

## Groundwater chemistry on deep peat lands three years after ash fertilization

Grundvattenkemin tre år efter askgödsling  
på djupa torvmarker i Norrland



Photo: Jenny Tjernlund

**Jenny Tjernlund**









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Examinator / *Examiner*: Ulf Skjällberg

SLU, Inst för skogens ekologi och skötsel / *SLU, Dept of Forest Ecology and Management*



I denna rapport redovisas ett examensarbete utfört vid Institutionen för skogens ekologi och skötsel, Skogsvetenskapliga fakulteten, SLU. Arbetet har handledts och granskats av handledaren, och godkänts av examinator. För rapportens slutliga innehåll är dock författaren ensam ansvarig.

*This report presents an MSc/BSc thesis at the Department of Forest Ecology and Management, Faculty of Forest Sciences, SLU. The work has been supervised and reviewed by the supervisor, and been approved by the examiner. However, the author is the sole responsible for the content.*



# Foreword

This is a master thesis written at the department of Forest ecology and management at the Swedish university of agricultural sciences. The thesis comprises 30 credits. This thesis work is an integrated part of the research project “*Effects of woodash fertilization in old-drained peatland forests*”, led by Tord Magnusson and Björn Hånell. The project is funded by Värmeforsk Service AB, within the program “Miljöriktig användning av askor.” The aim with this project is to find out if the ash produced at biomass boilers can be used for fertilization, without having any negative consequences for the environment. The experimental areas are all located on drained peatlands owned by the forest company Holmen AB. Samples were collected by Tord Magnusson and Jenny Tjernlund.

I want to begin to thank Tord Magnusson for being a great supervisor, his help and broad knowledge, which made me find the small paths to the bigger roads. I also want to thank my mom, Katarina Lahti for always being there for me, my sisters Frida and Julia Tjernlund for their encouragement and support. Thanks to Daniel Persson who makes me smile even on days I rather prefer not to. A big thank to my reinforcement Julia Ingelmark that always answers my questions and finds a way to help me.

Jenny Tjernlund

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# Summary

Ash fertilization in peat lands can be an effective tool in order to: i) increase tree growth, ii) supplying nutrients and iii) counteract acidification. This study focus on effects of ash fertilization on groundwater quality. Acid/base properties, dissolved nutrients, dissolved organic carbon and concentrations of methyl mercury, were studied. How ash fertilization affect the concentrations of methyl mercury in the groundwater is not previously examined and are therefore a further object of this study.

In this study 44 groundwater samples were collected from five different drained peat lands, situated in North Sweden and North Central Sweden. Three of the peatlands are considered to be nutrient poor and two are characterized as nutrient rich. The data was used to examine if groundwater quality from ash fertilized plots where different from control plots, three years after ash fertilization. The following water chemistry parameters where analyzed: pH-value, acid neutralizing capacity (ANC), major cations, ammonium, phosphate, strong acids anions inclusive nitrate, dissolved organic matter (DOC) and methyl mercury (MeHg).

No significant differences were found between plots fertilized with 0, 5 and 10 ton ash, with respect to: the pH-value, the ANC, major cations, nitrate, phosphate, anions, DOC, MeHg. A weak significant difference where found in ammonium concentration between ash fertilized plots and control plots. Ammonium concentration was lower in ash fertilized plots at three of the five peatlands.

Keywords: Ash fertilization, forested peatlands, groundwater chemistry, methyl mercury, pH, ANC, nitrate leaching.



# Sammanfattning

Askgödsling på torvmarker kan vara ett effektivt verktyg för att: i) öka trädens tillväxt, ii) tillföra näringsämnen och iii) motverka försurning. Föreliggande studie är inriktad mot kemiska effekter på grundvattnet. Syra/bas egenskaper, lösta näringsämnen, löst organiskt kol och halter av metylkvicksilver, studerades. Hur askgödsling påverkar koncentrationen av metylkvicksilver i grundvattnet inte tidigare undersökt och är därför ytterligare ett syfte med denna studie.

I denna studie samlades totalt 44 grundvattenprover in från fem olika dränerade och beskogade torvmarker, belägna i norra mellan Sverige. Tre av torvmarkerna är näringsfattiga och två karaktäriseras som näringsrika. Prover från askgödslade ytor jämfördes med prover från kontrolltor, tre år efter askgödsling. De vattenkemiska parametrar som analyserades var: pH-värde, ANC, dominerande katjoner, ammonium, fosfat, anjoner till starka syror (inkl. nitrat), DOC och MeHg.

Inga signifikanta skillnader fanns mellan ytor gödslade med 0, 5 och 10 ton aska, med avseende på: pH-värdet, ANC, dominerande katjoner, nitrat, fosfat, anjoner, DOC och MeHg. En svag signifikant skillnad återfanns för ammonium koncentrationen mellan askgödslade ytor och kontrolltor. Ammonium koncentrationen var lägre på ask gödslade ytor på tre av de fem torvmarkerna.

Nyckelord: Askgödsling, skogsbevuxna torvmarker, grundvattenkemi, metylkvicksilver, pH, ANC, nitrat utlakning.



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# Introduction

## Background

Ash fertilization on drained peatlands may be used to increase forest growth in an area of 190 000 hectares in Sweden (Hånell & Magnusson 2005). Ash fertilization is economically feasible at sites where ash induce a growth response to the trees. Such areas are peat-covered land, with proper drainage and medium site productivity (Magnusson 2009, Pavilainen & Päivänen 1995; Hånell & Magnusson 2005; Augusto et al. 2008; Moilanen et al. 2005). Tree growth increases after ash fertilization for mainly two reasons: i) ash contains phosphorus (P) and potassium (K), which in peatlands exist in such low concentrations that they may limit tree growth (Egnell 1998; Magnusson 1996) and ii) ash increases the pH value in the peat soil, which further increases the organisms' activity, so more nitrogen becomes available for tree uptake (Martikainen 1984).

According to EU directives, 49 % of all the consumed energy in Sweden should have a renewable origin in year 2020 (Europaparlamentets och rådets direktiv 2009/28/EG). In 2012, this goal was already reached and 51% of all the consumed energy had a renewable origin (Regeringskansliet 2013). The high demand for renewable energy sources has led to an increased harvest of branches and tops at final cutting (Andersson 2009; Bioenergiportalen 2013-07-02). This has resulted in increased losses of nitrogen (N), P and K from the harvested sites, of which the two latter often are critical on peat soil sites (Magnusson 1996). Further on, nutrient uptake by trees is normally an acidifying process in boreal forest ecosystems, something that is counteracted later when the trees are decomposed by soil organisms. This will not happen if whole tree harvesting is used (Skogsstyrelsen 2008). Whole tree harvesting causes 1.5-5 times greater loss of nutrients from the soil compared to when only the stem is harvested (Olsson et al. 1996). Depletion of nutrients also reduces the concentration of base cations in the soil which leads to a decreased ability to buffer against acidic inputs to the soil (Skogsstyrelsen 2008).

Every year, 100 000- 150 000 tons of dry wood ash is produced in Sweden. Most of the ash is deposited through costly solutions for the ash producers (Naturvårdsverket 2003). This ash could preferably be used to close the nutrient cycle, by returning it to forest land where trees growth may be limited by P and K (Pavilainen & Päivänen 1995). This is often the case on peatlands where waterlogging hinders tree roots from reaching down to the mineral soil, the ultimate source of P and K (Magnusson 1996). Ash fertilization has two more positive effects on the soil status, i) it increases the pH value by containing calcium oxide, hydroxide and carbonates which consumes hydrogen ions upon dissolution (Etiègni & Campbell 1991) and ii) increases the soils ability to buffer the soil solution against acidic inputs by containing base cations, mostly magnesium (Mg) and calcium (Ca) ions (Saarsalmi 2001a).

During 2011, 15 000 ha forestland where fertilized with ash in Sweden (Andersson & Hildingsson 2013). According to the Swedish forestry act paragraph 30§, ash should be



returned to areas where whole trees have been harvested, in order to avoid i) nutrient depletion and ii) lowering the soils capacity to buffer against acidic inputs.

According to the general recommendations to paragraph 30§, ash has to be stabilized before used as fertilizer. An ash dose should not be larger than 3 ton ash/ha within a ten year period and not larger than 6 ton ash/ha within a whole stand rotation. Ash fertilization should not be performed closer than 25 meters away from lakes, streams and undrained wetlands. This is an expression of the precautionary principle recommended when ash fertilization is used for production-enhancing measures.

## **Ash properties**

Pure wood ash consists mainly of Calcium (Ca), Silicon (Si), Aluminium (Al), Potassium (K), Magnesium (Mg) and phosphorous (P) (Etiègni & Campbell 1991; Aronson & Ekelund 2004). The major component Ca appears as calcium oxide (CaO), calcium hydroxide (Ca(OH)<sub>2</sub>) and carbonate (CaCO<sub>3</sub>). Depending on dominating form, the ash upon wetting gives the solution a pH value of 10-14. (Campbell 1990). During combustion of wood in furnaces, two different ashes are formed, fly ash and bottom ash (Augusto et al. 2008).

The temperature during combustion plays a major role in deciding the concentrations of certain elements. Boron (B) and K transform to gas form at higher temperatures (Pitman 2006). Combustion of wood in 500 C° forms ash mainly consisting of carbonates and bicarbonates. At a temperature of 1000 C° oxides becomes more dominant, and this is the temperature most boilers work at (Augusto et al. 2008).

The overall solubility of an ash depends very much on the content of the major salt ions e.g SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> (Steenari & Lindqvist 1997). The elements that are leached from the ash first, are those elements that are bound into soluble salt complexes. Those elements are K, sulphur (S), boron (B) and sodium (Na) (Augusto et al. 2008).

Ash is often enriched in trace metals and there is a concern about increased concentrations of heavy metals in the soil after ash fertilization. Some heavy metals are toxic to animals and humans even in low concentrations (Nieminen et al. 2005). Because of this the Swedish Forest Agency has recommended maximum concentrations of heavy metals in ash (Table 1). Cadmium is one heavy metal that has been shown to become more bioavailable after ash fertilization (Egnell et al. 1998). Cadmium (Cd) concentrations in ash normally range between 9-12 mg/kg ash and zinc (Zn) in concentrations of 130-1400 mg/kg ash. 100% of the Cd and 70% of the Zn becomes soluble when exposed to pH-values between 3 and 4. Cu and Pb exist in more insoluble forms in the ash (Zhan et al 1996).



Table 1. Recommended maximum concentrations of potentially toxic elements in (mg/kg) dry ash used for forest fertilization (Skogstyrelsen 2008).

<b>Element</b>	<b>Maximum concentrations in mg/kg dry ash</b>
Boron (B)	800
Copper (Cu)	400
Zinc (Zn)	7000
Arsenic (As)	30
Lead (Pb)	300
Cadmium (Cd)	30
Chromium (Cr)	100
Mercury (Hg)	3
Nickel (Ni)	70
Vanadium (V)	70

Loose ash can have negative impacts on the vegetation and on soil organisms because the pH change is too rapid (Pitman 2006). To make the ash less reactive, i.e. more insoluble, a hardening process is used. The ash is hardened by supply of water and CO<sub>2</sub>. This makes more easily soluble calcium oxides and hydroxides to form less soluble calcium carbonates (Steenari & Lindqvist 1997). The hardening process also reduce the i) pH value, ii) solubility of heavy metals and iii) solubility of phosphorous from the ash (Nieminen et al. 2005).

## **Ash fertilization and forest growth on peatland**

In mineral soil no significant growth response has been found (Jacobson 2003; Augusto et al. 2008). A lack of growth response seems to be the case on nitrogen limited soils, such as most soils in the boreal region. The ash itself does not contain any nitrogen (Saarsalmi et al. 2006; Jacobson 2003). However, several studies have shown an increased forest growth after ash fertilization on peatlands (Augusto et al. 2008; Moilanen et al. 2005; Moilanen et al 2002; Ernefors et al. 2010). In contrast to mineral soils in the boreal forest, peatlands contain large amounts of N. Most of this N is bound in humified peaty organic matter, which however, may have an exceedingly low decomposition rate (Paavilainen & Päivenen 1995). Forest growth on peatlands is often also limited by low concentration of P and K, and on nitrogen rich peatlands any of these substances may be more limiting than N. (Magnusson 2009). P and K becomes available for tree uptake by weathering of the mineral soil, but on peatland the high ground water table hinders tree roots from reaching down to these nutrients (Egnell 1998).

Ash contains P and K and can therefore increase forest growth if applied. Furthermore, ash fertilization starts a number of processes that indirectly promotes forest growth, e.g. when pH-value is raised the microbial activity increases and this leads to more available nitrogen and phosphorous for tree uptake (Moilanen et al. 2005).



## Ash fertilization and the response on soil properties

### *pH-value*

Ash fertilization increases the pH-value in the top soil, defined as the top 0-5cm of the soil (Saarsalmi et al. 2001b; Arvidsson & Lundqvist 2003; Nohrstedt 2001; Saarsalmi et al. 2006), (Kronnäs et al. 2012; Ludwig et al. 2002). This effect can last for several years (Saarsalmi et al. 2001b). Ash fertilization has also been shown to increase the pH value in streams where the runoff water comes from fertilized areas (Ring 2006; Johansson 2014). In the groundwater an increased pH-value after ash fertilization can have a time lag (Augusto et al. 2008).

Ash increases the pH value when applied to soil because it contains high concentrations of CaO, MgO, K<sub>2</sub>O and NaOH which upon wetting produces the bases O<sub>2</sub><sup>-</sup>, OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup> that neutralizes H<sup>+</sup> ions in the soil solution (Saarsalmi et al. 2006).

### *ANC*

ANC in a soil is defined as its ability to buffer against acidic inputs. If a soil has high ANC, it has a high capacity to neutralize acidic inputs to the soil. (Reuss & Johnson 1986). If a soil has a high ANC it can neutralize a certain input of protons by cations bound to exchange sites. Those cations are Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup>. When acidic inputs comes into the system those cations are exchanged for protons and goes out in the soil solution, where it can follow water movement and be leached out or assimilated by plants. If there is a higher input of protons compared to cations that can be released from exchange sites, then the pH will decrease. Eventually, solid aluminum hydroxide starts to dissolve and act as a buffer (Stumm & Morgan 1981).

ANC can increase in the runoff water after ash application and this effect may last for several years after the treatment, up to ten years. Several conditions decide the effect on ANC, when ash is applied: i) the size of the ash dose, ii) the composition of the ash, iii) the proportion of the catchment that is fertilized and v) the degree of acidity in the soil (Johansson 2014).

### *Base cations*

After ash fertilization the concentration of K, Mg, and Ca increases in the humus layer and mineral soil (Saarsalmi et al. 2001b; Saarsalmi et al. 2006; Ring et al. 2011; Nilsson & Lundin 1996; Moilanen et al. 2002; Geibe et al. 2003; Arvidsson & Lundqvist 2003; Ludwig et al. 2002; Augusto et al. 2008). Base saturation (BS) of the soil is increased when Ca, Mg, K and Na concentrations is increased in the soil after ash fertilization (Arvidsson & Lundqvist 2003).

Several studies have also found an increased Na concentration in the top soil (Augusto et al. 2008; Saarsalmi et al. 2001b; Saarsalmi et al. 2006). Na is bound in the form of very soluble salts in the ash which mean that Na is quickly released into the soil after ash fertilization (Piirainen et al. 2012; Ring et al. 2006).

Mg, Ca, K and Na concentrations in the groundwater may be unaffected after ash fertilization (Ring et al 2011).



### *Acidic cations and heavy metals*

Ash contains higher concentrations of heavy metals compared to the background value in the soil (Piirainen et al. 2012). Nevertheless, the increased soil pH caused by the ash, may actually decrease the mobility of many heavy metals, because they become more insoluble (Augusto et al. 2008; Piirainen et al. 2012).

Metal ions such as aluminum and iron can be bound to the humus and form either mobile or immobile complexes. Metal ions mobility depends on what type of humus complexes they bind to. Metal ions bound to soluble low molecular weight organic acids become more mobile while metal ions bound to larger humic complexes may form insoluble complexes. How stable the metal-organic bonds are depends on the charge of the metal ion, where increasing charge of the metal ion means that it binds more tightly to organic molecules (Russell 1988). An increased dissolved organic matter (DOC) concentration normally leads to more mobile metals as well (Piirainen et al. 2012).

Aluminum concentration has been shown to decrease in both humus and soil layer after ash fertilization (Saarsalmi et al. 2001b; Geibe 2003). Aluminum concentrations have also shown to increase after ash fertilization (Lundell et al. 2001; Ludwig et al. 2002). A decreased aluminum concentration in the soil solution can be explained by the increased pH value which makes Al to be less soluble as it precipitates as insoluble  $\text{Al}(\text{OH})_3$  (Geibe 2003).

Cadmium (Cd) is a toxic metal even in trace quantities. Cd is easily leached from ash and might elevate the Cd concentration in the soil (Nohrstedt 2001). Wood ash normally contains concentrations of Cd between 2-21 mg/kg (Jacobson 2003).

Other metals that may increase in concentration after ash fertilization are: Pb (Ludwig et al. 2002), Mo, B, Li (Ring et al. 2011), Zn, B, Cr, Cu, Mn (Saarsalmi et al. 2001b), Cr (Ring et al. 2011; Saarsalmi et al. 2006) and Fe (Geibe 2003).

Concentrations of the heavy metals: Al, Fe, Mn, Zn, Cr, Cu, Cd, As, Ni, Pb, Ti and Mo, have not been shown to increase in berries after ash fertilization (Moilanen et al. 2006).

### *$\text{SO}_4^{2-}$ and $\text{Cl}^-$*

$\text{SO}_4^{2-}$  concentrations can after one year become elevated after ash fertilization, in both the runoff water coming from ash fertilized areas and in the topsoil (Piirainen et al. 2012; Geibe et al. 2003; Ring et al. 2011; Ludwig et al. 2002). In the long perspective for up to 54 years  $\text{SO}_4^{2-}$  concentrations can be elevated in the ground water (Moilanen et al. 2002).  $\text{SO}_4^{2-}$  is bound to easily soluble salts in the ash and is upon wetting released (Ring et al. 2006).  $\text{Cl}^-$  also exists in easily soluble forms in the ash and  $\text{Cl}^-$  concentration is also increased shortly after ash fertilization (Piirainen et al. 2012; Geibe et al. 2003; Norström et al. 2011). The strength of these effects varies with the composition of the ash; the relation between oxyhydroxide- and carbonate anions on one hand, and strong acid anions on the other (Steenari & Lindqvist 1997). Increased  $\text{SO}_4^{2-}$  can also be a result of redox changes that comes from the increased tree growth after ash fertilization, which lowers the ground water table so reduced sulphur gets available for oxidation in the peat (Russel 1988).



## *Nitrogen (N)*

On N rich soils there has been a concern about nitrate leaching after ash fertilization. The results are contradictory, some studies have not found any effects on nitrate concentration after ash fertilization (Nohrstedt 2001; Ring et al. 2006; Kronnäs et al. 2012). One study has found an increased  $\text{NO}_3^-$  concentration at all depths down to 100 cm down in the soil (Ludwig et al. 2002). Yet another study found increased concentrations of total N and  $\text{NO}_3^-$  in the ground water 54 years after ash fertilization (Moilanen et al. 2002). Nitrification in the top organic layer was found to be stimulated by ash fertilization in coniferous forest soil, probably due to the increased pH value (Martikainen 1984).

Peat soils contain large amounts of organically bound nitrogen. When pH is raised the mineralization rate increases and the pool of ammonium then increases in the soil. If the groundwater surface in the peat land is low there is much available oxygen in the peat, oxygen that can be used first by ammonia-oxidizing organisms, which transform ammonium to nitrite and in a second step used by bacteria's from the genus *Nitrospira* and *Nitrobacter*, which transforms nitrite to nitrate. The raised pH value after ash fertilization favors the autotrophic nitrification. The nitrification process does not appear in very acid soils such as in soils with a pH value below 4. During the reaction when one ammonium molecule is transformed to nitrite, two hydrogen ions are set free into the soil solution. If  $\text{NO}_3^-$  stays in the soil, plant uptake of the  $\text{NO}_3^-$  ion is a alkalinizing process, but if not, the leaching of  $\text{NO}_3^-$  will cause a permanent acidification of the soil.  $\text{NO}_3^-$  is very easily leached out from the soil (Russel 1988).

## *Phosphorous*

In mineral soil phosphorous is adsorbed so soil particles by bonding to Al and Fe hydroxide, by substitution with hydroxyl groups. In organic soil P is bound to the organic matter by formation of inositol phosphate esters, phospholipids, phosphate linkage to sugars and by C-P bonding in phosphoric acid. Therefore, the phosphate concentration in the soil solution is determined by how much of the phosphate that forms less soluble complexes (or is bound to complexes) and this in turn is controlled by the: i) initial pH value in the soil solution and ii) concentration of Al and Fe hydroxide.

The highest concentration of free phosphate ions is found in soils with a pH value between 6 - 7. In acid soils, with pH values below 5.5, some of the aluminum exists as free ions, as  $\text{Al}^{3+}$  and phosphate exists as  $\text{H}_2\text{PO}_4^-$ . These substances react with each other and form insoluble complexes. In alkaline soils having pH values above 8, phosphate exists in the form of  $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$  and reacts with calcium, so insoluble complex is formed (Russel 1988).

Mineral soils contain high concentrations of Al and Fe hydroxide. This makes mineral soils effective in adsorbing phosphorous at low pH values. In peat soils, concentrations of those metals are normally low. Exceptions from this are nutrient rich fens that contain high concentrations of Al and Fe hydroxide. However, the ash contains high amounts of Al and Fe hydroxides that effectively can absorb P by formation of Al-P and Fe-P complexes (Pirainen et al. 2012). By this reaction the ash decreases the leakage of P because it is effectively adsorbed. This can be the main reason why little P leakage has been found after ash



fertilization (Ring et al. 2011; Nilsson et al. 1996) in comparison to liming, where P leakage has been found (Nieminen et al. 2007; Geibe et al. 2003).

Desorption of phosphate and increased phosphate concentration in the soil solution after liming, can be a result of the increased mineralization rate as the pH value increases. So there is some concern about leaching of P also after ash fertilization, since it is applied in amounts ten times more P than normal forest takes up during one year (Piirainen et al. 2012). Trees take up around 2-9 kg P/ha per year. The annual uptake by ground vegetation is 1-2 kg P/ha (Paavilainen & Päivenen 1995).

### *Dissolved organic matter*

Microbial activity in the soil can be measured by: i) DOC concentration in the soil or ii) gas exchange. After ash fertilization Geibe et al. (2003) found an increased DOC concentration in the topsoil and Norström et al 2011 found an increased DOC in stream water. On the contrary, no increases of DOC were found in the humus layer or in mineral soil by Piirainen et al. (2012) or by Saarsalmi et al. (2001b).

Ash increased the emissions of CO<sub>2</sub> from one drained mire treated with ash (Moilanen et al. 2002). Ash fertilization increased microbial respiration per unit microbial biomass with increased dose of ash from 1, 2.5 and 5 ton (Fritze et al. 1994). No effect on CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O gas exchange from the soil was detected after ash fertilization with 3.1 and 6.6 ton ash, for up to five years (Ernfors et al. 2010).

Increased DOC in water after ash fertilization has two main reasons, i) the functional groups of organic matter gets de-protonated and in that way hydrated and soluble and ii) increased mineralization rate because of increased pH-value (Nilsson et al. 2001).

## **Wetlands can have a net production of Methylmercury (MeHg)**

A net production of MeHg, CH<sub>3</sub>Hg<sup>+</sup> has been shown to occur in wetlands where an oxygen free environment exist (Tjerngren et al. 2011; Rudd 1995; St. Louis 1994; Hurley et al. 1995). This toxic form of Hg is fat-soluble and can therefore accumulate in the fat tissues of organisms (Morel et al. 1998). The formation of MeHg is catalyzed primarily by sulphate-reducing bacteria (SRB) living in the wetland (Matilainen. 1995). It is mainly five controlling factors which affect SRB activity and thus the potential of net production of MeHg. The things favoring SRB are: i) oxygen-free conditions (Ullrich et al. 2001), ii) a temperature of about 20 degrees (Bloom et al. 2004), iii) a sulfate concentration of 20-50 mg/l (Ullrich et al. 2001), iiiii) low pH (Miskimmin et al. 1992), iiiii) high DOC concentration with high C/N ratio (Ullrich et al. 2001).

Ionic mercury (Hg<sup>2+</sup>), as well as methyl mercury (CH<sub>3</sub>Hg<sup>+</sup>) are strongly bound to organic matter, by binding to the strongly reduced sulfur groups, and therefore MeHg follows DOC to a high extent (Karlsson et al. 2003). Methyl mercury (MeHg) and Hg has been shown to be lower in runoff water after lime application compared to control (Parkman & Munthe 1998)



# Purpose

The thesis aims to compare the groundwater quality from ash fertilized plots with control plots, three years after ash fertilization - with respect to the following water chemistry parameters:

- pH-value
- ANC
- Base cations
- Ammonium and nitrate
- Phosphate
- DOC
- Methyl mercury

Hypothesis:

There is no significant difference in the groundwater chemistry values: i) pH value, ii) the ANC iii) base cations, iv) ammonium and nitrate, v) phosphate, vi) DOC and vii) MeHg , between ash fertilized and control plots.



# Material and methods

## Material

Data for this study was collected from five different peat lands situated in North Sweden and North central Sweden. These five peatlands are divided into two groups according to their nutritional status. Three of the peatlands are classified as nutrient poor peatlands: Brönstjärn 1 (Br1), Brönstjärn 2 (Br2) and Medskogen (M). Two out of the five peatlands are classified as nutrient rich peatlands and those are Daltorpet (D) and Fönebo (F).

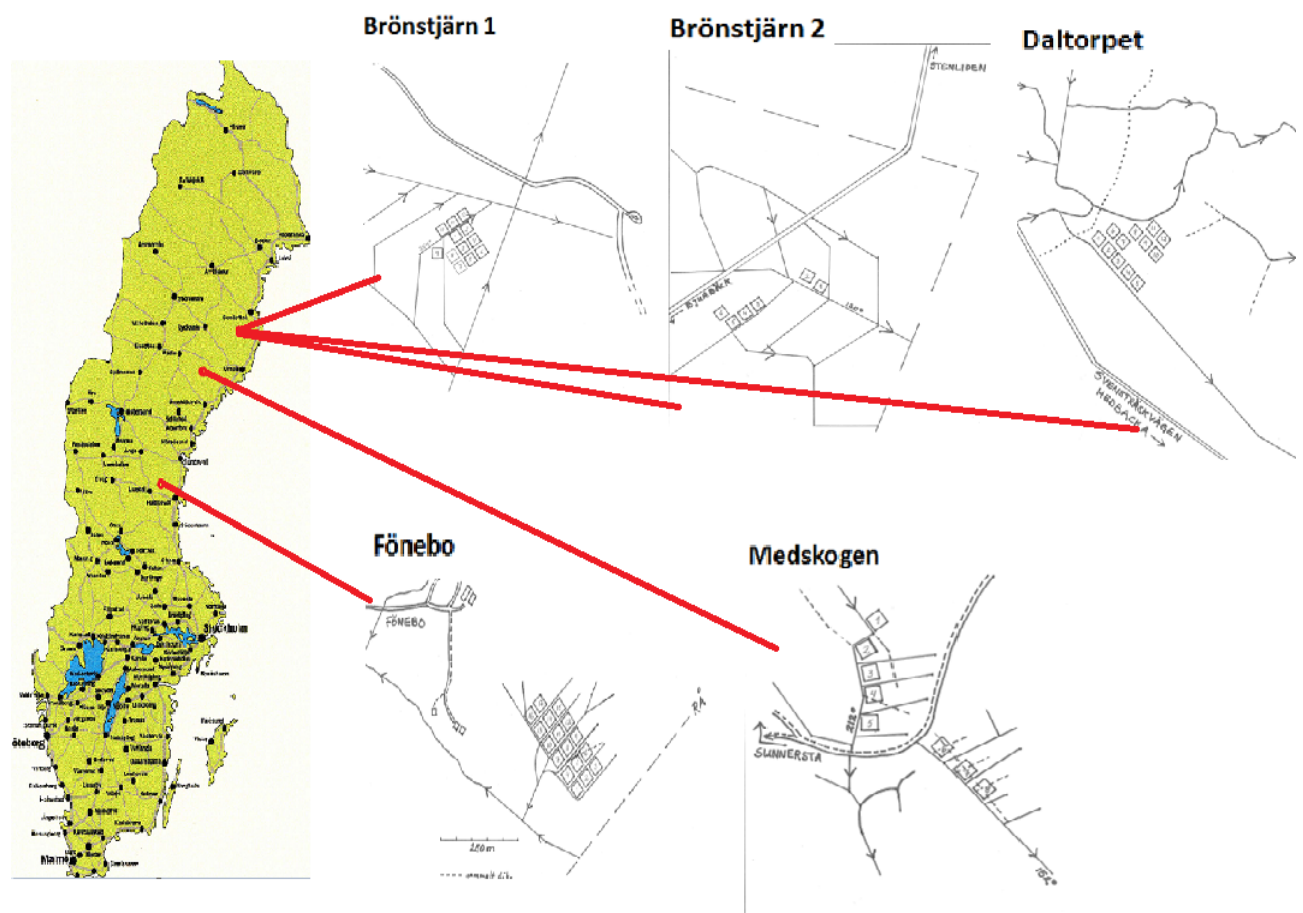


Figure 1 Trial sketches over the five different wetlands and where they are located in Sweden.

### Site description

Brönstjärn 1 is situated in Burtäsk, Lat 644057 Long 202446. Brönstjärn 1 has an area of 2.8 hectares and is a nutrient poor peatland and is classified as low sedge species type, however the dominating species in the field layer is hare's-tail cottongrass (*Eriophorum vaginatum* (L)) and Marsh Labrador tea (*Rhododendron tomentosum* (syn. *Ledum palustre*)). The thickness of the peat cover is at least 40 cm deep. The ditches have been cleared before the start of trial.



According to the company stand register the tree stand, consisting of Scots pine (*Pinus silvestris* (L)) has an average age of 85 years. The standing volume is estimated to 94 m<sup>3</sup>sk/ha. 12 plots with a size of 30\*30 m were laid out in this area. Plot 3, 6, 8 and 11 was treated with 0 ton ash/ha. Plot 2, 4, 7, and 12 was treated with 5 ton ash/ha and plot 1, 5, 9 and 12 was treated with 10 ton ash/ha

Brönstjärn 2 is situated in Burträsk, Lat 644120 Long 202500. Brönstjärn 2 is a nutrient poor peatland classified as low sedge to blueberry-horsetail type. The thickness of the peat cover is at least 40 cm deep. The ditches at Brönstjärn 2 have been cleared and the stand has been thinned before trial start. The stand is dominated by Scots pine with some Norway spruce (*Picea abies* (L.) Karst. and according to the company stand register it has an average age of 64 years. The standing volume is 191 m<sup>3</sup>sk/ha. The experimental setting on Brönstjärn 2 consists of 6 plots with a size of 30\*30m. Plot 2 and 3 has been given 0 ton ash/ha. Plot 4 and 5 has been given 5 ton ash/ha. Plot 1 and 6 has been given 10 ton ash/ha.

Medskogen, Solberg, Lat 634203 Long 172942. Is a nutrient poor peat land classified as low sedge to blueberry-horsetail type. The thickness of the peat cover is at least 40 cm deep. Ditches have been cleared before trial. The stand consists of equal parts of Scots pine and Norway spruce and some Silver birch (*Betula pendula*). According to the company stand register the average stand age is 70 years and the standing volume is 150 m<sup>3</sup>sk/ha. Here 9 plots of 30\*30 m were laid out. Plot 2, 6 and 9 was given 0 ton ash/ha. Plot 1, 5 and 7 was given 5 ton ash/ha. Plot 3, 4 and 8 was given 10 ton ash/ha.

Daltorpet, Burträsk, Lat 643343 Long 202824. Daltorpet is a nutrient rich peatland, with a peat layer deeper than 1 meter; it is dominated with blueberry-horsetail to low sedge type species. The stand is a mixed forest of Scots pine and Norway spruce. According to the company stand register the average stand age is 80 years and the standing volume 200 m<sup>3</sup>sk/ha. 12 plots was laid out at Daltorpet with an size of 30\*30 m. Plot 2, 5, 7 and 12 were given 0 ton ash/ha. Plot 4, 8, 10 and 11 were given 5 ton ash/ha. Plot 1, 3, 6 and 9 were given 10 ton ash/ha.

Fönebo, Lat 615501 Long 164536. Fönebo is a nutrient rich peatland dominated with blueberry and horsetail species. The peat thickness is over 1 meter. According to the company stand register the average age of the stand is 70 years and is dominated by Scots pine with some Silver birch. The standing volume is 235 m<sup>3</sup>sk/ha. Ditches was cleared before trial start. The trial at Fännsmyran consists of 17 plots with a size of 30\*40 m. 0 ton ash/ha was given on plot 2, 5, 7, 11, 13 and 16. 5 ton ash/ha was given on 1, 4, 9, 14 and 15. 10 ton ash/ha was given on 3, 6, 8, 10, 12 and 17.

### *Properties of the applied ash*

Plots where fertilized with a Finnish granulated wood ash (Ecolan T4000, F A Forest Oy). Composition of the applied ash in this study is displayed in table 2, 3, 4 and the pH-values of the ash upon wetting in table 5. Plots where fertilized with ash in November 2011 by precision spreading from helicopter.



Three composite samples were randomly collected from the big fertilizer bags delivered to the landings at each experimental area, in 2011. Each composite sample contained ash granules from 3-5 fertilizer bags. Additionally, an extra sample of partly dissolved ash granules collected from the ground surface in august 2014, was also analyzed. The dry composite samples were ground on a ball mill and thoroughly homogenized. Total elemental contents were analysed at the ALS Scandinavia Laboratory in Luleå, Sweden. Elements were determined by ICP-AES/ICP-SFMS, after digestion in 7M nitric acid/ lithiumtetraborate, respectively (ASTM methods D3683 and D3682). The pH value in the ash was determined at the Soil Laboratory at the department of Forest Ecology and Management, SLU. Activities were measured with a combination electrode in a 1:5 (v/v) ash:water solution, after shaking and equilibrating overnight.

The ash used in this study has a higher concentration of the element chromium (104 mg/kg dry substance), (table 2) than the recommended lowest limit by (Skogstyrelsen 2008) which is 100 mg/kg dry substance, (table 1).

Table 2 Mean value and standard error for major elements (% of dry substance) and loss on ignition at 1000°C (% of dry substance).

Substance	Mean value	Standard error
SiO <sub>2</sub>	32.13	0.366
Al <sub>2</sub> O <sub>3</sub>	7.95	0.284
CaO	23.63	0.401
Fe <sub>2</sub> O <sub>3</sub>	3.48	0.101
K <sub>2</sub> O	3.99	0.112
MgO	3.06	0.097
MnO	0.96	0.048
Na <sub>2</sub> O	2.02	0.082
P <sub>2</sub> O <sub>5</sub>	2.16	0.049
TiO <sub>2</sub>	0.33	0.004
LOI 1000°C	12.10	0.125

Table 3 Mean value and standard error for elements in the ash (mg/kg dry substance).

Element	Mean value	Standard error
S	13 833.33	7 986.68
Ba	1 613.33	931.46
Zn	1 640.00	946.85
Sr	739.00	426.66
B	129.67	74.86
Zr	105.33	60.81
Cr	104.00	60.04



Table 4 Mean value and standard error for trace elements in the ash (mg/kg dry substance).

Element	Mean value	Standard error
Cu	85.47	49.34
Pb	67.30	38.86
Ni	52.93	30.56
V	46.10	26.62
Y	21.83	12.61
Co	14.40	8.31
As	14.33	8.28
Cd	8.29	4.78
Nb	7.58	4.38
Mo	6.87	3.97
Sc	5.51	3.18
Sn	2.86	1.65
Be	1.35	0.78
Hg	0.22	0.13

Table 5 pH-value in water of three different ash composite samples.

Sample	pH-value
1	12.47
2	12.34
3	12.21

## Methods

### *Sampling*

Water sampling began on 1 September, 2014 and ended 12 September, 2014. Water samples were taken from temporary groundwater wells. Altogether 44 groundwater samples were taken. Groundwater wells was drilled with a soil auger (Eijkelkamp) equipped with an open-blade drilling head 7,5 cm diameter, which is pushed down to depth of ca 0,7 m and takes up a peat core of approximately 7.5 cm diameter. Thereafter the groundwater was allowed to seep in and fill the well up to the ground water table.

The water sample was taken up from the well by using a hand evacuation pump connected to sample bottle by a PTFE tubing. The tube was attached to a stick so that the opening did not touch the muddy bottom of the well. The tube was rinsed with ion-free water between different sampling sites. Water samples for MeHg were taken in acid-washed glass bottles. Water samples for other analyzes were taken in clean polyethylene bottles. Bottles were labeled according to the code of the plot.



Water samples were transferred within ca 2 hrs to a cooling bag, with a temperature close to 0 °C. On return back from the field in the evening the samples were frozen, leaving a headspace for expansion. Before analysis, frozen samples were thawed and carefully decanted into new clean bottles – without filtration.

### *Analytical methods*

Methyl mercury in sampled groundwater was analyzed at the ALS Scandinavia Laboratory in Luleå, MeHg was determined by GC-ICP-MS after sequential steps of i) isotopic dilution, ii) extraction and iii) ethylation, according to the ALS method MEHG-V. All other water analyses were made at the Soil Laboratory, dept of Forest Ecology and Management, SLU, Umeå. pH was measured on a Mettler – Toledo Sevencompact instrument equipped with a Mettler – Toledo Inlab combination electrode. DOC/TOC was measured on a Shimadzu TOC-V instrument. Nitrate and phosphate was measured on an Omniprocess Autoanalyzer AA3 instrument. Remaining anions were measured on a Dionex ICS90 with AS-DV autosampler and a AS22 Dionex column.

### *Calculation and statistical method*

The results obtained were compiled in Excel, including calculation of the mean and standard error. Analysis of variance (ANOVA) was used for the statistical evaluation of differences in mean values between different treatments. The specific method applied was ANOVA for randomized block trial. This was done in Minitab, by using the function general linear model. Also an ANOVA model with interaction factor, Site \* Treatment was used. In order to test if the chosen statistical method was valid for this type of trial, the residual plots were examined. Correlation between, i) DOC and MeHg and ii)  $SO_4^{2-}$  and MeHg were performed in Minitab.

ANC was calculated by the formula:

$$ANC = ((Ca^{2+} + Mg^{2+} + K^+ + Na^+) - (SO_4^{2-} + Cl^- + NO_3^-))$$



# Results

## pH-value, ANC and Al

Groundwater data from the five different drained peatlands was evaluated with ANOVA in order to decide if pH value, ANC and aluminum concentrations differ between plots treated with 0, 5 and 10 tons of ash. The average pH value, ANC and aluminum concentrations were compared between treatments for each peatland and for all peatlands summed together.

The results of the statistical analysis shows that the pH-value is not significantly different between plots treated with 0, 5 or 10 tons of ash, neither when looking at all peatlands combined ( $p = 0.876$ ), or when testing at the five peatlands separately. (Figure 1). On the contrary, the pH-value at the five different peatlands are significantly different from each other ( $p = 0.000$ ).

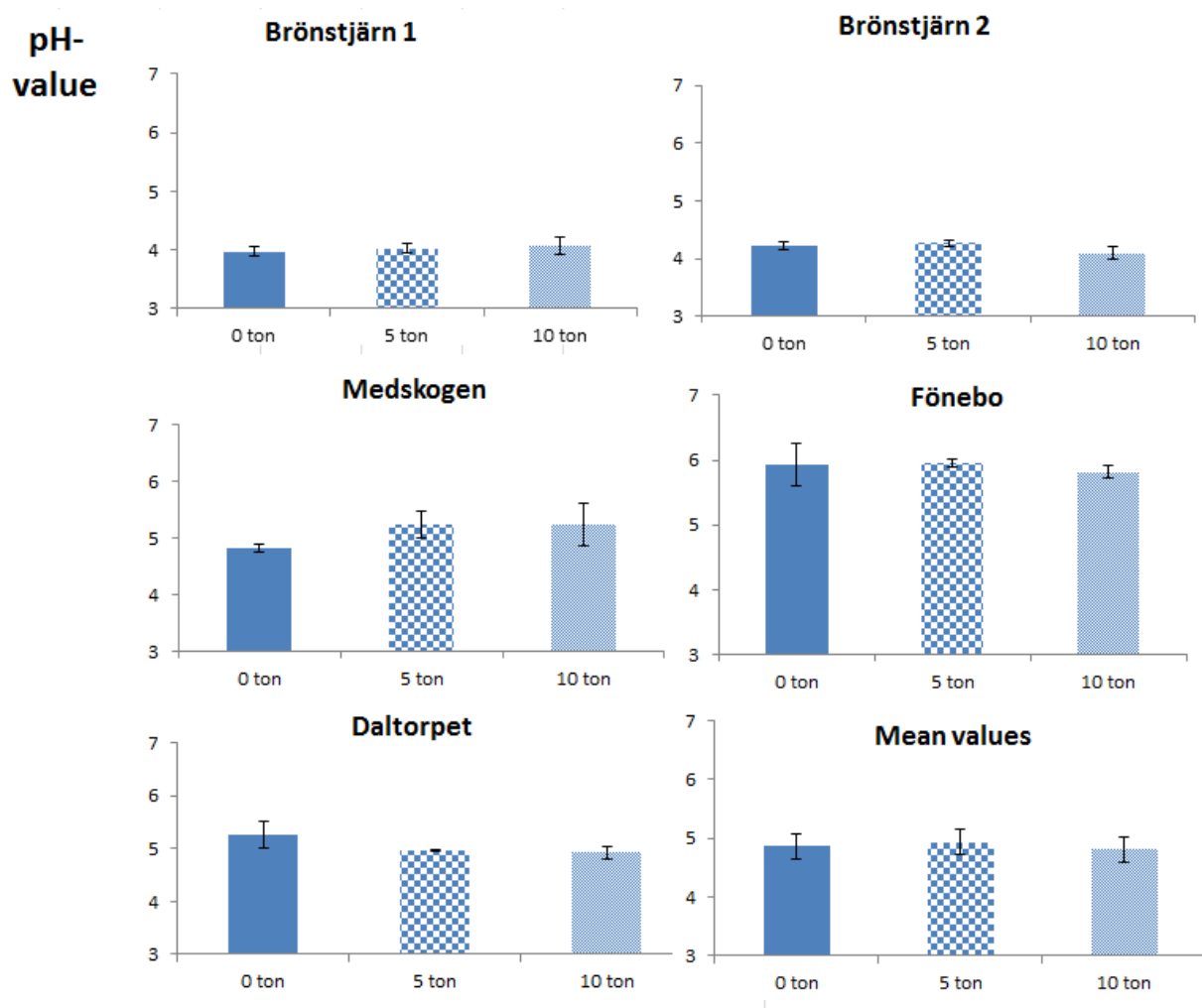


Figure 1 Average pH-value in the groundwater for the different treatments at the five different peatlands. Standard error given with error bars.



Mean ANC is not significantly different between the treatments ( $p = 0.943$ ). (Figure 2). The results from the five drained peatlands separately show contradictory results. (figure 2). B1 and B2 show trends of increasing ANC, while ANC decreases with fertilization dose at peatland F. The inclusion of an interaction factor (Treatment \* Site) in the ANOVA model reveals that the interaction factor is weakly significant ( $p = 0.043$ ).

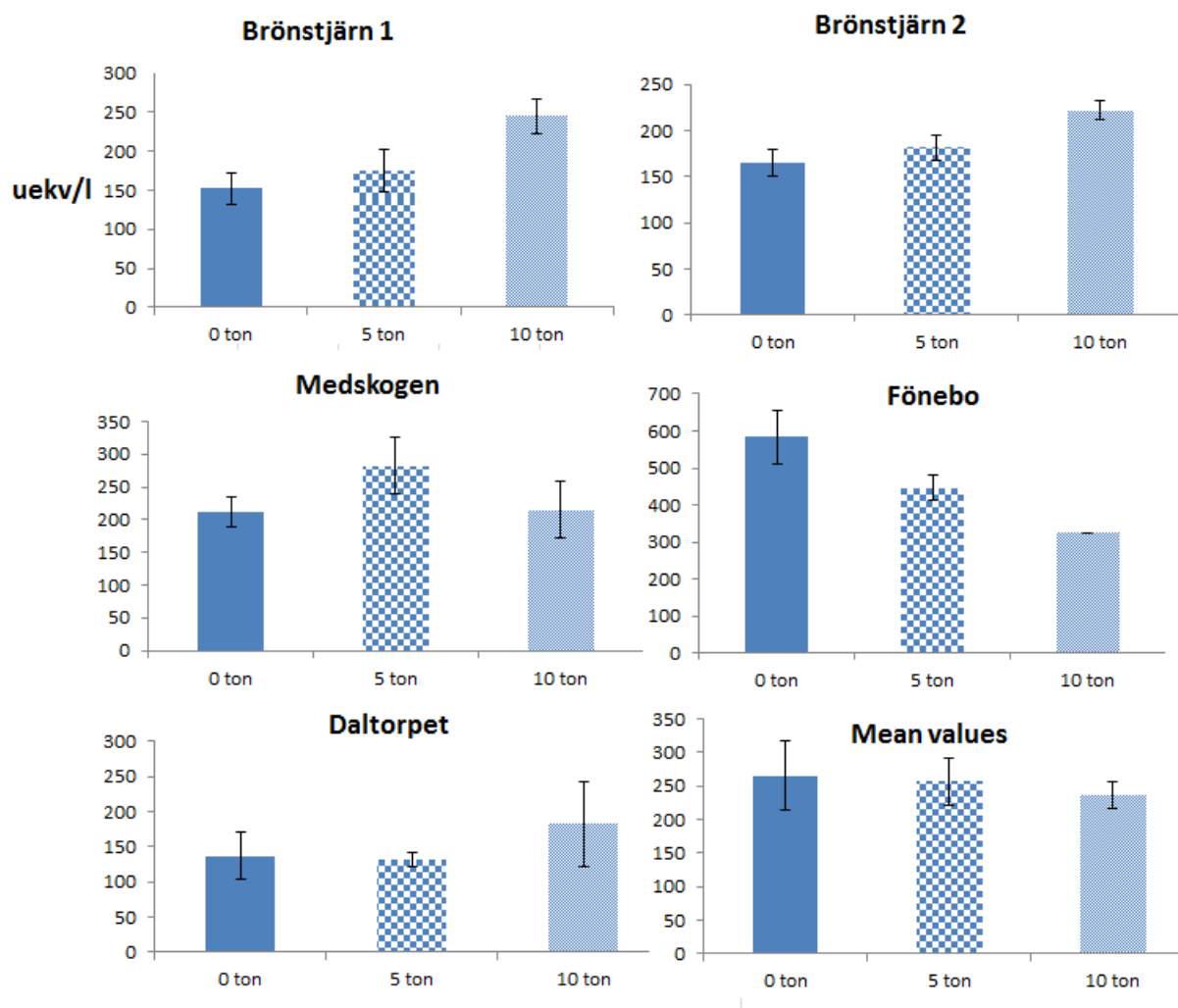


Figure 2 Average ANC (µekv/l ) for each treatment and site. Standard error given with error bars.

The concentrations of aluminum in the peat groundwater was not different between ash treatments ( $p = 0.912$ ). (Table 6). Aluminum concentrations are relatively well correlated to DOC ( $r = 0.64$ ).



Table 6 Average Al concentration (mg/l) in the ground water at the five wetlands where plots are treated with 0 ton, 5 ton and 10 ton ash. Mean value is calculated for all wetlands. Standard error indicated by “\*”.

Site	Al					
	0 ton		5 ton		10 ton	
B1	1.44	0.21*	2.19	0.26*	2.22	0.15*
B2	1.31	0.28*	0.94	0.05*	1.02	0.01*
M	0.90	0.07*	0.70	0.22*	0.49	0.20*
F	1.66	1.02*	0.64	0.19*	0.95	0.19*
D	0.73	0.01*	1.29	0.22*	1.70	0.40*
Mean value	1.24	0.26*	1.16	0.19*	1.29	0.21*

## Base cations

Ash fertilization have no statistical significant effect on the Ca concentration in the groundwater at the five drained peatlands ( $p = 0.408$ ). (Table 7, figure 3).

The results of the average K concentration for all peatlands summed. shows an increasing average K concentration in the groundwater with increasing dose ashes (figure 5). However the effect of treatment is non-significant ( $p = 0.093$ ). (Table 7, figure 3).

Ash treatment has no effect on the Mg concentration at these peatlands. ( $p = 0.498$ ). (Table 7, figure 3).

The treatment effect on average Na concentration is not significant ( $p = 0.298$ ). Na concentration increases slightly with increasing ash dose. (Table 7, figure 3).

The ANOVA factor site has a great impact on the Ca and Mg concentration ( $p = 0.000$ ). The site has a weak significant effect on Na concentration ( $p = 0.039$ ), but no significant effect on K concentration ( $p = 0.772$ ).



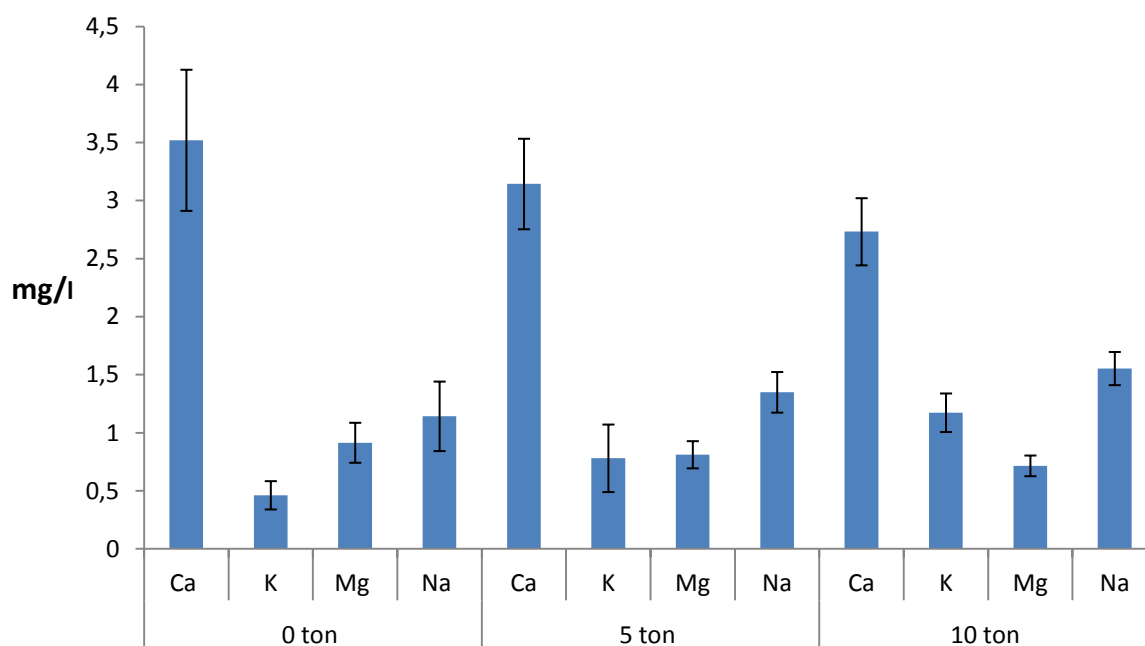


Figure 3 Average Ca. K. Mg and Na concentrations for all wetlands calculated on plots treated with 0. 5 and 10 ton ash. Standard error given with error bars.

Table 7 Average Ca. K. Mg and Na (mg/l) concentrations calculated per site and treatment. Standard error marked with “\*”.

Site	Ca <sup>2+</sup>						K <sup>+</sup>					
	0 ton		5 ton		10 ton		0 ton		5 ton		10 ton	
B1	1.95	0.35*	2.14	0.34*	2.61	0.38*	0.23	0.01*	0.35	0.11*	1.01	0.15*
B2	2.71	0.17*	2.39	0.09*	2.55	0.19*	0.26	0.01*	0.55	0.04*	1.39	0.25*
M	2.78	0.31*	3.05	0.18*	2.39	0.68*	0.18	0.04*	1.65	1.09*	0.76	0.08*
F	7.19	0.79*	5.46	0.36*	3.60	0.05*	0.79	0.24*	0.53	0.05*	1.63	0.14*
D	2.29	0.59*	2.07	0.38*	2.74	1.06*	0.94	0.43*	0.72	0.26*	1.35	0.75*



Site	Mg <sup>2+</sup>						Na <sup>+</sup>					
	0 ton		5 ton		10 ton		0 ton		5 ton		10 ton	
B1	0.46	0.09*	0.49	0.08*	0.61	0.08*	0.51	0.15*	0.84	0.17*	1.59	0.24*
B2	0.78	0.06*	0.78	0.08*	0.81	0.17*	0.85	0.42*	1.24	0.14*	1.25	0.18*
M	0.74	0.07*	0.74	0.10*	0.71	0.24*	0.52	0.05*	1.32	0.38*	1.59	0.42*
F	1.98	0.16*	1.48	0.14*	0.93	0.05*	2.43	0.86*	1.91	0.43*	1.68	0.26*
D	0.37	0.03*	0.43	0.07*	0.57	0.25*	1.39	0.09*	1.43	0.17*	1.62	0.23*

## Phosphorous. ammonium and nitrate

Average phosphorus concentrations in the groundwater for the five drained peatlands included in this study did not increase after ash fertilization. Plots treated with 0, 5 and 10 ton ash are not significantly different between each other ( $p = 0.526$ ). (Table 8, Figure 6). Data from plots treated with 0 ton ash on peatland B2 and 5 ton on peatland M include outliers-, as shown by the large standard errors. (Table 8).

Table 8 concentrations of  $\text{PO}_4^{2-}$  ( $\mu\text{g/l}$ ) at the different sites and treatments. Standard error with \*.

Site	$\text{PO}_4^{2-}$					
	0 ton		5 ton		10 ton	
B1	9.87	3.44*	14.53	6.27*	8.89	1.22*
B2	36.55	18.12*	1.46	0.12*	3.77	0.82*
M	6.75	2.50*	57.90	41.73*	4.33	1.07*
F	4.79	0.99*	3.87	0.36*	5.74	1.19*
D	3.34	1.04*	3.38	0.19*	9.02	1.27*



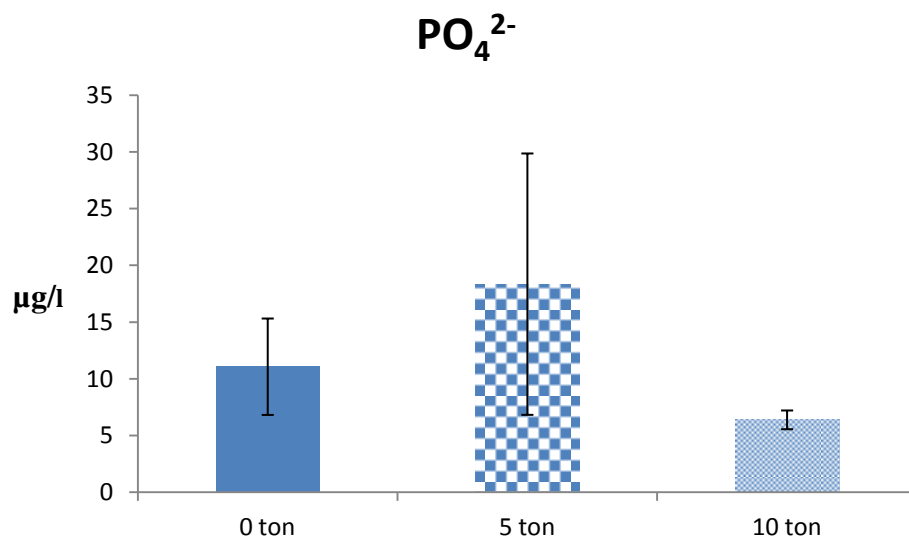


Figure 4 average  $\text{PO}_4^{2-}$  concentrations in the groundwater for all wetlands summed. Standard error given with error bars.

Average  $\text{NH}_4^+$  concentrations show a decreasing trend with increasing ash dose (figure 7), but the mean values are not significantly different from each other ( $p = 0.136$ ). However, when including the interaction factor between site and treatment in the ANOVA model, the treatment factor becomes significant ( $p = 0.000$ ). Ash doses 5 and 10 ton/ha both show lower  $\text{NH}_4^+$  concentrations than the control at the three sites B1, B2 and D. (Table 9).

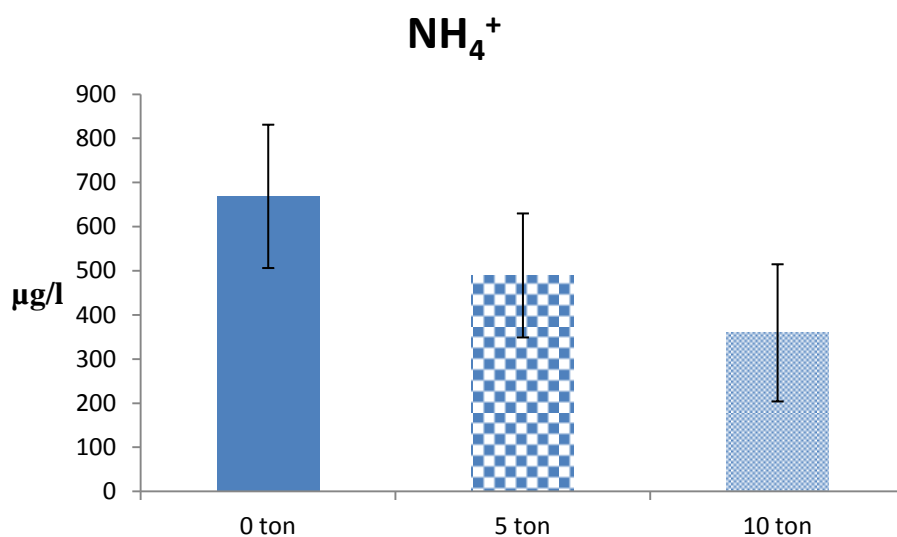


Figure 5  $\text{NH}_4^+$  concentration in the groundwater for plots treated with 0, 5 and 10 ton ash. Standard error shown with error bars.



Average  $\text{NO}_3^-$  concentrations on the five peatlands summed together seems to be unaffected after ash fertilization ( $p = 0.701$ ).

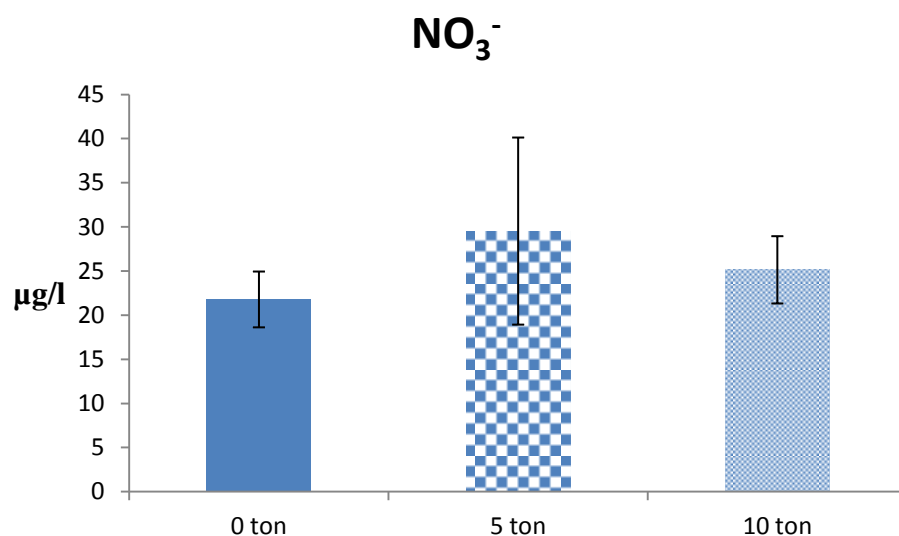


Figure 6 average  $\text{NO}_3^-$  concentrations in the groundwater for the different treatments. Standard error shown with error bars.

Table 9  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentrations (µg/l) in the groundwater for the five sites and treatments.

Site	$\text{NH}_4^+$					
	0 ton		5 ton		10 ton	
B1	236.5	113.2*	105.0	22.3*	119.8	42.7*
B2	1216.3	205.9*	37.5	10.8*	19.0	5.8*
M	194.4	135.9*	583.8	77.1*	198.6	105.4*
F	1455.9	91.9*	1303.1	137.2*	1533.1	6.5*
D	298.4	13.6*	154.5	68.3*	125.2	61.4*

Site	$\text{NO}_3^-$					
	0 ton		5 ton		10 ton	
B1	27.81	2.25*	26.91	4.48*	27.95	4.07*
B2	32.79	5.36*	15.72	0.37*	24.20	5.52*
M	12.87	2.78*	19.06	8.65*	18.89	5.75*
F	12.54	6.77*	8.09	0.96*	29.44	11.05*
D	29.01	5.28*	95.17	43*	26.98	14.57*



## DOC and MeHg

Average DOC concentrations do not significantly differ between plots treated with 0, 5 and 10 ton ash, ( $p = 0.504$ ). (Figure 7, table 10).

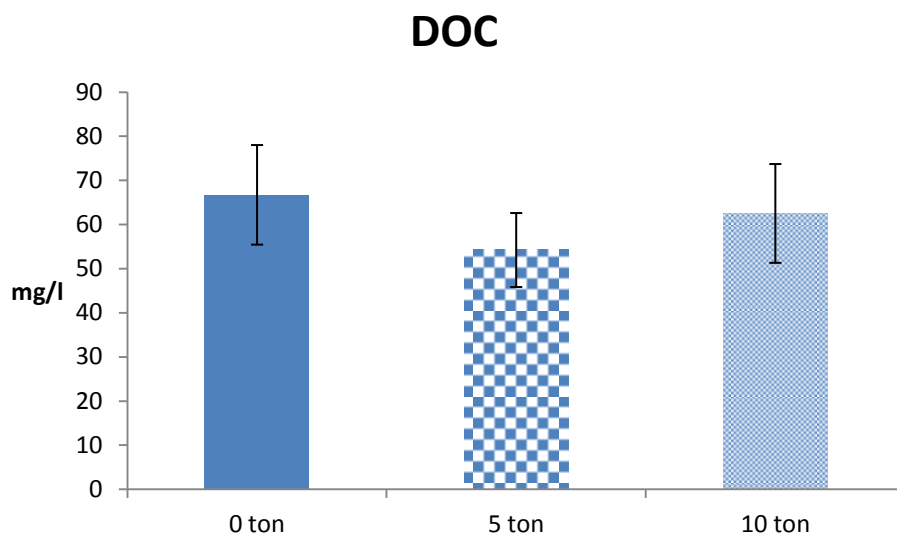


Figure 7 average DOC concentrations on plots treated with 0, 5 and 10 ton ash. Standard error given with error bars.

Average MeHg concentrations for ash fertilized plots are not significantly different from the control ( $p = 0.782$ ). Average MeHg concentrations for plots fertilized with 10 ton ash are numerically somewhat higher compared to plots fertilized with 0 and 5 ton ash, but such a pattern is vaguely indicated only at site F. (Figure 7, table 10).

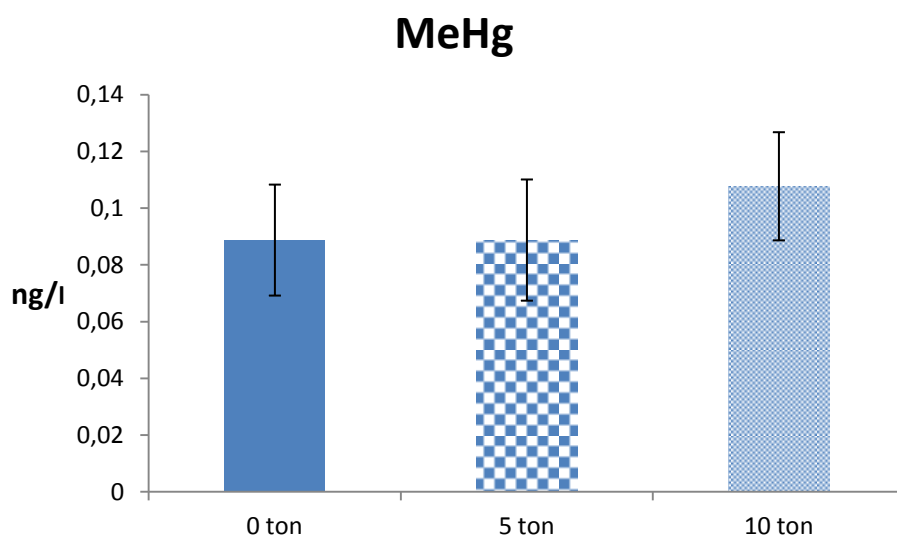


Figure 8 Average MeHg concentrations for treatments 0, 5 and 10 ton ash. Standard error with error bars.



There is a weak positive correlation between DOC and MeHg (simple correlation coefficient  $r = 0.339$  and  $p = 0.038$ ), (not shown).

Table 10 MeHg (ng/l) and DOC (mg/l) concentrations in groundwater at the different wetland treated with 0. 5 and 10 ton ash. Standard error given with \*.

Site	MeHg						DOC					
	0 ton		5 ton		10 ton		0 ton		5 ton		10 ton	
B1	0,12	0,05*	0,08	0,02*	0,10	0,04*	91,93	2,41*	93,10	4,29*	103,92	10,73*
B2	0,20	0,03*	0,05	0,02*	0,20	0,01*	99,03	15,84*	62,46	2,11*	93,54	16,75*
M	0,06	0,03*	0,14	0,07*	0,05	0,01*	55,27	4,32*	53,98	18,04*	36,30	13,48*
F	0,04	0,02*	0,09	0,04*	0,14	0,03*	66,31	34,03*	34,01	5,47*	53,69	15,00*
D	0,05	0,01*	0,06	0,02*	0,08	0,02*	14,29	1,15*	18,16	0,85*	17,38	0,66*

## Residual anions

Fluoride concentrations are almost the same for plots treated with 0, 5 and 10 ton ash ( $p = 0.266$ ).

Average chloride concentrations between treatments are not statistically different from each other ( $p = 0.924$ ).

Sulfate concentration increases with increasing ash dose, figure 11, however the concentrations are not significantly different ( $p = 0,166$ ). No correlation was found between sulfate and MeHg (simple correlation coefficient  $r = -0.198$  and  $p = 0.232$ ).

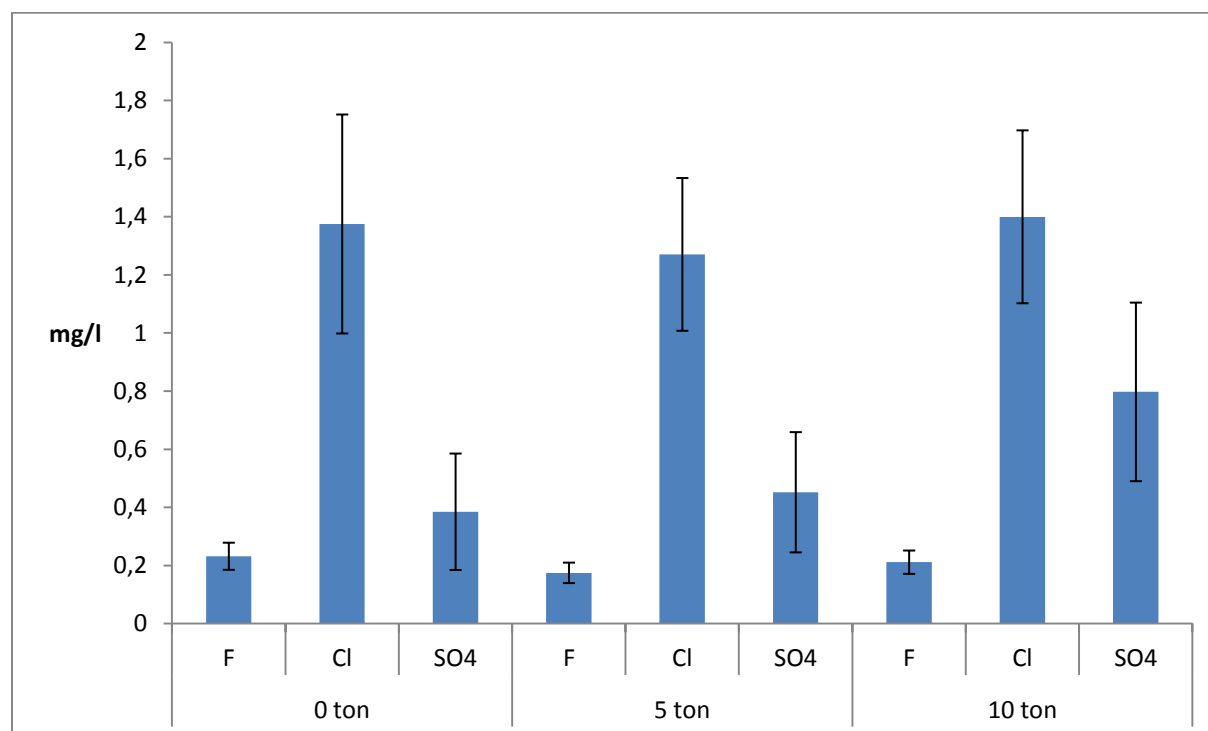


Figure 9 Average fluoride, chloride and sulfate concentrations (mg/l) summed for all sites and the treatments 0, 5 and 10 ton ash. Standard error with error bars.



## Discussion

The major aim of this thesis was to investigate if the groundwater chemistry coming from plots treated with 5 and 10 ton ash were different compared to groundwater coming from non-fertilized plots. No significant differences were found for pH-value. ANC and concentrations of: Al, Mg, K, Ca, Na, PO<sub>4</sub>, NO<sub>3</sub>, F, Cl, SO<sub>4</sub>, DOC and MeHg. The only variable that was significantly different between plots treated with 10, 5 and 0 ton ash was NH<sub>4</sub><sup>+</sup>. NH<sub>4</sub><sup>+</sup> concentration in this study was shown to decrease with increasing ash dose at the sites B1, B2 and D (table 4).

### pH-value

After ash fertilization the pH-value increases in the topsoil. Normally in the range of 0.3-2.4 units (Saarsalmi et al. 2001b). In our study we did not measure the pH-value in the soil. The groundwater samples collected at less than 1m depth, did not show any significant differences in the pH-value between fertilized and non-fertilized plots. Moilanen et al. 2002 analyzed groundwater samples from a depth of 0.9 m and also found no significant effect on the pH-value. Some studies have found a decreased pH value in the groundwater after ash fertilization (Eriksson et al. 1998; Geibe et al. 2003; Ludwig et al. 2002). The total acid/base effect of wood ash is always an alcalinization, but due to a dissolution time-lag pH-value in the soil solution may initially decrease.

Ash contains base cations balanced by Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> in soluble salts, which dissolves quickly after ash fertilization and then has an indirect acidifying effect on the soil water. This phenomenon is called exchangeable acidity and arises when base cations dissolved from these Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> salts, displace H<sup>+</sup> on cation exchange sites of the organic matter. Protons will not be neutralized, but will acidify the soil solution. The cations bound to carbonates are taking longer time to dissolve and when they are dissolved it raises the base saturation of the cation exchange sites and also neutralizes the displaced proton. It would be interesting to go back and measure the pH-value in the groundwater on these five peatlands 10 years after ash fertilization to see if the pH-value is increased then, when the full alkalizing effect of carbonates has been released.

### ANC

In a meta-analysis of ash and lime treatments of forest soils/catchments, Johansson (2014) concluded that both ash and lime doses, ranging from ca 2 to 12 ton/ha, significantly increased the ANC in stream waters. In the present study, values of ANC was not statistically different between the treatments 0, 5 and 10 ton ash ( $p = 0.943$ ). However, when an interaction factor between site and treatment was added in the ANOVA analysis, a weak significant difference appeared ( $p = 0.043$ ). This means that the ash had different effects on different peatlands. ANC increased with increased ash dose at sites B1 and B2, contrasted to that ANC decreased with increasing ash dose at site F.



## Base cations

For the base cations measured, Ca, K, Mg and Na, no significant differences were found between the treatments 0, 5 and 10 ton ash. K was the variable closest to have a significant difference ( $p = 0.093$ ) between 0 and 10 ton ash. K concentrations were higher in plots treated with 5 and 10 ton ash compared to the control. This might be due to that K is bound in ash to easily soluble salts, and therefore are one of the first elements to be set free in the soil solution after ash fertilization. When K is released to the soil solution it follows the water movement downward through the soil profile to the groundwater (Augusto et al. 2008). Most studies on soil chemistry after ash fertilization have however found an significantly increase in concentrations of Ca, K, Mg and Na in both mineral soil (Saarsalmi et al. 2006) and on drained peatland (Ring et al. 2011) & (Nilsson & Lundin 1996).

Mg and Ca ions are held more strongly in soils with a dominating fraction of permanent charge compared to soils with a pH-dependent charge. This makes organic soil more sensitive to leakage of Mg and Ca ions (Russel & Wild 1988). So the expected result should be an increased concentration of these elements in the groundwater. On organic soils the pH-value determines how many available cation exchange sites that is available to bind  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $K^+$  and  $Na^+$  ions. Ash increases the pH-value so more CEC sites gets available to bind  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $K^+$  and  $Na^+$  ions. Due to this,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $K^+$  and  $Na^+$  might be efficiently adsorbed in the top layers of these five peatlands and as a result no significantly elevated concentration of these elements were shown in this study.

The characteristics of the peat also have a major role in deciding how easily elements are leached down to the groundwater. Nutrient poor peats like sphagnum type have a higher leakage of potassium and sulfate compared to more nutrient rich peats (Pirainen et al. 2012). Leakage of  $K^+$  do not seem to be influenced by type of site in this study ( $p = 0.766$ ). There is not seen any more leakage of  $K^+$  at peatland B1, B2 and M, which are nutrient poor peatlands compared to peatland F and D considered as nutrient rich peatlands.

## Aluminum and methyl mercury

In this study the only metals studied except the base cations, where Al and MeHg. There is much work done on how ash fertilization effects the Al concentration. For MeHg there is today no published study on the effects after ash fertilization on MeHg concentrations. Studies on Al concentrations shows contradictory results Saarsalmi et al. (2001b) & Geibe (2003) have found a decreased Al concentration after ash fertilization. This is explained by the increased pH-value induced by the ash which makes Al to fall out as aluminium hydroxide, which is insoluble. On the other hand Lundell et al. (2001) & Ludwig et al. (2002) found increased Al concentrations after ash fertilization; this might be due to a higher mineralization rate that often results in a higher concentration of mobile DOC which Al strongly binds to and follows. In this study no differences in Al concentrations were found after ash fertilization ( $p = 0.912$ ).



MeHg concentration were not significantly different between treatments ( $p = 0.782$ ). Sulfate-reducing bacteria (SRB) thrives in environments with a  $\text{SO}_4^{2-}$  concentration that lies between 20-50 mg/l (Ullrich et al. 2001). At all sites and treatments the  $\text{SO}_4^{2-}$  concentration was far below that (2 mg/l) and the  $\text{SO}_4^{2-}$  concentration did not increase with increasing ash dose.

A weak positive correlation between DOC and MeHg was found in this study. (correlation coefficient  $r = 0.339$  and  $p = 0.038$ ). MeHg binds to thiol-groups in the organic matter (Skylberg, 2008). According to Qian et al. (2002) in most soils the thiol-groups exist in excess compared to the amount of MeHg, so this would mean that most of the MeHg is bound to the organic matter and therefore follows the movement of DOC to a great extent (Karlsson et al. 2003). The DOC concentration in the groundwater did not differ between treatments in this study ( $p = 0.504$ ).

Earlier studies in peatlands have found the highest net production of MeHg during summer, because SRB methylation rate is at an optimum at 20 degrees (Bloom et al. 2004). So, if there is a significant net production of MeHg in any of these wetlands our samplings in early September appear appropriate. However there can be a time lag before the MeHg might be transported down to the groundwater, which depends on the percolation rate of water in the peat. Hydraulic conductivity decreases with increasing depth. Also, the summer 2014 was a very dry summer. The groundwater levels in early August were exceptionally low, which can have affected the results.

### **$\text{PO}_4^{3-}$ , $\text{NO}_3^-$ and $\text{NH}_4^+$ concentrations**

Concerning the results of  $\text{PO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  concentrations, only  $\text{NH}_4^+$  was detected to differ between treatments when an interaction factor between site and treatment was used in ANOVA ( $p = 0.000$ ). There was a decreasing trend of  $\text{NH}_4^+$  concentration with increasing ash dose at site B1, B2 and D. According to Russel et al. (1988) an increased pH-value leads to increased mineralization rate, which results in an increased release of  $\text{NH}_4^+$  to the soil. The formed  $\text{NH}_4^+$  is in oxygen rich environments and at high pH-values quickly transformed to  $\text{NO}_3^-$ . pH-values above 4 intensifies the nitrification process. So with this fact the trend of decreasing  $\text{NH}_4^+$  concentration at sites treated with 5 and 10 ton ash, might be due to intensified conversion of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  compared to control sites, due to the higher pH-value in the topsoil at ash treated sites. Significantly increased  $\text{NO}_3^-$  concentrations at ash treated sites were, however not apparent in the groundwater samples ( $p = 0.701$ ). Another possible explanation to the decreasing  $\text{NH}_4^+$  concentration in the groundwater at ash treated plots, may be that the cation exchange capacity is increased in the surface peat since CEC increases with increasing pH-value and decreasing water content. When pH increases in the soil,  $\text{H}^+$  is deprotonated from OH-groups and carboxyl groups and this results in negatively charged sites on the organic matter, which then attract positively charged ions such as  $\text{NH}_4^+$ . A further possible explanation for declining  $\text{NH}_4^+$  levels with increasing ash dose, might be that the ash promotes increased forest growth and the trees are competing harder for available nitrogen in the soil.

In my study the phosphorus concentration was not increased in the groundwater three years after application, ( $p = 0.526$ ), (fig 4). This is in line with findings by (Ring et al. 2011;



Nilsson et al. 1996) that did not find an increased P concentration in the groundwater. There can be three possibly reasons behind this: i) the amount of phosphate that gets immobilized by soil organisms can be high. Phosphate is only available when the soil organisms needs of phosphate has been satisfied. Mineralization of P happens at a C: P ratio of around 200:1; ii) phosphorous has a low solubility from the ash (Ring et al. 2011; Nieminen et al. 2005) and iii) ash contains Fe and Al hydroxides which has been shown to efficiently adsorbs P (Pirainen et al. 2012).

## **SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup>**

The most soluble salts (K<sup>+</sup> and Na<sup>+</sup> -chlorides and -sulphates) should, according to Arvidsson (2003), dissolve within a 6 years period. In this study the Cl<sup>-</sup> concentration where not higher in ash fertilized plots compared to control plots, (p = 0,924), (figure 9). The SO<sub>4</sub><sup>2-</sup> concentrations were also not significantly higher in fertilized plots compared to control, although the mean value of SO<sub>4</sub><sup>2-</sup> where higher compared to control.

## **Implications**

The fact that most of the variables in this study were not significantly different between ash fertilized and control plots, may be due to the sampling of groundwater instead of sampling of soil solution in the unsaturated zone. This may indicate that most elements in the ash are efficiently retained in the surface peat, or that the ash dissolves very slowly. The ash used in this study was a granulated and very well hardened wood ash, with relatively high silicon content (15%) and moderate calcium content (16%). Furthermore, an analysis of a single composite sample consisting of 3 year old granules retrieved from the forest floor at one of the field sites, revealed concentrations of approximately 75% of the initial, for the cations Na, K, Ca and Mn. P and Mg appeared to be retained even stronger.

According to a study by Ring et al. 2011, most variables were significantly different between ash fertilized and control plots, when the soil solution was sampled at a depth of 30-40 cm in the peat. The relatively low groundwater level at the time of sampling in the present study, may have added to this discrepancy between this study and Ring et al. (2001). However I think this study at these five peatlands confirms that there is a low risk of undesirable leakage of e.g. nitrate, ammonium nitrogen and phosphate. Because of this I see ash as an effective tool that can be used for i) promoting forest growth, ii) counteracting acid depositions and iii) closing the nutrient cycling after harvest. However, the maximum dose of 3 ton ash/ha, which is currently recommended by The Forestry Board, is probably too low to raise the alkalinity of the peat groundwater. This conclusion is in agreement with Nohrstedt (2001), who concludes that 3 ton/ha is insufficient to substantially raise the alkalinity in runoff water from mineral soils.



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