THE EFFECT OF MINING WASTE WATER ON GREENHOUSE GAS FLUXES AND ECOSYSTEM RESPIRATION IN TWO BOREAL PEATLANDS

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ABSTRACT

Metal mining produces waste water that include pollutants such as nitrate, ammonium, sulfate and heavy metals. Natural peatlands are an inexpensive method of treating mining waste water before releasing it back to natural water bodies and thus, this method has been frequently used in Finland and around the world.

The aim of this study was to investigate the effects of mining waste water on the chemical and microbiological processes and greenhouse gas emissions of two northern boreal peatlands. For this purpose, the fluxes of three main gases contributing to global warming, carbon dioxide, methane and nitrous dioxide, were studied by a gas chamber method. Samples were collected from two treatment peatlands influenced by mining waste water, and from an adjacent pristine peatland.

The results suggest that mining waste water highly effects the greenhouse gas dynamics and underlying processes of boreal peatlands. Peatlands used for waste water treatment had larger nitrous oxide and significantly lower methane fluxes than the untreated site. Results show higher nitrous oxide emissions with high nitrogen loads from the waste water. Compounds, such as sulfate, in mining waste water also seem to limit methane emissions from treatment peatlands. This is likely caused by increased activities of sulfate reducing microbes that dominate methanogens in competition over resources. The effect of the drastically higher N_2O emissions to global warming potential is counterbalanced by the effect of the greatly lower CH_4 emissions. Mining effluents also seem to influence the processes controlling ecosystem respiration and carbon dioxide balance of these wetlands. Ecosystem respiration rates were significantly higher on treatment plots closest to the waste water inlets on both peatlands, possibly because of changes in wetland nutrient status.

Boreal peatlands are heterogenic environments that are affected by various microbial and chemical processes. Northern soils are also subjected to year-round changing weather conditions. It was only possible to study a small part of these factors in the scope of this thesis. Nevertheless, this study gives valuable new insight on the effects that mining waste water have on the treatment peatlands greenhouse gas balance, a scarcely studied topic so far.

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ABBREVIATIONS

Al	aluminium
As	arsenic
C	carbon
CH_4	methane
Cl^-	chloride
CO_2	carbon dioxide
Cu	copper
EC	electrical conductivity; reflects the ability of material to conduct electrical current through it
ER	ecosystem respiration; sum of respiration of living organism in an ecosystem
Fe_3^+	ferric iron
GEP	gross ecosystem photosynthesis; total fixed carbon from photosynthesis by primary producers in an ecosystem (including photorespiration)
GPP	gross primary production; total fixed carbon from photosynthesis by primary producers in an ecosystem without photorespiration
H	hydrogen
IPCC	Intergovernmental Panel on Climate Change
Mn_{2+}	manganese
N	nitrogen
NEE	net ecosystem exchange; net primary production minus carbon losses in heterotrophic respiration
NH_4^+	ammonium
NO_2^-	nitrite
NO_3^-	nitrate

NPP	net primary productivity; gross primary production (GPP) minus autotrophic respiration (by plants)
N_2O	nitrous oxide
P	phosphorus
pH	negative logarithm of the nitrogen ion concentration (-log $[H^+]$;, ranging from 0 to 14 (7 is neutral)
PO_3^{4-}	phosphate
RP	reference plot; plot 0 on the reference peatland
S	sulfur
SO_4^{2-}	sulfate
TOC	total organic carbon
TP	treatment plot; study plot on either treatment peatland (A or B)

1 INTRODUCTION

Mining industry has been increasing for years in Finland and around the world. Mines produce vast amounts of polluted waste water that needs to be treated before release to the environment. Wetlands and peatlands are a commonly used waste water purification method in Finland and globally. Use of wetlands, especially pristine peatlands, for this purpose can have major effects on their microbiology, vegetation and greenhouse gas balances, but studies on this matter are scarce.

Boreal peatlands have a significant role in global greenhouse gas balance. Pristine peatlands act naturally as sources of methane (CH_4), but as sinks of carbon dioxide (CO_2). Nitrous oxide (N_2O) emissions from peatlands are greatly controlled by availability of nitrate (NO_3^-), which is usually limited, and thus peatlands often act as sinks or sometimes as small sources, of N_2O.

This thesis reports the influence of mining drainage and process waste waters have on two treatment peatlands that were formerly natural mires. The two treatment peatlands were studied in June, July and August of 2014. The study has been conducted in close co-operation with *Wetlands geochemical interaction mechanisms and optimizing the purification efficiency on mines* -project by the University of Oulu. The project was funded by Niemi Foundation and scholarships to the author were provided by Maaperän tutkimus- ja kunnostusyhdistys ry (MUTKU) and Maa- ja vesitekniikan tuki ry.

2 MINING WASTE WATERS

The number of gold and other metal mines is increasing. These produce large amounts of mining waste water (Kauppila et al. 2011, Palmer et al. 2015). Waste waters come from all mining operations, from mining drainage, mineral extraction, processing (e.g. beneficiation) and metallurgical extraction (i.e. collection of industrial minerals) (Lottermoser 2010, Pöyry 2010). All mining discharges are different in composition (Wood 2012). Nevertheless, these process and drainage waters often contain substances such as sulfate (SO_4^{2-}), phosphate (PO_4^{3}), and N compounds (e.g. NO^{3-}, NH^{4+}). Mining waste waters can also contain other hazardous substances such as metals (e.g. iron, nickel, copper, mercury, zinc), metalloids (e.g. arsenic, antimony) and radioactive compounds depending on the ore composition. Also, lead, acids, baces, salts and process chemicals can be present in mine waste waters (Kauppila et al. 2011, Palmer et al. 2015). Waste water can cause problems by releasing suspended and dissolved solids as well (Wood 2012, Lottermoser 2010). Table 1 presents the measured compounds in waste water at the studied metal mine in 2014.

Table 1. Waste water composition and input to the treatment peatlands A and B of the studied metal mine in 2014 (Based on environmental monitoring data provided by the mine company).

Compounds	TP A input (kg d^{-1})	TP B input (kg d^{-1})
Total-N	53.9	72.1
Ammonium-N	31.7	12.0
Nitrate-N	19.0	58.3
Nitrite-N	1.92	0.62
Sulfate	16400	4780
Suspended solids	5.45	11.8
Fe	0.22	0.21
Mn	2.61	0.51

Mining of sulfidic ores can lead to acid mine drainage due to weathering and oxidation of sulfides (Lottermoser 2010, McLemore 2008, Wood 2012). Sulfides are common in minerals and can be found for example in metallic and phosphate ores and mineral sands. Pyrite (FeS_2) is the most common sulfide mineral. Oxidation of pyrite has been proven taking place even in permafrost areas. Acid drainage can be released from tailing damns, waste rock dumps and spoil heaps, heap leach piles, underground and open pit mines (Lottermoser 2010, Wood 2008). High pH can release increased amounts of arsenic (As) and sulfur (S), aluminum (Al), ferric iron (Fe^{3+}), copper (Cu) and manganese (Mn^{2+}) from the ground (Wood 2012, Lottermoser 2010). Not all mining waste waters are acidic, but even alkaline and neutral waters may hold high concentrations of metals. Acidity is highly dependent on the geology of the mining site (Wood 2012). Excavation of tunnels also demands chemicals. Ammonium nitrate is widely used in explosives used for excavation of tunnels (Hämäläinen 2015, McLemore 2008). Nitrate (NO_3^-) is also known as a fertilizer and is one of the most water soluble of anions (McLemore 2008).

Process water quality and composition depend on the techniques applied in mineral and hydrometallurgical processes. In hydrometallurgy, several different types of chemicals are used. These are flotation reagents (e.g. oils, xanthates), modifiers (e.g. pH regulating lime and ammonia, sulfates, nitrates), flocculants and coagulants (e.g. metal hydroxides and sulfates), hydrometallurgical agents (e.g. sulfuric acid, cyanide) and oxidants (e.g. peroxide and chlorides). Cyanide leaching is the dominant method of gold extraction and cyanide compounds (CN^-) can be used also as flotation agents in the extraction of base metals (Lottermoser 2010, Pöyry 2010, McLemore 2008, Kauppila et al. 2011). Instead of cyanide, other leaching agents such as ammonia (NH_3), thiocyanate (SCN^-) or thiosulfate ($S_2O_3^{2-}$) can be used (Lottermoser 2010). Thiocyanate, ammonia and nitrates are also degradation products of cyanide and common in mining wastes (McLemore 2008). Cyanide reduction is commonly used method of decreasing CN^- levels in the waste water, and this is generally conducted by pumping them to tailing damns before further release to the environment (Lottermoser 2010, Pöyry 2010).

Climate (i.e. rain fall and temperature) is a big controller of the amount and quality of mining waste water produced (McLemore 2008). Water that cannot be recycled, needs to be processed for example by clarification, chemical or passive treatment before it is released to the environment (McLemore 2008, Palmer et al. 2015, Kauppila et al. 2011). In passive treatment systems, such as wetlands and settling ponds, natural chemical and biological processes are used to reduce amounts of harmful compounds in mining waste water. These treatment systems also include constructed and natural wetlands which are good at retaining substances such as metals and suspended solids. Removal of metals in passive treatment works by formation and precipitation of metal oxides and hydroxides, microbial sulfate reduction, organic complexation reactions, exchange with other cations on negatively charged sites and direct plant uptake. Wastes can be also attached to substrate materials, adsorbed or by metal exchange and by microbial reduction (Gusek & Figueroa 2009, Wood 2012). Removal on nutrients, and other harmful substances, by using wetlands is cost and energy efficient. Non-treated waste waters are a higher risk in causing eutrophication and other deterioration consequences to downstream water systems and overall water quality (Nichols 1983).

3 GREENHOUSE GAS EMISSIONS FROM NATURAL PEATLANDS

Peatlands, also called mires, are wetlands where most of the dead, decomposing plant matter (i.e. detritus) is accumulated to the soil surface. High water table slows down decomposition rates in peatlands, where carbon is accumulated into new plant biomass. Peatlands can be divided into nutrient poor ombotrophic bogs and nutrient rich minerotrophic fens. Northern peatlands cover around 3-4 million km^2 and contain 10-20 % of global carbon (C) storage (Frolking et al. 2013, Laine et al. 2013, Winde 2011). This C storage can be transformed into dissolved or particulate organic matter - or to gaseous compounds, such as CO_2 and CH_4. Carbon dioxide and CH_4 fluxes have had a net cooling effect of about -0.4 W m^{-2} through the Holocene and they are still accumulating in carbon. Nowadays, CO_2 and CH_4 are major components contributing to global warming. Another significant greenhouse gas, N_2O can also be produced in peatlands microbiological processes (Frolking et al. 2013).

Greenhouse gases have different global warming potentials (GWPs) based on their radiative forcing capacity and lifetime in the atmosphere (IPCC 2007). These are usually presented in comparison to the GWP of CO_2, i.e. as CO_2 equivalents, or as calculated radiative forcing increases (Table 2).

Table 2. Carbon equivalents (CO_2 eq.), global warming potentials (GWP) for a 100-years period and increased radiative forcing potentials of carbon dioxide (CO_2), methane (CH_4) and nitrous dioxide (N_2O) (IPCC 2013 & IPCC 2007).

GHG	CO_2 equivalent	GWP (100-yrs)	Increased radiative forcing (W/m^2)
CO_2	1.00	1.00	1.94
CH_4	21.0	28.0	0.50
N_2O	310	265	0.20

Vegetation on peatlands consists mostly of woody plants such as trees and shrubs, graminoids (e.g sedges, grasses) and forbs (i.e herbaceous plants). Unlike most terrestrial environments, peatlands are usually dominated by bryophytes such as mosses and lichens. Bryophytes have no roots or vascular systems and their metabolic rates are strongly influenced by their leaf water content. Bryophytes are quick responders to seasonal changes and it has been proposed that they are mainly responsible for net ecosystem productivity in early spring, and maybe to a lesser extent in the fall. These nonvascular plant species are usually the first ones to cycle nutrients, but nutrient additions have been found to promote the growth of vascular plant species because they compete better for light than bryophytes (Frolking et al. 2013).

3.1 Methane emissions

Peatlands release large amounts of methane to the atmosphere. Northern peatlands are one of the largest sources of atmospheric CH_4 releasing 10 - 65 x 10^{12} g CH_4 y^{-1}, around 25 - 40% of global CH_4 emissions (Walter et al. 2001, Mikaloff Fletcher et al. 2004, Strack et al. 2008). The net CH_4 emissions are determined by the amounts of produced, consumed (Hynninen 2011) and transported CH_4 in soil and water (van Hulzen et al. 1999).

Methane is produced through methanogenesis by methanogenic archaea such as Methanobacteriaceae, Methanosarcinaceae and *Methanoregula* (Hynninen 2011, Strack et al. 2008). Methanogenesis is a form of anaerobic respiration of microbes and a part of anaerobic decomposition. Both aceticlastic and hydrogenotrophic pathways are used for CH_4 production (Pester et al. 2012). CO_2, formate, acetate and methylated compounds work as carbon source (i.e. electron acceptors) in the process. Substrates used for this are formed by fermentative bacteria, so peat quality and pH also play a role in CH_4 production (Pester et al. 2012). Freshwater wetlands provide high amounts of substrates for CH_4 production in organic matter. In natural wetlands, CH_4 production is also supported by low availability of oxidizing agents (e.g. O_2, NO_3^-, Fe^{3+} and SO_4^{2-}) for other carbon degradation processes (Liikanen et al. 2006). Production rate, and less so oxidation, of CH_4 is also linked to soil temperature and water table level (Bubier et al 1995, Yu et al. 2013).

Methane emissions in the north are highly influenced by temperature changes that control the rate of microbial activity, making it highly seasonally and annually variable (van Hulzen et al. 1999, Bubier et al. 1995, also Mikaloff Fletcher et al. 2004). Estimates suggest high emissions during summer and very low ones in winter. It is estimated that an increase of 1 °C in soil temperature can lead to 20% increase in wetland CH_4 emissions (Walter et al. 2001). Van Hulzen et al. (1999) found a ten degree (°C) increase in temperature increasing CH_4 production by 1.3 – 28 times. CH_4 production was shown to increase up to temperature of 30 °C. At lower temperatures (> 4 °C) electron acceptors and methanogenic biomass were found to be the limiting factors for methanogenesis (van Hulzen et al. 1999). Since methanogenesis takes place in anoxic environments, water table height has also been shown to have a great effect on CH_4 emissions. An increase of approximately 20% in precipitation, has shown to increase CH_4 emissions by 8% (Walter et al. 2001).

Methane can be transported to the atmosphere by diffusion through the soil or bubbling (i.e. ebullition), or can also be diffused through vascular plant species. Methane can be partly oxidized into CO_2 during transportation by methanotrophic microbes i.e. methanotrophs (Bubier et al. 1995). Methanotrophs consume CH_4 in an aerobic oxidation process. This process is common in peatlands and often associated with mosses such as *Sphagnum*. In a study by Kip et al. (2010) methanotrophic oxidation has been seen to increase with temperature and being

especially pronounced in submerged mosses. Vascular vegetation can also provide fresh substrates for CH_4 production. Due to vegetation and higher water tables, fens usually emit more CH_4 than bogs. Emissions are largely variable both temporally and spatially (Bubier et al. 1995).

Wetland also have sulfur reducing micro-organisms that can affect CH_4 cycling and carbon mineralization. Sulfur reduction is thermodynamically preferable to methanogenesis (or fermentation), therefore reducing CH_4 production (Pester et al. 2012, van Hulzen et al. 1999). Methanogenesis could be limited due to sulfate reducing bacteria consuming hydrogen and acetate, which are essential to methanogenesis, when SO_4^{2-} is present (Oremland & Polcin 1982, Pester et al. 2012). Competition over methylated compounds has not been detected on studies (Oremland & Polcin 1982). Northern peatlands have shown high sulfate reduction potentials in the laboratory studies (Moore & Basiliko 2006).

3.2 Nitrous oxide emissions

Nitrous oxide (N_2O) is produced in the denitrification process, usually in the anoxic layer of the wetlands called the catotelm (Nichols 1983, Yu et al. 2013, Winde 2011, Huang et al. 2014). Under anoxic conditions, facultative anaerobic bacteria use NO_3^- instead of oxygen (O_2) as terminal electron acceptor for respiration. Organic compounds (i.e. carbon sources) are used as electron donors. Nitrate (NO_3^-) is converted to nitrite (NO_2^-), then to nitric oxide (NO), nitrous oxide (N_2O) and finally to nitrous gas N_2. In case of incomplete denitrification N_2O is released into the atmosphere as the end product (Nieminen 1998). Naturally wetlands produce low amounts of N_2O or are even N_2O sinks (Strack et al. 2008).

N_2O production is dependent on available NO_3^- (Silvan et al. 2005). Nitrate (NO_3^-) is oxidized from ammonium (NH_4^+) during nitrification processes that occur under the oxic conditions e.g. in the surface layer, the acrotelm (Strack et al. 2008, Yu et al. 2013, Winde 2011, Nichol 1983). These processes are conducted by ammonia-oxidizing microbes. Examples of denitrifying bacteria are *Pseudomonas*, *Achromobacter*, *Bacillus* and *Micrococcus* (Palmer et al 2010, Liikanen et al. 2006).

The two main microbial reactions producing N_2O are nitrification and denitrification (Robertson & Groffman 2007):

nitrification	$NH_3 \rightarrow NH_2OH \rightarrow NO_2^- \rightarrow NO_3^-$ or N_2O
denitrification	$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$

For denitrification, NO_3^- needs to diffuse down to anoxic portion of the soil (Nichols 1983) and naturally this often works as limiting factor in the process (Strack et al. 2008). Other factors that control microbial nitrification and denitrification processes are the availability of soil moisture, pH, soil and air temperature (Strack et al. 2008), also soil redox potential (Palmer et al. 2010). Water table level and overall moisture conditions on peatlands control the formation of oxic and anoxic conditions and therefore the location of and extend of microbial processes in peat. Nitrous oxide emissions have found to higher on peatlands with lower water tables due to increased nitrification activity and availability of NO_3^- for denitrification (Liikanen et al. 2006). N_2O is formed mostly on neutral and close-to-neutral pH conditions, but also acid-tolerant denitrification has been recorded especially in peatlands (Palmer et al. 2010, Kolb & Horn. 2012, Maljanen et al. 2009). Denitrification usually increases with temperature (Palmer et al. 2010), but peat soils have also shown ability to produce N_2O even in conditions below zero Celsius (Maljanen et al. 2009, Palmer et al. 2011). N_2O emissions have shown potential for very high temporal variability possibly due to soil freezing and thawing (Strack et al. 2008, Maljanen et al. 2009, Palmer et al. 2011, Liikanen et al. 2006). In northern areas, soil can be frozen up to six months of the year. N_2O emissions are often limited by ice and snow that prevents diffusion and gas exchange (Maljanen et al. 2009).

Nitrification and denitrification processes are enhanced when organic compounds and exudates are present (Strack et al. 2008, Nieminen 1998). Denitrification is often limited by the lack of easily degradable organic carbon. In peatlands, denitrification has also been shown to be limited by availability of NO_3^- (Nichols 1983, Palmer et al. 2010). Bogs usually have lower emissions due to lower pH and N availability than fens. Nitrogen fertilization can enhance N_2O production at least on the forested and agricultural peatlands. Demand of N can also result in higher N_2O emissions on the winter period when plant uptake is lacking and moisture levels are more constant (Nieminen 1998, Strack et al. 2008). Also, ammonia-oxidizers have shown to thrive in conditions of high total NH_4^+ and organic carbon (Huang et al. 2014).

Nitrite (NO_2^-) can also be oxidized to NO_3^-. Nitrous oxide can be formed as a by-product of nitrate reduction (Palmer et al 2010, Liikanen et al. 2006). Also, chemodenitrification of nitrate to N_2O is possible under anoxic, low pH conditions. In cryoturbated, largely water-filled peat, denitrification, instead of nitrification, can be the major source of N_2O in some cases (Palmer et al. 2010).

3.3 Carbon dioxide emissions and ecosystem respiration

Natural peatlands act as net sinks for carbon dioxide (CO_2) and in northern peatlands 200 - 450 x 10^{15} g of carbon is stored representing up to 30 % of global soil C (Gorham 1991, Strack et al. 2008). Carbon is fixed by plants from the atmosphere by photosynthesis and stored to the peat where it gradually decomposes. Decomposition takes place under anoxic conditions and hence hydrological changes greatly effect CO_2 emissions (Gorham 1991).

Plants allocate CO_2 to their biomass by autotrophic respiration which also returns CO_2 to the atmosphere during respiration and decomposition of plant material. CO_2 is also released by microbial, bacterial and fungal dominated, i.e. heterotrophic respiration, during decomposition process. Combined auto- and heterotrophic respiration is called ecosystem respiration (ER). The amount of ER is highly dependent on soil temperature and moisture (Malmer et al. 2005). Total ecosystem CO_2 exchange (NEE) is the difference between plant uptake (GEP) and ER (Strack et al. 2008). It was estimated that Northern peatlands are net sinks for atmospheric CO_2 around 47 g CO_2-C m^{-2} y^{-1} (Gorham 1991). More recent estimates have been lower, but with wide confidence intervals, showing net CO_2 exchange (NEE) sinks between 7 - 359 g CO_2 m^{-2} y^{-1} (Strack et al. 2008).

Productivity of vegetation drives photosynthesis and ER. This is controlled by temperature, the hydrological conditions and nutrient status of the peatland (Strack et al. 2008, Yu et al. 2013). Generally, CO_2 production increases with lower water table, because this produces more oxic conditions and higher decomposition rates of organic matter (Liikanen et al. 2006). ER and substrate quality are also dependent on the plant species (Strack et al. 2008). Plant species in peatlands are dominated by nonvascular plants, such as mosses, due to high water coverage

and soil saturation (Belyea 2013). Naturally low amounts of CO_2 are being produced from ecosystem exchange in the peatlands and soil respiration contributing to the net primary production (Moore & Basiliko 2006). Microbial activity and decomposition are limited under waterlogged conditions and acidic waters due to limited oxygen convection, diffusion and pH preferences (Yu et al. 2013). In northern areas, soils can be frozen up to six months a year. Frozen peat slows down decomposition and also transportation to gaseous forms (CO_2 and CH_4) (Frolking et al. 2013).

4 MINING WASTE WATER TREATMENT IN PEATLANDS

Constructed wetlands have been used for over 50 years for treatment of many kinds of wastewaters, including municipal and industrial ones (Sheoran & Sheoran 2006). Natural wetlands have the capacity to remove effluent substances, especially nutrients (Nichols 1983). Constructed wetlands utilize the same processes that take place in natural wetlands, such as waste purification by vegetation, soil and microbial processes, but in a designed and controlled manner (Sheoran & Sheoran 2006). Natural wetlands can provide a more diverse purification processing than totally constructed wetlands due to the soil properties and biochemistry and flow patterns. These include chemical and physical processes, oxidation and reduction, precipitation, sedimentation and plant uptake (Palmer et al. 2015, Ronkanen & Kløve 2009, Winde 2011). Wetlands prolong flow time and provide wide surface for filtration and adsorption, adhesion and aggregation on the surfaces of plant roots, soil and mineral particles (Palmer et al. 2015, Ronkanen & Kløve 2009, Vymazal 2014). Vegetation acts as a filter and settling place for organic and inorganic particulate matter, nutrients and other substances. It also acts as substrate provider for decomposing micro-organisms (Nichols 1983). Co-precipitation, sorption and cation exchange are methods for removal of contaminants. Effectivity of these processes depends on physical, chemical and biological variables such as substrates, pH, waste water quality and plant species (Sheoran & Sheoran 2006). Purification can be ongoing and may improve with age or degrade as peat gets saturated. Best retention has been discovered on areas closest to the waste water distribution ditch (Palmer et al. 2015).

Peatlands used for waste water treatment typically have higher water level than natural peatlands and hydrological conditions vary because of constant surface and subsurface water flow (Vymazal 2014). Water flow brings also oxygen to the peatlands (Wood 2012), but reduces oxygen diffusion rates to the peat soil. Oxygen gets to the wetlands also through plant photosynthesis (Vymazal 2014). Peat becomes more transmissive with higher water table and less transmissive with lower one. Therefore, water is discharged faster with more hydrological loadings (Belyea 2013). If hydraulic loading to the wetlands are very high, nutrients may only be removed by sedimentation (in case of particulate forms) because of the short retention time. Retention time is increased in deeper water peatlands but reactions with wastewater nutrients and soil are decreased (Nichols 1983, Reddy et al. 1978, Winde 2011). Another one of the soil characteristics controlling removal and retentions capacities, is the cation exchange capacity of the peat. Ammonium (NH_4^+) is generally retained by cation exchange while NO_3^-, as it remains in soluble form, is more likely to be retained by vegetation or microbes if any. Potential for cation exchange of peat is generally high and therefore NH_4^+ is highly retained (Hynninen 2011). Highest NH_4^+ cation exchange capacity has been discovered in the surface peat of treatment peatlands (Ronkanen & Kløve 2009).

Nitrogen (N) is removed by ammonification, nitrification-denitrification, adsorption, ions exchange, sedimentation, volatilization, precipitation, biological assimilation and plant uptake (Ronkanen & Kløve 2009, Vymazal 2014). Denitrification is a viable method for removal of N from wetland wastewaters. As mentioned earlier (in chapter 3) this process turns NO_3^- into its gaseous form N_2 (Nichols 1983). It has been discovered by Reddy et al. (1978) that in NO_3^- containing waterlogged soils the denitrification pace was determined by NO_3^- concentration and the diffusion rate from the water to the soil (Nichols 1983). Bacterial and algae fixation of N into forms more available for plants can reduce nitrogen's removal capacity. These are common e.g. in mosses such as *Sphagnum.* Large amount of N supply has been detected to decrease fixation amounts. Nitrate (NO_3^-) removal might be reduced by general favoring of NH_4^+ by plants instead of it as N supplement. Plants take up nutrients but also release them back to water and soil which can lead to net N leaching. With non-rooted plants, such as *Sphagnum,* which take nutrients from the water directly, N intake can be considerably higher (Nichols 1983). Inorganic N can be largely obtained by vegetation and therefor have smaller effects on denitrification (Moore & Basiliko 2006). Naturally wetlands are small nutrient sinks. Peat acts as permanent sink accumulating nutrients into soil. Retention takes places mostly in

growing season especially in the spring and is low otherwise. Peat can be saturated and then release nutrients stored earlier (Nichols 1983). Nutrient addition can also alter the vegetation composition of wetlands (Liikanen et al. 2006). Dead vegetation leads often to net export of nutrients in certain times of the year. Assimilated nutrients can leach out during winter and autumn leading to low overall retention efficiency. This might still benefit downstream ecosystems and prevent eutrofication due to nutrients being bound in growing season and released partly in non-available form (Nichols 1983).

Peatlands are generally considered to retain metal and metalloids well. Removal of metals and other substances depends also highly on the water-soil contact (Vymazal 2014, Winde 2011). Peatlands provide very good retention to As, antimony (Sb) and nickel (Ni) (Palmer et al. 2015). Removal of chromium (Cr), Cu and selenium (Se) are also found to be good (Sheoran &Sheoran 2006). In an ongoing treatment peatland, iron have been found to be retained poorly which suggests that ongoing waste water loads are not sustainable (Palmer et al. 2015). Natural wetlands have found to degrade, or even die, in quality in this use, mostly by the low pH and high metal concentrations (Gusek & Fugueroa 2009, Wood 2012). Lower anoxic layer enable the reduction of such compounds as Fe^{3+}, Mn^{4+} and SO_4^{2-}. Micro-organisms produce sulfide (S^{2-}) from SO_4^{2-} (Sheoran & Sheoran 2006). Also, water flow provides oxygen that aerates surface peat. Amount of SO_4^{2-} is high due to ongoing water from processes and drainage, sulfate precipitation is likely and reduction possible. Sulfate reduction on treatment peatlands used for some years have also been found to be poor (Palmer et al. 2015).

The lifetime of treatment peatlands seems to be limited (Palmer et al. 2015). General lifetime of treatment wetland is 20 - 30 years, and its adsorption capacity might decrease over time (Ronkanen & Kløve 2009, Palmer et al. 2015, Sheoran & Sheoran 2006). This capacity is highly dependent on the input water quality (Sheoran & Sheoran 2006). Contaminants may also leach out due to circumstances such as snowmelt or mine closure (Palmer et al. 2015).

5 METHODS

5.1 Study site and environmental variables

Monitoring and measurements were conducted from June to August 2014. The study site was located near a metal mine in the Finnish Lapland (68° N). Mine has been operating since 2008. The ground in the area is volcanic and sediment rocks rich in iron, magnesium and gold deposits (Pöyry 2010). Mean annual temperature is -0.5 C°, precipitation 500-600 mm a^{-1} and evaporation 200-300 mm a^{-1}. Snow covers the ground in October and melts in May (Palmer et al. 2015, Pöyry 2010).

Study sites are natural, open peatlands. The pristine reference area is situated about 200 m north of the wastewater distribution ditch on treatment peatland A (Fig. 1). This pristine site is unaffected by mine process waters according to EC and tracer studies by Palmer et al. (2015).

The two treatment peatlands used in this study have been used for purification of pretreated drainage and process waters which are then discharged to nearby river. Treatment peatland B, size 17 hectares, is used for treating mine drainage waters from open pit and underground mines. Treatment peatland A, size 44 hectares, is used for treating process effluent waters pretreated in tailings ponds. Treatment peatland B has been used since 2006 and treatment peatland A since 2010. Mean conduction rate to treatment peatland B: 6500 m^3 d^{-1} and treatment peatland A: 2700 m^3 d^{-1}. Inlet waters include high loads of SO_4^{2-}, N, phosphorus (P), metals and metalloids: iron (Fe), Mn_2^{+}, As, antimony (Sb), nickel (Ni). Highest N, P and SO_4^{2-} loading are in process waters. As, lead (Pb), nickel (Ni) loadings on the other hand are highest in drainage waters (Palmer et al. 2015).

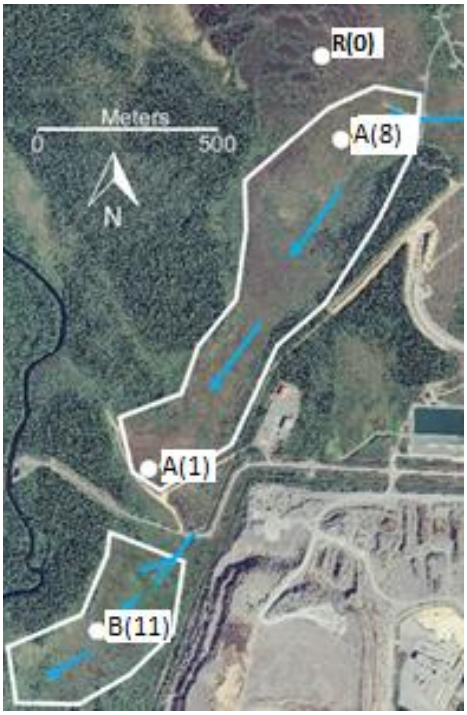

Figure 1. Treatment peatlands A (with TP 1 & 8) and B (with TP 11) and the waste water inlets and flow paths, as well as the reference peatland (with RP 0) (modified from aerial photograph provided by the National Land Survey of Finland, Orthophoto-data, in March 2015).

Both peatlands are minerotrophic, poor (mesotrophic) fens. Vegetation consists of mosses (e.g. *Spaghnum), Eriophorum augustifolium, Carex sp. and Trichophorum cespitosum*. Peat was shown to be only slightly decomposed on surface layers of both treatment peatlands and the reference peatland (H4, von Post scale), but more decomposed on the deeper layers (H5-6, von Post scale, < 30 cm from the surface on treatment sites and < 10 cm on reference site). It has been shown with tracer studies by Palmer et al. (2015) that in these peatlands process waters evenly spread to the whole acrotelm. Waste concentrates higher in surface layers, but infiltrate to deeper layer as well, even 70 cm deep. Majority of contaminants are retained in the first 100 m from the distribution ditch.

In order to characterize *in situ* condition at the time of gas sampling, a vegetation assessment was conducted and soil temperatures, surface water pH and EC were measured manually from all study plots.

5.1.1 Air and ground temperature

Air temperature was measured on each measurement and reference plot during the time of sampling. Soil temperature was measured from 5, 10 and 20 cm depth in peat by using a ground thermometer.

5.1.2 Vegetation assessment

Vegetation on the peatlands was assessed from photographs. Photographs for the vegetation assessment were taken from each collar every sampling time. These were send for analyses to Prof. Eeva-Stiina Tuittila for University of Eastern Finland for species composition and surface coverage analysis.

5.2 Surface water sampling and chemical properties

5.2.1 Surface water sampling

Surface water samples (á 30 ml) were gathered from each study plot on same occasions as the gas chamber samples. Surface water was sampled from inside each study collar. When this was not possible due to weather conditions, samples were collected right outside the collars.

5.2.2 pH and electrical conductivity

Soil pH was measured in the laboratory from water samples using a WTC pH340 pH-meter. Electrical conductivity (EC) was also measured from surface water samples in the laboratory (WTW Fennolab pH/Cond 340i EC-meter).

5.2.3 Total organic carbon

Total organic carbon (TOC) was measured from surface water samples with TOC/TNb Analyzer Multi N/C 2100S (Analytik Jena AG). Analyzes were conducted by a laboratory technician from the Department of Environmental Science with Savonia University of Applied Sciences' equipment in Technopolis.

5.2.4 Anion analysis

Surface water samples were analyzed with ion chromatograph (Dionex 120) which separates ions based on their affinity to the ion exchanger. Ion chromatograph was used to determine concentrations of NO_3^-, Cl^-, SO_4^{2-} and NO_2^- from the water samples.

4.5 mM Na_2CO_3 + 0.8 mM $NaHCO_3$- (20 ml/2 l MilliQ-H_2O) was used as an eluent. Standards of 0, 0.5, 1, 2.5, 5, 10 mg l^{-1} were used for calibration. Samples were diluted 1:2, except in TP 8 where they were diluted 1:10 to get results (mg N l^{-1}). For sulfate analyses samples were diluted even down to 1:1000.

The chromatograph peak areas were used for calculation of a standard curve. The slope of the linear standard curve was used in the concentration calculations of NO_3^-, SO_4^{2-} and Cl^- (Formula 1) in the water samples.

$$\textit{Anion concentration (mg/l) = Peak area x slope x dilution factor} \qquad (1)$$

5.2.5 Ammonium analyses

Ammonium (NH_4^+) was analyzed from surface water samples spectrofotometrically with Ultrospec 3000 Pro. Standards 5.0, 2.5, 1.25, 0.625, 0.3125 and 0 mg l^{-1} made from stock solution (100 mg NH_4-N l^{-1}). Two sample replicates were used. To measure the content, color

formation between NH_4^+ and reagents was analyzed. 1 ml of sodium phenate, 1.5 ml 0.01% sodium nitroprusside and 1.5 ml 0.02 M sodium hypochlorite were added to each sample (á 1 ml). Ammonium and reagents produced increasing amounts of blue color with more NH_4^+ present (Fig. 2).

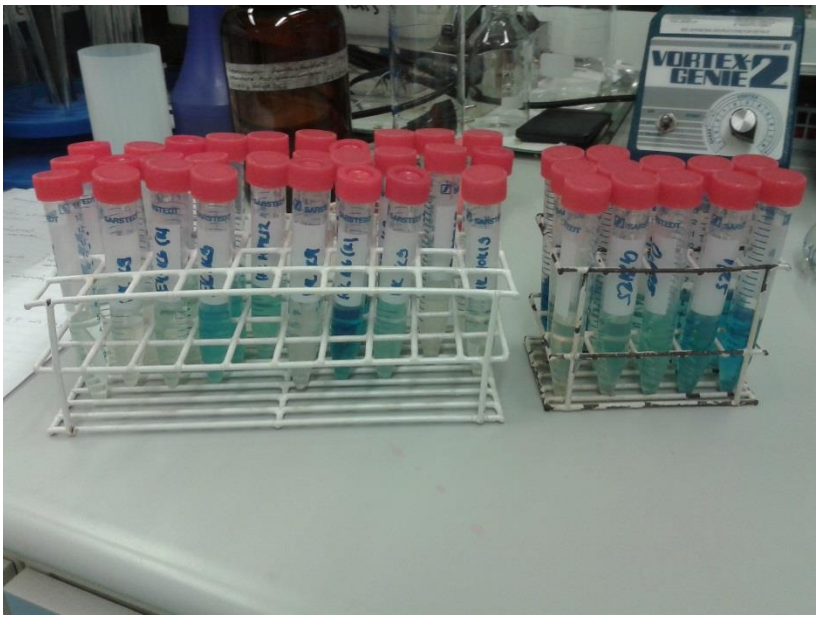

Figure 2. Ammonium samples with reagents.

Absorbance was measured at a wavelength of 630 nm. Samples were diluted 1:1, except August and September collars 1-3 were diluted to 1:10. Reference samples were not diluted. Absorbances from the spectrometer were calculated to concentrations (mg NH_4^+-N l^{-1}) using the standard curve and dilution factor (Formula 2).

$$\textit{Concentration of } NH_4^+ \textit{ (mg/l) = Absorbance x slope x dilution factor} \qquad (2)$$

5.3 Gas sampling by chamber method

For gas sampling and flux measurement, static chambers (e.g. Maljanen et al. 2009) were used. A surface area of 0.36 m^2 of the wetland was isolated by a collar (Fig. 3) and a chamber on top to measure the concentrations of CO_2, N_2O and CH_4 at certain time points. Gas concentrations increased or decreased in the headspace of the chamber in time due to microbial activity (i.e. production or consumption of the gas). With CO_2, only dark respiration rates were measured, not the net CO_2 balances.

Figure 3. Study plot with collars

Three treatment plots (plots 1, 8 on treatment peatland A and plot 11 on treatment peatland B) were used as well as one reference plot (0) on an adjacent pristine peatland area (Fig. 1). Three replicate chambers were used on each plot. Chambers were 20 or 32 cm high and 60 x 60 cm in size. Collars (h 30 cm, n=3) were sealed air-tight with water (also described by Silvan et al. 2005). Results from collars that were not air-tight (< 10 % of all results) were omitted. Air was circulated in the chambers during the measurements with fans to exclude the influence of plants. Short boardwalks were built on each measurement station (Fig. 3) to minimize the disturbance (e.g. Silvan et al. 2005).

Gas samples were collected 16th and 17th of June, 22nd of July as well as 25th and 26th of August. Samples of 30 ml were taken with a 60 ml polypropylene syringe every five minutes (from 5 to 25 minutes) after closing the chambers. Chamber, soil (at 3 to 20 cm when possible) and air temperatures were measured at every study plot.

5.4 Gas sampling by silicone gas collectors

Gas samples were also collected from silicone gas collectors (as described by Maljanen et al. 2009.) Samples of 30 ml were taken with syringes from pre-installed silicon tubes (Ø 1.0 cm, wall thickness 0.3 cm, length 110 cm, V = 86 cm^3) that were inserted horizontally in the peat. Four tubes were used in each study plot: two at 5 cm depth and two at 20 cm depth. Similar syringes were used for analyzing gas collector samples as were used in the chamber method described earlier (Chapter 5.3). The peak areas of standards and samples from GC were used to calculate (Formula 3) the concentrations of CH_4, N_2O and CO_2. Results represent the concentration of these gases (µl l^{-1}) equilibrium in the silicone tube.

5.5 Gases dissolved in the surface water

Water samples were taken from the surface water inside each chamber collar (when possible) using syringes. Three replicate samples were collected from all four study plots and 30 ml of water was collected from each collar.

The amount of dissolved gases in water samples taken from the waterlogged peat surface was quantified using a headspace equilibration technique within 24 h of sampling. Nitrogen-filled syringes (30 ml water + 30 ml N_2) were equilibrated by shaking vigorously for 3 minutes to separate the gases for analysis. The CH_4, N_2O and CO_2 gas concentrations were analyzed as described in chapter 5.6. Formula 6 was also used for calculating dissolved gas concentrations in the surface water (µl l^{-1}). The concentrations of the each measured gas in the gas phase (µmol l^{-1}), were calculated with Formula 3 (Sander 1999).

$$Temperature\ dependence\ of\ Henry's\ law\ constant = H * (EXP(TempCoeff * (1/Tkelvin) - 1/298.15))) \quad (3)$$

where H = Henry's Law constant, TempCoeff = temperature coefficient (-DH/R [K])

and T_{kelvin} *= temperature* [K].

Henry's Law solubility constants (*H*) and temperature coefficients (*-DH/R*) specific for each gas are shown in Table 3 (Sander 1999).

Table 3. Henry's Law solubility constants (H) and temperature coefficients (-DH/R) for methane (CH_4), carbon dioxide (CO_2) and nitrous oxide (N_2O).

GHG	H [M/atm]	temp-coefficient -DH/R [K]
CH_4	0.00140	1600
CO_2	0.0350	2400
N_2O	0.0250	2600

Simple description of Henry's laws as a function of temperature can be seen in Formula 4 (Sander 1999).

$$kH = k\Theta H * exp\left(((-\Delta solnH)/R) * (1/T - 1/T\Theta)\right) \quad (4)$$

*where Henry's Law volatility constant (kH) = (M/atm) = (mol_{aq}/dm^3)/atm**

*and $\Delta solnH$ = enthalpy of solution**.*

* Commonly used, but official SI unit kH = (mol_{aq}/m^3)/Pa, converted by kH [M/atm] = 101.325 × kH [(molaq/m3 aq)/Pa].

** Here, the temperature dependence is: −d ln kH d(1/T) = ΔsolnH R.

5.6 Gas analysis

Agilent Technologies 7890B GC-System gas chromatograph and Gilson auto sampler (GX-271) were used for gas analyses. System had electron capture (EC), flame ionization (FI) and thermal conductivity (TC) detectors. Standards gas containing 0.836 µl l^{-1} of N_2O, 2.02 µl l^{-1} of CH_4, and 398 µl l^{-1} of CO_2 was used for daily calibrations. This GC –method was used for analyzing gas samples from chambers, ambient air and soil air from gas collectors and dissolved gases from water samples.

Gas flux results from chambers were calculated using Excel and a linear regression model (e.g. Silvan et al. 2005) with measured increase/decrease of gas concentration in time as showed in Formula 5. Results were then converted to mg m^{-2} h^{-1} (in case of CH_4 and CO_2) and µg m^{-2} h^{-1} (in case of N_2O) units.

$$F\left(\frac{\frac{mg}{m2}}{d}\right) = \frac{\frac{pkV}{RT} \text{ x M}}{A\ x\frac{1}{60}h} \quad (5)$$

F=flux, p=pressure (1, 01325 kPa), k=slope (CO2 ppm min^{-1}, N2O ppb min^{-1}), V=chamber capacity (m^3), R=gas constant (8.3143 J mol-1 x K^{-1}), T = chamber temperature (K), M=molar mass of gas (g mol^{-1}), A=collar's surface area (m^2)

The peak areas of standards and samples from GC were used to calculate (Formula 6) the concentrations of CH_4, N_2O and CO_2.

$$GHG\ consentration\ (ppm) = \frac{Area}{(standard\ mean\ area\ x\ standard\ concentration)} \quad (6)$$

5.7 Global warming potential

Global warming potential was calculated using measured daily fluxes of CH_4 and N_2O. These were weighed with their CO_2 equivalents (Table 2) and fluxes from the reference area and measurement sites were compared to see the net global warming potential.

5.8 Statistical analysis

Results were tested with Kolmogorov-Smirnov normality test (IBM SPSS Statistics 21). Methane and N_2O fluxes from chamber method were not normally distributed ($p < 0.05$) where ER rates (i.e. CO_2 fluxes) were ($p > 0.05$). Gas concentrations from silicone gas collectors or water samples were not normally distributed ($p < 0.05$).

Because data was not normally distributed, except in case of ER rates, non-parametric tests were used for analysis of all other samples. Non-parametric Mann-Whitney U-test was used to analyze CH_4 and N_2O fluxes, surface water samples and silicone gas collector samples ($p < 0.05$). Independent samples T-test was used as a parametric test for testing ER rate results ($p < 0.05$) only.

Correlation tests were used for analyzing correlation between gas flux and water and soil air results, and between these results, measured environmental and chemical parameters. Spearman's rank correlation test was used for all non-parametric tests ($p < 0.05$) and Pearson's two-tailed test of significance ($p < 0.05$) for assessing correlation for parametric samples (i.e. ER rates).

6 RESULTS

6.1 Environmental variables

6.1.1 Air and peat temperature

Mean air temperature during measurement period was lowest (min. +5.9 °C; TP 11) in June and highest in July (max. +28.5 °C; TP 1). Variations between different measured temperatures on separate study plots fall between natural variations and no distinctive difference can be shown between the reference and treatment plots (Table 4).

Measured mean peat temperature did not show great differences between the reference and treatment plots at any measurement depths (Table 4). Highest measured peat temperature was +22.3 °C on the RP 0 (at 5 cm depth) and +21.5 °C on TP 1 (at 5 cm) which was the highest of the TPs. Both were measured in June. Lowest measured mean temperature was +6.3 °C on the reference (at 10 cm) and, of the treatment peatlands it was +4.8 °C on plot 11 in June (at 10 and 20 cm). Generally, peat temperatures were slightly higher on plots on treatment peatland A (TPs 1 and 8) than on treatment peatland B (TP 11) or on the reference peatland (RP 0).

Table 4. Measured mean air temperature (°C) and mean peat temperatures (°C) at 5, 10 and 20 cm depth in June, July and August on each TP (1, 8, 11) and RP (0).

	Measurement dates											
	16/17.6.2014				**22.7.2014**				**25/26.8.2014**			
Study plot	**0**	**1**	**8**	**11**	**0**	**1**	**8**	**11**	**0**	**1**	**8**	**11**
Mean Air temp. (°C)	10.7	6.6	15.6	5.9	27.5	28.5	26.4	26.3	10.8	12.6	11.8	11.3
Mean peat temp. (°C) 5 cm	6.7	10.7	10.7	7.0	22.3	21.5	19.3	22.1	10.4	12.1	12.1	10.2
Mean peat temp. (°C) 10 cm	6.3	10.1	9.7	4.8	19.6	20.6	18.5	21.0	10.1	11.3	11.8	10.3
Mean peat temp. (°C) 20 cm	7.5	10.1	9.8	4.8	16.7	17.8	16.8	18.6	10.1	10.5	11.4	10.8

6.1.2 Vegetation

Vegetation coverage and species compositions varied between all study plots (Fig. 4). TPs 1 and 8 on treatment peatland A consisted of same species (mostly of *Eriophorum angustifolium*, 10 and 25 % coverage respectively, and *Carex lasiocarpa*, 22 and 18 % respectively), expect for *Carex chordorhiza* which was discovered on TP 1 (12 % coverage) but not on TP 8. Overall vegetation coverage on TP 8 was slightly higher (60 %) than on TP 1 (51 %) (Table 5).

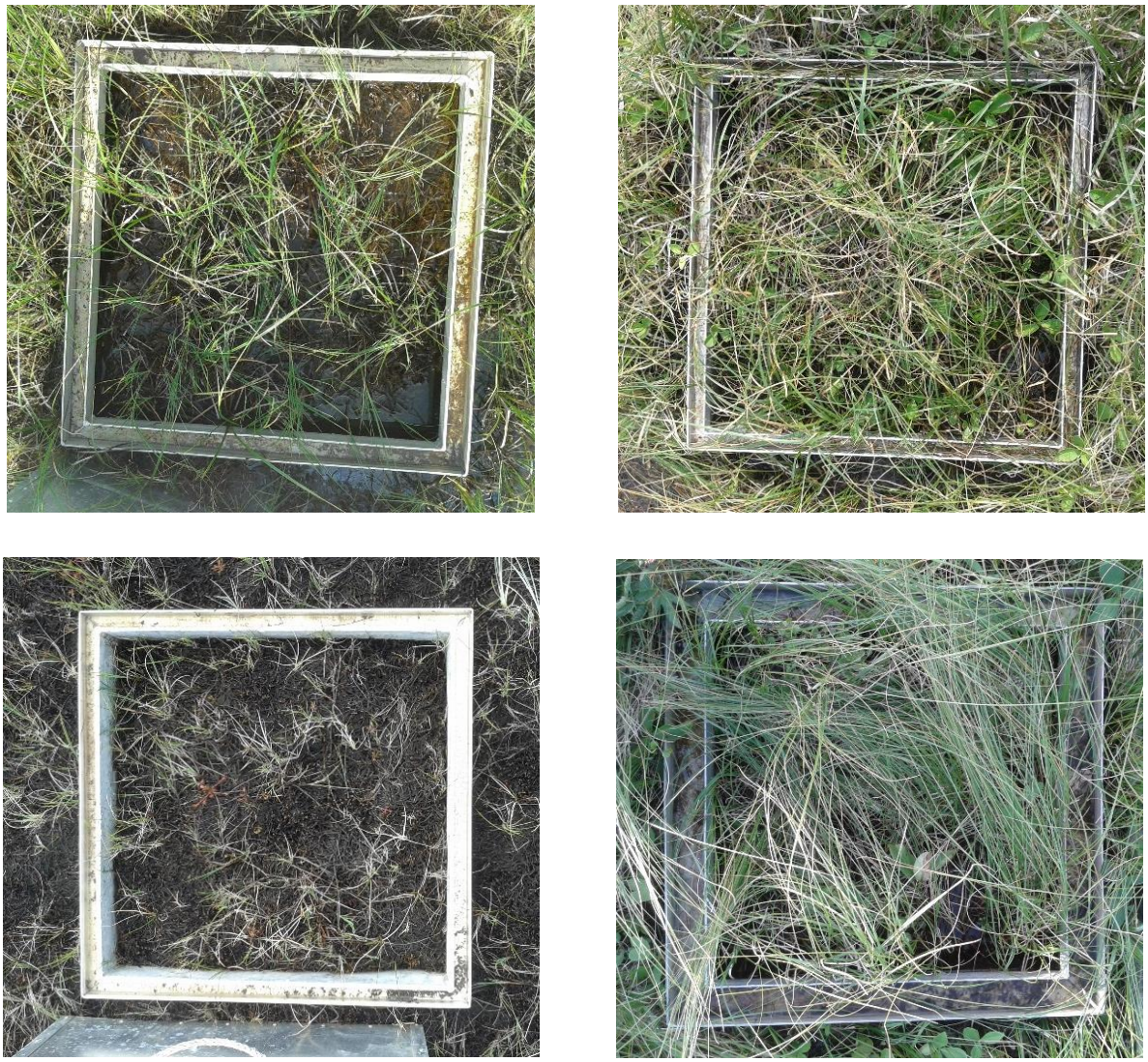

Figure 4. Vegetation in July on treatment peatland A TP 1 (collar 8) top left (a); treatment peatland A TP 8 (collar 1) top right (b) and on the reference peatland RP 0 (collar 4) down left (c) and on treatment peatland B TP 11 (collar 12) down right (d).

Treatment plot 11 on treatment peatland B was dominated by *Carex lasiocarpa* (50 % of all coverage). Also, *Menyanthes trifoliate* was common (29 % coverage). In total, more species (6) and higher surface coverage (85%) was discovered on TP 11 (treatment peatland B) than either of treatment plots (TP 1 or 8) on treatment peatland A (Table 5).

Table 5. Surface coverage (%) of different vegetation species on the study plots on treatment peatland A (TPs 1, 8) and B (TP 11) and on the reference peatland (RP 0).

	RP 0 (%)	**TP 8 (%)**	**TP 1 (%)**	**TP 11 (%)**
Warnsdorfia sp.	85	0	0	0
Carex livida	11	0	0	0
Drosera rotundifolia	3	0	0	0
Eriophorum angustifolium	1	25	10	4
Carex lasiocarpa	0	18	22	50
Menyathes trifoliata	0	13	3	29
Betula nana	0	3	3	1
Carex chordorhiza	0	0	12	0
Carex rostrata	0	0	0	3
Caltha palustris	0	0	0	1
Other	0	0	0	0
Total	99	60	51	85

The reference plot (0) had higher vegetation surface coverage (99%) than any of the treatment plots (51 – 85 %). Reference plot 0 consisted almost solely of *Warnsdorfia sp.* (85%) and *Carex livida* (11 %). Species were all different than on either treatment sites, except for *Eriophorum angustifolium* which was represented by 1% (Table 5).

6.2 Chemical properties

6.2.1 pH

Mean measured pH values from the surface water in June, July and August were between 6.43 and 7.54 (Table 6). Lowest measured mean pH value was on the RP 0 (always < 6.76) throughout the measurement period. pH values on TP 11 (Mann-Whitney U=0.000, p=0.001) and TP 1 (U=15, p= 0.043) were significantly higher than values on RP 0. Measured mean pH value on TP 8 was not statistically higher than on RP (U=20.5, p=0.077).

Highest pH values were measured always on TP 11 (> 7.26). pH values on TP 1 (U=0.000, p=0.001) and TP 8 (U=6, p=0.007) were significantly lower than on TP 11. pH values were not statistically lower on TP 1, compared to TP 8 (U=35, p=0.923).

Table 6. Measured mean pH values and standard deviation (SD) of three replicants in June, July and August on the RP (0) and TPs (1, 8, 11).

	June		**July**		**August**	
Plot	**pH**	**SD**	**pH**	**SD**	**pH**	**SD**
0	6.76	0.12	6.43	0.10	6.65	0.14
1	6.79	0.37	6.82	0.14	6.96	0.28
8	7.34	0.24	6.53	0.18	6.87	0.14
11	7.45	0.12	7.26	nd*	7.54	0.04

**note SD, only one sample*

6.2.2 Electrical conductivity

A clear difference was seen in measured EC values between the reference plot (0) and the treatment plots (Table 7). The mean EC value from the TPs varied between 1690 and 10 600 µS cm^{-1} while maximum EC value on the reference plot was only 130 µS cm^{-1}. EC values were significantly higher on TPs 8 (U= 0.000, p= 0.000), 1 (U=0.000, p=0.001) and 11 (U=0.000, p=0.001) than on the RP 0.

There was also a statistically significant variation between the EC values on the treatment plots. Highest measured EC values were throughout the measurement period on TP 8 (> 9650 µS cm^{-1}) and lowest on TP 11 (< 1690 µS cm^{-1}). Measured mean EC values were significantly lower on TP 11 (U=0.000, p=0.001) and TP 1 (U=0.000, p=0.001) than on TP 8. EC values were also significantly higher on TP 1 than on TP 11 (U=0.000, p=0.001). TP 1 showed the highest variation on EC (Table 7).

Table 7. Measured mean electrical conductivity (µS cm^{-1}) values and standard deviation (SD) of three replicants in June, July and August on the RP (0) and TPs (1, 8, 11).

	June		July		August	
Plot	**EC**	**SD**	**EC**	**SD**	**EC**	**SD**
0	30.7	2.52	130	44,9	43.3	4.04
1	5270	3270	7960	421	6250	2170
8	9650	130	9940	528	10600	26.5
11	1803	5.29	1690	nd*	1690	3.06

**note SD, only one sample*

6.2.3 Total organic carbon

Total organic carbon (TOC) concentrations varied from 3.00 to 35.0 mg C l^{-1} (Table 8). Overall highest TOC concentrations were measured in July. Measurements showed consistently higher TOC concentrations in the RP 0 (always > 27.3 mg C l^{-1}) compared to the TPs 8 (U=0.000, p=0.000), 1 (U= 0.000, p=0.001) and 11 (U=0.000, p=0.001) (Table 8).

TOC values also varied between the treatment plots, where TP 1 showed the highest concentrations. TOC concentrations were significantly higher on TP 1 than on TP 11 (U=5, p=0.008), but not statistically higher than ones on TP 8 (U=18, p=0.083). There was no statistically significant difference on TOC values between TPs 8 and 11 (U=21, p=0.266).

Table 8. Measured mean total organic carbon (mg C l^{-1}) concentrations and standard deviation (SD) of three replicants in June, July and August on the RP (0) and the treatment plots (1, 8, 11).

	June		**July**		**August**	
Plot	**TOC**	**SD**	**TOC**	**SD**	**TOC**	**SD**
0	27.3	2.60	35.0	4.77	27.7	2.83
1	10.8	5.78	15.7	1.60	9.22	0.910
8	7.48	3.51	12.4	1.91	3.00	0.910
11	4.39	3.26	5.22	nd*	6.61	5.98

**note SD, only one sample*

6.2.4 Anions

Nitrate (NO_3^-) (Fig. 5), SO_4^{2-} (Fig. 6) and Cl^- (Fig. 7) were measured from surface water samples. Nitrite (NO_2^-) concentrations were also measured but they were lower than the detection limit (< 0.01 mg l^{-1}).

The lowest measured NO_3^- concentration throughout the measurement period were found on the reference plot 0 (0.01 - 0.30 mg l^{-1}). Nitrate concentrations on TPs 8 (U=0.000, p=0.000) and 11 (U=0.000, p=0.001) were significantly higher than on the RP 0, but concentrations on TP 1 (U=28, p=0.440) were not (Fig. 5). Highest mean NO_3^- concentrations were measured on TPs 8 (7.82 - 10.8 mg l^{-1}) and 11 (4.42 – 11.0 mg l^{-1}). Lowest NO_3^- concentrations of the treatment plots were always measured on TP 1 (0.15 - 0.53 mg l^{-1}) (Fig. 5). Mean NO_3^- concentrations on TP 11 were statistically higher than on TP 1 (U=0.000, p=0.001). Results from TP 8 were also higher than on TP 1 (U=0.000. p=0.001). No statistically significant difference was discovered between TPs 11 and 8 (U=22, p=0.315).

Measured SO_4^{2-} concentrations were significantly lower on the RP 0 (< 13.6 mg l^{-1}) than on the TPs 1 (U=0.000, p=0.001), 8 (U=0.000, p=0.000) and 11 (U= 0.000, p=0.001) on all sampling occasions (> 963 mg l^{-1}) (Fig. 6). Highest SO_4^{2-} concentrations were always measured

on TP 8 (9070 – 11010 mg l^{-1}). Sulfate concentrations were on 4450 – 5850 mg l^{-1} on TP 1 and 962 – 8280 mg l^{-1} on TP 11. Sulfate concentrations were significantly higher on TP 8 than on TPs 11 (U=0.000, p=0.001) and 1 (U=1.000, p=0.001). No statistically significant difference was seen between TPs 1 and 11 (U=13, p=0.083).

Mean Cl^- concentrations measured on the RP 0 were 0.68 – 3.84 mg l^{-1}, where on the treatment plots these were always over 14.5 mg l^{-1}. TPs 1 (U=0.000. p=0.001), 8 (U=0.000, p=0.000) and 11 (U=0.000, p=0.001) had significantly higher Cl^- concentrations than RP 0 (Fig. 7). Chloride concentrations measured from the surface water were always highest on TP 11 (30.6 - 43.6 mg l^{-1}). These were somewhat lower on TPs 8 (20.5 – 29.6 mg l^{-1}) and 1 (14.5 – 20.3 mg l^{-1}). Chloride concentrations were significantly higher on TP 11 than on TP 1 (U=0.000, p=0.001) or 8 (U=4, p=0.004). Concentrations of Cl^- were also higher on TP 8 compared to TP 1 (U=8, p=0.007).

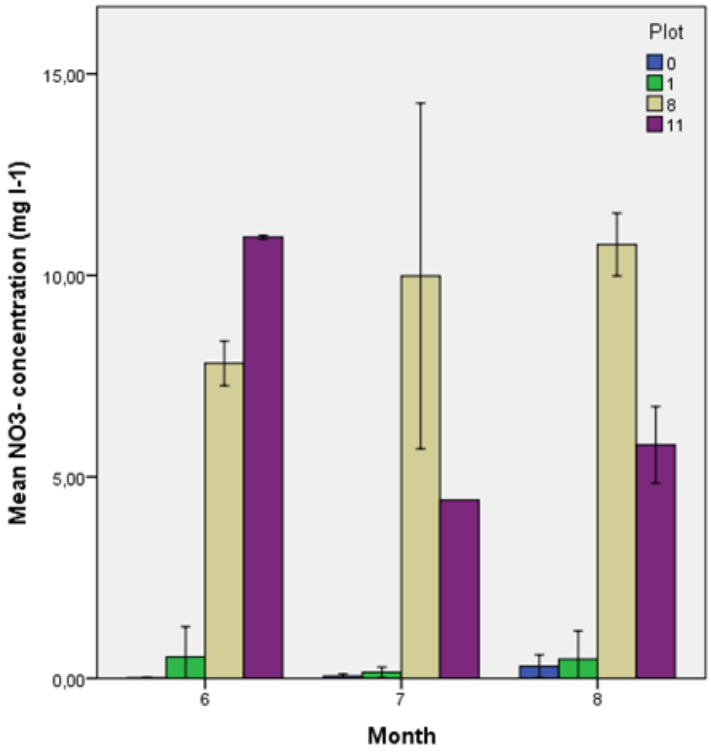

Figure 5. Mean measured nitrate (NO_3^-) concentrations of three replicates in surface water samples on the RP (0) and TPs (1, 8, 11) in June (6), July (7) and August (8) (Error Bars: +/- 1 SD, could not be calculated if under three samples per plot).

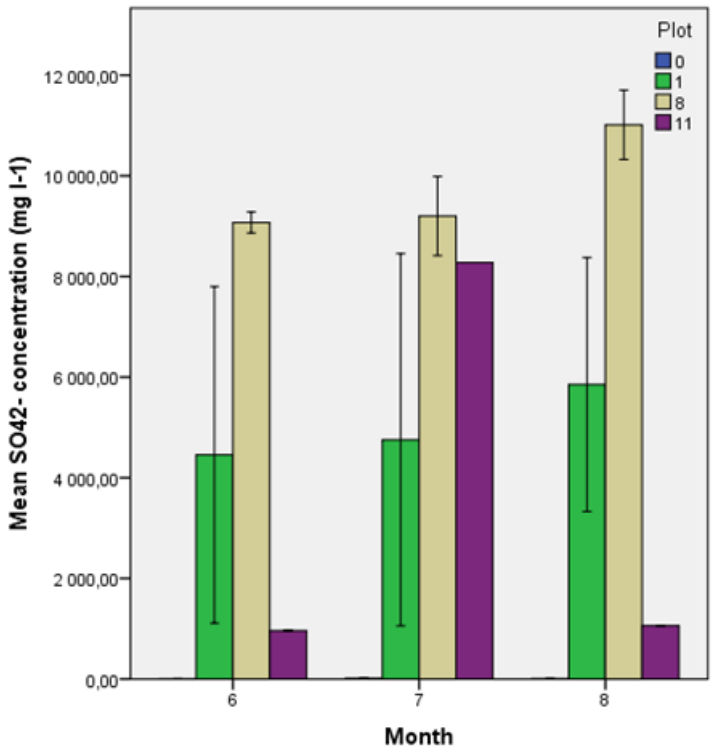

Figure 6. Mean measured sulfate (SO_4^{2-}) concentration of three replicates in surface water samples on the RP (0) and TPs (1, 8, 11) in June (6), July (7) and August (8) (Error Bars: +/- 1 SD, could not be calculated if under three samples per plot).

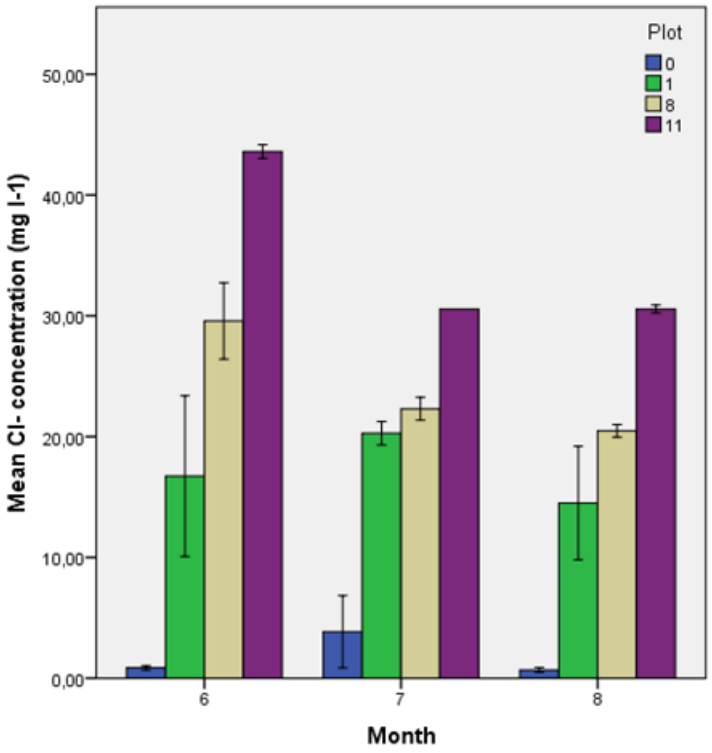

Figure 7. Mean measured chloride (Cl^-) concentration of three replicates in surface water samples on the RP (0) and TPs (1, 8, 11) in June (6), July (7) and August (8) of 2014 (Error Bars: +/- 1 SD, could not be calculated if under three samples per plot).

6.2.5 Ammonium

Measured mean NH_4^+ concentrations were significantly higher on TP 8 (7.97 – 24.7 mg l^{-1}) than on any other study plots, especially in August (Fig. 8). Ammonium concentrations were significantly higher on TP 8 than on TPs 1 (U=1.000, p=0.000), 11 (U=0.000, p=0.001) or on the RP 0 (U=4, p=0.001).

Ammonium concentrations on the RP were low in June (0.14 mg l^{-1}) and August (0.28 mg l^{-1}), but peaked on July (3.89 mg l^{-1}). Mean concentration of NH_4^+ on TPs 1 (0.23 – 1.00 mg l^{-1}) and 11 (0.11 – 0.24 mg l^{-1}) were low in general. Results from the RP 0 were not statistically different from results on TP 1 (U=40, p=0.965) or TP 11 (U=13, p=0.050). Ammonium concentrations were significantly higher on TP 1 than TP 11 (U= 12, p=0.039) though.

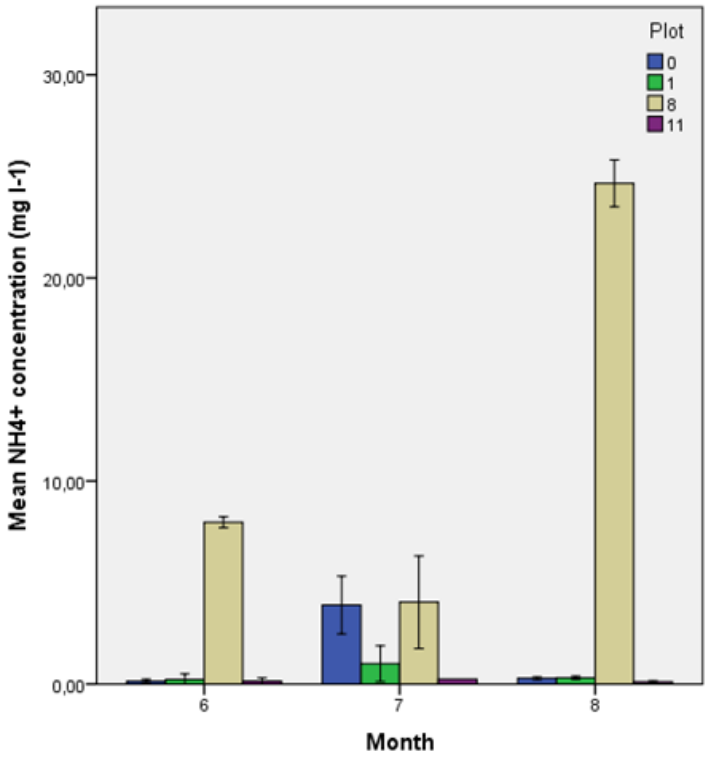

Figure 8. Mean measured ammonium (NH_4+) concentration of three replicates in surface water samples on the RP (0) and TPs (1, 8, 11) in June (6), July (7) and August (8) of 2014 (Error Bars: +/- 1 SD, could not be calculated if under three samples per plot).

6.3 Gas flux rates measured with static camber method

6.3.1 Methane fluxes

Mean CH_4 fluxes from the RP were highest in July (1.04 mg $m^{-2}h^{-1}$) and slightly lower (1.02 mg $m^{-2}h^{-1}$) in June. These were only about half of that in August (0.50 mg $m^{-2}h^{-1}$). Methane fluxes on the RP 0 (Fig. 9) were significantly higher than on any of the TPs: 8 (U=6, p=0.007), 1 (U=8, p=0.007) or 11 (U=7, p=0.01).

Methane emissions measured on the treatment plots throughout the summer were very small. TP 8, nearest the waste water inlet, actually showed a negative CH_4 flux in June (-0.18 mg $m^{-2}h^{-1}$) as did TP 11 (-0.01 mg $m^{-2}h^{-1}$) indicating uptake of methane. No uptake was measured in July or August. The mean CH_4 flux was close to zero on TP 1 (0.00 mg $m^{-2}h^{-}$) in June. In July, there was a small emission on TPs 1 (0.01 mg $m^{-2}h^{-1}$) and 11 (0.03 mg $m^{-2}h^{-1}$) but not on TP 8 (0.00 mg $m^{-2}h^{-1}$). In August, there were bit higher CH_4 emissions on TPs 1 (0.03 mg $m^{-2}h^{-1}$), 8 (0.03 mg $m^{-2}h^{-1}$) and 11 (0.05 mg $m^{-2}h^{-1}$). No statistically significant difference was discovered between the treatment plots themselves, nor between the two treatment peatlands. There was no significant difference between TPs 1 and 11 (U=25, p=0.728), 1 and 8 (U=24, p=0.643) or 11 and 8 (U=19, p=0.482).

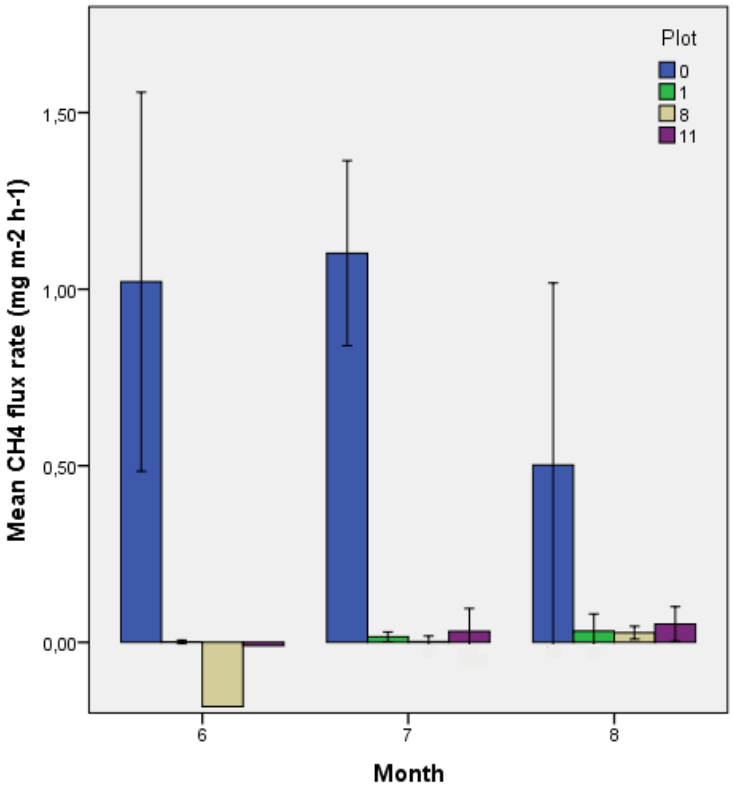

Figure 9. Mean methane (CH_4) fluxes of three replicates in June (6), July (7) and August (8) on treatment peatlands A (TPs 1 and 8) and B (TP 11) and on the reference peatland (RP 0) measured with gas chamber method (Error Bars: +/- 1 SD, could not be calculated if under three samples per plot).

6.3.2 Nitrous oxide fluxes

Nitrous oxide fluxes were highest in June, and generally decreased towards the fall. Highest N_2O fluxes were measured on TP 8, nearest the waste water inlet, in June (363 µg $m^{-2}h^{-1}$) (Fig. 10). These emissions were around one third of that in July (110 µg $m^{-2}h^{-1}$) and even lower in August (22.3 µg $m^{-2}h^{-1}$). Measured mean N_2O fluxes were slightly negative on the RP 0 (-2.87 µg $m^{-2}h^{-1}$) in June and generally low trough out the measurement period (< 10.6 µg $m^{-2}h^{-1}$). Treatment peatlands 1 and 11 showed low positive fluxes as well, even an uptake (-0.48 µg $m^{-2}h^{-1}$) was seen on TP 1 in August. Nitrous oxide fluxes were higher on TP 8 than on the RP 0 (U=2, p=0.002). Fluxes of N_2O were also higher on TP 8 than on TP 1 (U=3, p=0.004) and TP 11 (U=6, p=0.018). Results did not show statistically significant differences between fluxes on the RP 0 and TPs 1 (U=35, p=0.923) or 11 (U=22, p=0.315). There was no statistically significant difference in N_2O fluxes (U=17, p=0.203) between TPs 1 and 11 either.

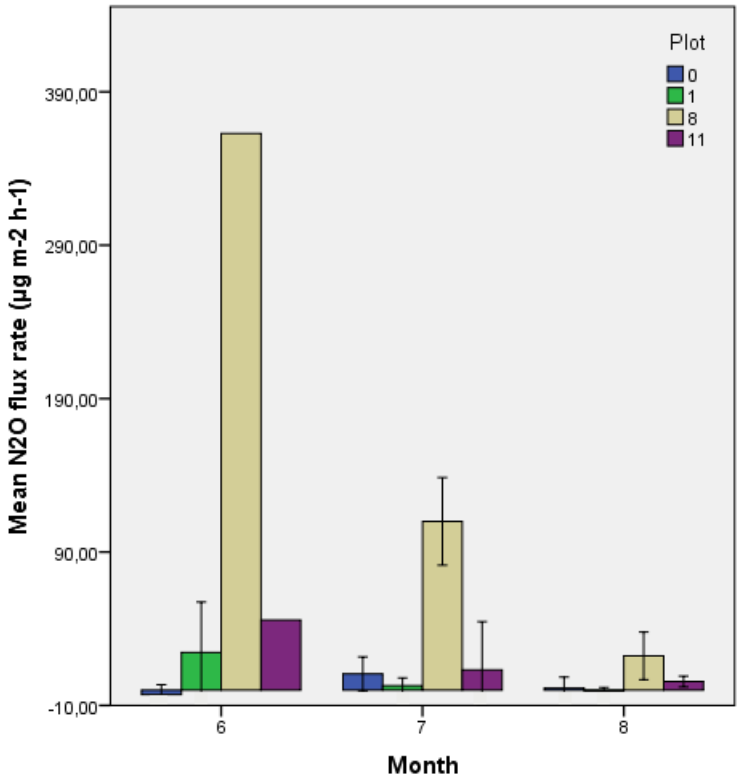

Figure 10. Measured nitrous oxide (N_2O) fluxes in June (6), July (7) and August (8) on treatment peatlands A (TPs 1 and 8) and B (TP 11) and on the reference peatland (RP 0) measured with gas chamber method (Error Bars: +/- 1 SD, could not be calculated if under three samples per plot).

6.3.3 Ecosystem respiration

Highest measured ER rates in each plot were in July, except for RP 0 which peaked in June (Fig. 11). In June, the highest respiration rates were measured on TP 11 (472 mg $m^{-2}h^{-1}$) and the lowest were measured on TP 1 (32.4 mg $m^{-2}h^{-1}$). In July measured rates were slightly higher on TP 8 (613 mg $m^{-2}h^{-1}$) than on TP 11 (611 mg m^{-2} h^{-1}) and still lowest on TP 1 (243 mg $m^{-2}h^{-1}$). In August TPs 8 and 11 showed again higher (always > 270 mg $m^{-2}h^{-1}$) respiration rates than TP 1 or RP 0 (always >133 mg $m^{-2}h^{-1}$).

Ecosystem respiration rates were strongly lower on the reference plot (0) than on TPs 11 (t(10) -2.334, p=0.041) than on TP 8 (t(10)=-2.328, p=0.042). Ecosystem respiration rates were not significantly lower on RP 0 than TP 1 (t(14)=1.150, p=0.269). Fluxes also varied between the treatment plots and were significantly higher on TP 11 (t(9)=-3.243, p=0.010) and TP 8 (t(9)=-3.246, p=0.009) compared to TP 1. No statistically significant difference was seen between TPs 11 and 8 (t(12)=-0.023, p=0.982).

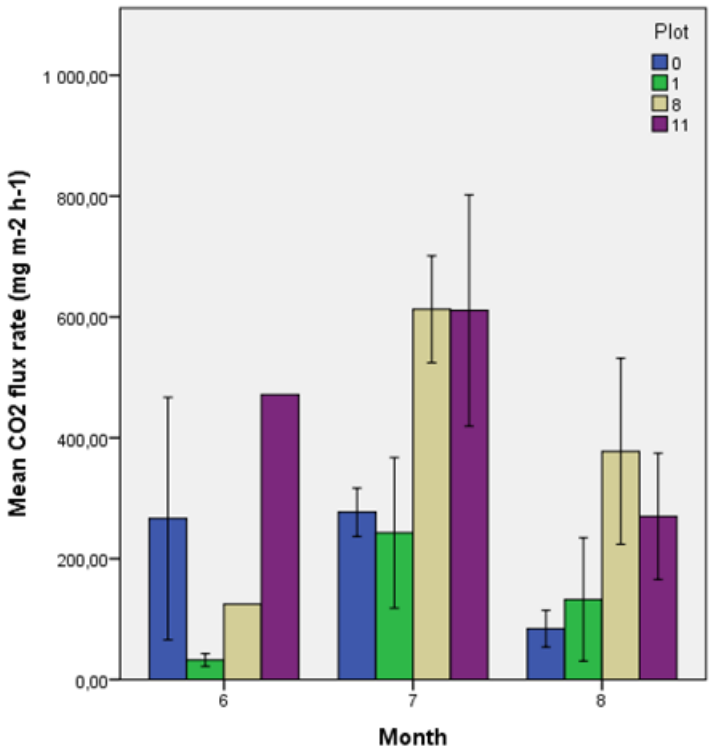

Figure 11. Measured ecosystem respiration rates (CO_2 flux rate) in June (6), July (7) and August (8) on treatment peatlands B (TP 11) and A (TPs 1 and 8) and the reference peatland (RP 0) measured with gas chamber method (Error Bars: +/- 1 SD, could not be calculated if under three samples per plot).

6.4 Measured gas concentrations from silicone gas collectors

6.4.1 Methane concentrations in soil air samples

Concentrations of CH_4 were clearly higher on the reference plot (0) than any of the treatment plots (1, 8 or 11) at both measurement depths (5 and 20 cm). At 5 cm depth, measured concentrations were up to 54700 µl l^{-1} in June. These were clearly higher in June and August than in July (10.4 µl l^{-1}) (Fig. 12). At 20 cm similar pattern was detected. Highest measured CH_4 concentration was 162100 µl l^{-1} in August and lowest (2300 µl l^{-1}) in July (Fig. 13). No statistically significant difference between the two study depths was discovered (r_s=0.425, n=21, p=0.055).

Measured CH_4 concentrations on TPs 1 (2.16 – 4.03 µl l^{-1}) and 11 (1.94 – 2.67 µl l^{-1}) at 5 cm depth were rather constant throughout the measurements (Fig. 12). Results on TP 8 were rather high (82.7 µl l^{-1}) in June, smaller (1.99 µl l^{-1}) in August and non-existent (0.00 µl l^{-1}) in July. Concentrations on RP 0 were significantly higher than concentrations on TPs 1 (U= 5.000, p=0.037) and 11 (2.000, p=0.018), but not statistically higher than concentrations on TP 8 (U=4.000, p=0.088).

TP 1 showed the highest concentrations of CH_4 of the TPs at 20 cm depth (Fig. 13) in June (332 µl l^{-1}) and July (13.9 µl l^{-1}), but lowest (1.23 µl l^{-1}) in August. Highest CH_4 concentrations at 20 cm depth in August were measured on TP 11 (11.1 µl l^{-1}). Otherwise, results from TPs 11 and 8 were under 6.80 µl l^{-1}. Methane concentrations on the RP 0 at 20 cm depth were significantly higher than on any of the treatment plots: TP 8 (U=0.000, P=0.004), TP 1 (U=1.000, p=0.006) or TP 11 (U=0.000, p=0.004).

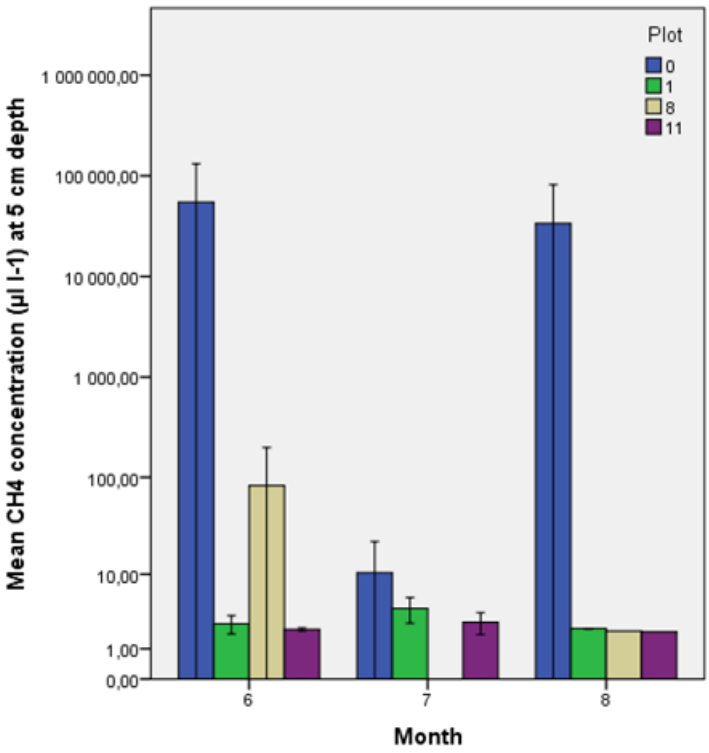

Figure 12. Mean methane (CH_4) concentrations of three replicates at 5 cm depth in June (6), July (7) and August (8) measured from silicone gas collectors. Results from the RP (0) and TPs (1, 8 and 11) (Error Bars: +/- 1 SD, could not be calculated if under three samples per plot). Note the logarithmic scale.

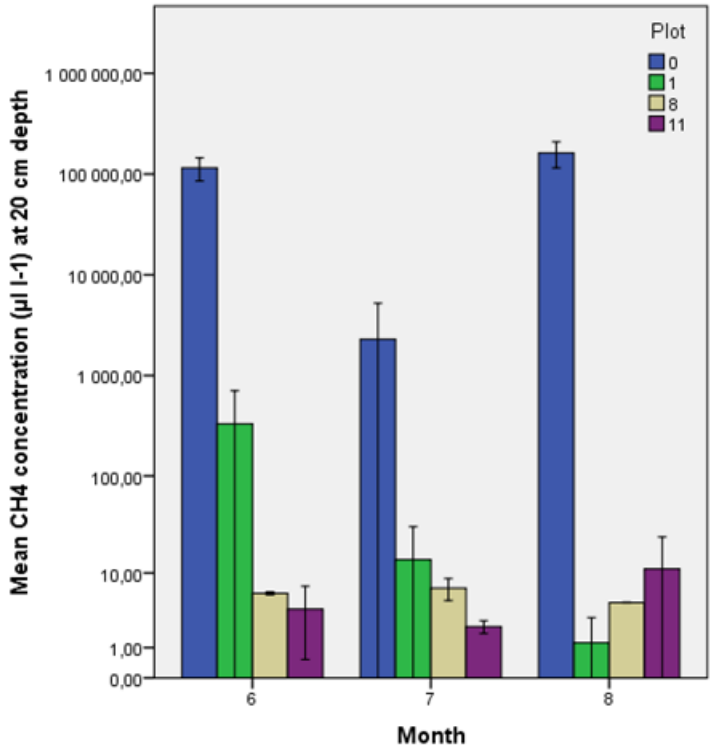

Figure 13. Mean methane (CH_4) concentrations of three replicates at 20 cm depth in June (6), July (7) and August (8) measured from silicone gas collectors. Results from the RP (0) and TPs (1, 8 and 11) (Error Bars: +/- 1 SD, could not be calculated if under three samples per plot). Note the logarithmic scale.

6.4.2 Nitrous oxide concentrations in soil air samples

Nitrous oxide concentrations (Fig. 14) were highest on TP 8 (max. 485 000 µl l^{-1}) at both depths, 5 and 20 cm, throughout the measurement period, but were greatly lowered towards the fall (min. 405 µl l^{-1}). Measured N_2O concentrations were lowest on the RP 0 (260 – 291 µl l^{-1}). TP 11 had significantly higher (354 – 531 µl l^{-1}) ($U=4.000$, $p=0.045$) and TP 8 had even higher ($U=0.000$, $p=0.011$) measured concentrations of N_2O at 5 cm than RP 0. Nitrous oxide concentrations from were not significantly lower on TP 1 (331 – 1741 µl l^{-1}) than RP 0 at 5 cm ($U=7.000$, $p=0.078$). No statistically significant difference in the N_2O concentrations between TPs 8 and 11 at 5 cm depth was shown ($U=2.000$, $p=0.050$).

Nitrous oxide concentrations at 20 cm depth (Fig. 15) seemed to vary less between measurement times, but a similar pattern to 5 cm results was detectable. Concentrations in TP 8 were clearly highest (4670 – 17 760 µl l^{-1}). The concentrations in the RP 0 were even lower (max. 252 µl l^{-1}) than measured ones at 5 cm. At 20 cm depth, the RP 0 had significantly lower measured N_2O concentrations than TPs 11 ($U=0.000$, $p=0.006$) or 8 ($U=0.000$, $p=0.004$), but not statistically lower ones than TP 1 ($U=9.000$, $p=0.150$). Between the treatment plots, N_2O concentrations were only significantly higher on TP 8 than TP 1 ($U=2.000$, $p=0.010$). No statistically significant difference was discovered between the two depths ($r_s=0.373$, $n=21$, $p=0.096$).

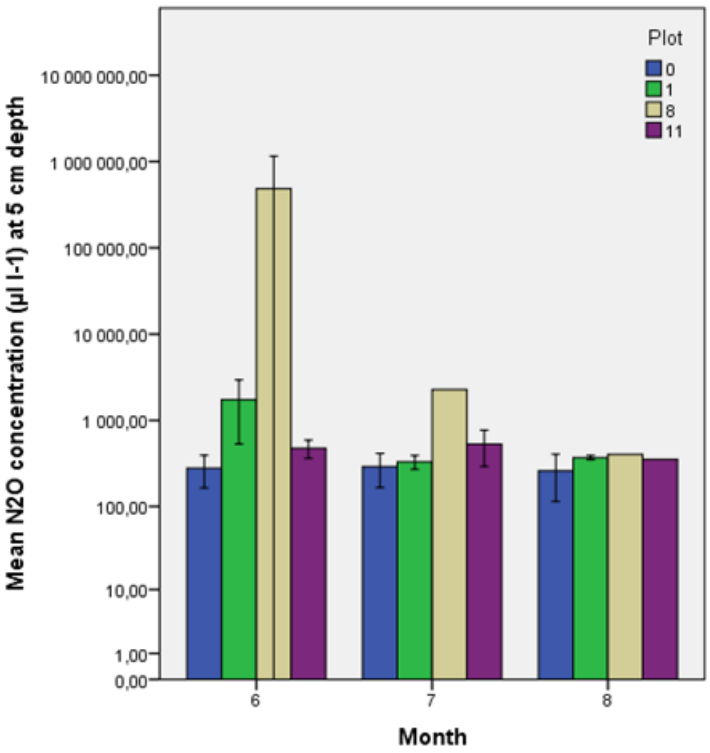

Figure 14. Mean nitrous oxide (N_2O) concentrations of three replicates at 5 cm depth in June (6), July (7) and August (8) measured from silicone gas collectors. Results from the RP (0) and TPs (1, 8 and 11) (Error Bars: +/- 1 SD, could not be calculated if under three samples per plot). Note the logarithmic scale.

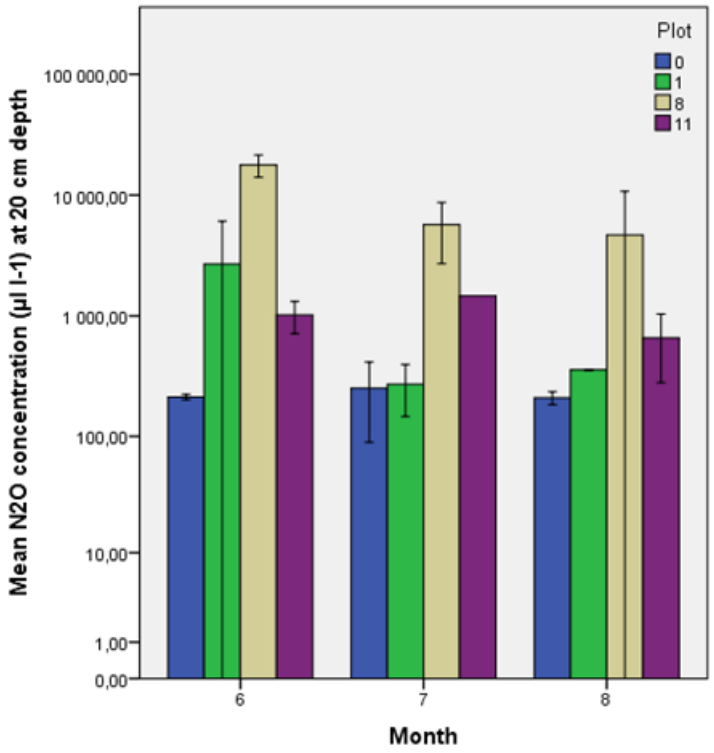

Figure 15. Mean nitrous oxide (N_2O) concentrations of three replicates at 20 cm depth in June (6), July (7) and August (8) measured from silicone gas collectors. Results from the RP (0) and TPs (1, 8 and 11) (Error Bars: +/- 1 SD, could not be calculated if under three samples per plot). Note the logarithmic scale.

6.4.3 Carbon dioxide concentrations in soil air samples

Carbon dioxide concentrations at 5 cm depth varied between measurement times (Fig. 16). Highest CO_2 concentrations were measured in TP 8 in June (58700 µl l^{-1}), TP 1 in July (17200 µl l^{-1}) and RP 0 in August (1000 µl l^{-1}). The RP 0 showed high concentrations in June (7550 µl l^{-1}) and August, but somewhat lower concentrations in July (620 µl l^{-1}). No statistically significant difference was discovered between the ER rates on RP 0 and the TPs 8 (U=11.000, p=0.831), 11 (U=7.000, p=0.144) or 1 (U=11.000, p=0.262).

Carbon dioxide concentrations on TP 11 were low (401 – 897 µl l^{-1}) and significantly lower than on TP 1 (U=1.000, p=0.011). There was no statistically significant difference between the measured CO_2 concentrations of TPs 11 and 8 (U=5.000, p=0.221) or between those of TPs 1 and 8 (U=8.000, p=0.394).

Measured mean CO_2 concentrations in 20 cm depth (Fig. 17) varied more than on the upper depth (5 cm). Distinctively low CO_2 concentrations, lowest of all study plots, were measured on the RP 0 in July (238 µl l^{-1}). Concentrations on RP 0 were highest of the study plots in June (14600 µl l^{-1}) and August (27000 µl l^{-1}). The TPs showed slightly less variation between measurement times than the RP 0. In the summer period TP 1 had measured CO_2 concentrations of 1390 – 16600 µl l^{-1}, TP 8 4790 – 11 744 µl l^{-1} and TP 11 3760 – 6530 µl l^{-1}. There was no statistically significant difference between measured CO_2 concentrations on the RP 0 and TP 8 (U=14.000, p=0.522), 11 (U=12.000, p=0.337) or 1 (U=13.000, p=0.423). No statistically significant difference was seen between the TPs 8 and 1 (U=15.000, p=0.613) or between TPs 8 and 11 (U=14.000, p=0.522) or between TPs 11 and 1 (U=16.000, p=0.749) either. There was no statistically significant difference (r_s=0.373, n=21, p=0.096) between CO_2 concentrations measured at the two depths (5 and 20 cm).

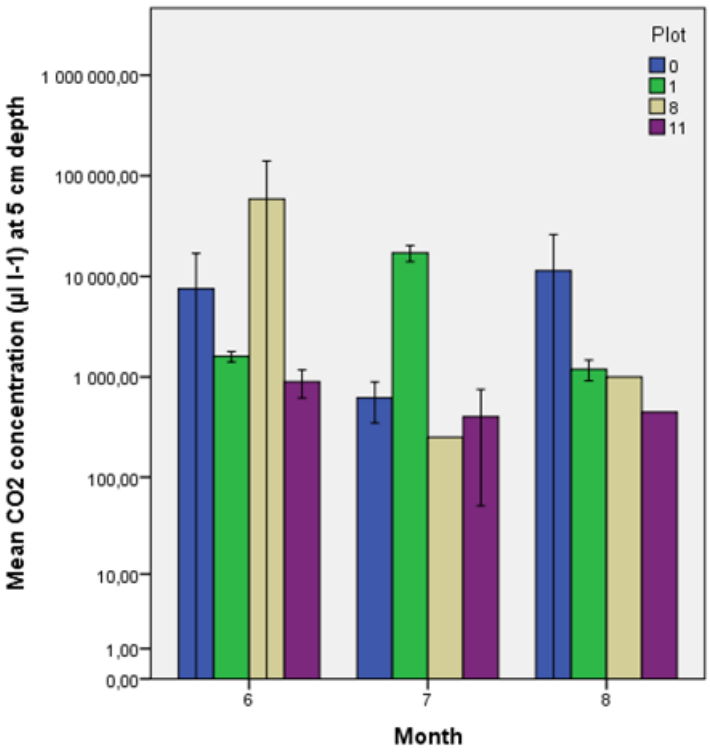

Figure 16. Mean carbon dioxide (CO_2) concentrations of three replicates at 5 cm depth in June (6), July (7) and August (8) measured from silicone gas collectors. Results from the RP (0) and TPs (1, 8 and 11) (Error Bars: +/- 1 SD, could not be calculated if under three samples per plot). Note the logarithmic scale.

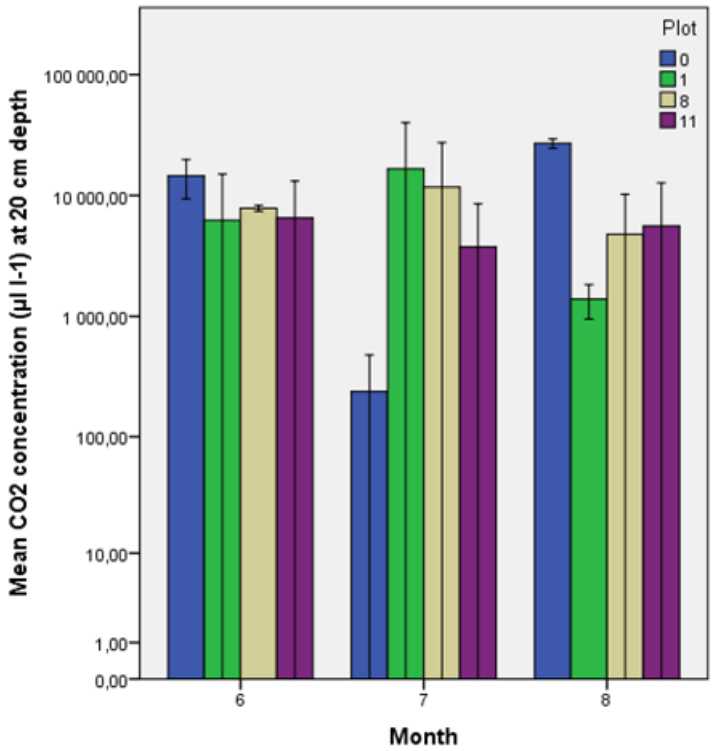

Figure 17. Mean carbon dioxide (CO_2) concentrations of three replicates at 20 cm depth in June (6), July (7) and August (8) measured from silicone gas collectors. Results from the RP (0) and TPs (1, 8 and 11) (Error Bars: +/- 1 SD, could not be calculated if under three samples per plot). Note the logarithmic scale.

6.5 Dissolved gases in surface water

6.5.1 Methane concentration in surface water

Highest amounts of dissolved CH_4 in water samples in June were found on TP 1 (9.02 µmol l^{-1}). Levels on the reference plot were nearly a third of this (3.67 µmol l^{-1}) and no CH_4 was measured from TPs 8 or 11 (Fig. 18). In July and August clearly highest CH_4 concentrations were measured on the RP (0) and were 0.98 µmol l^{-1} and 2.85 µmol l^{-1} respectively.

Low amounts of CH_4 were measured on TP 1 (0.05 µmol l^{-1}) and on TP 8 (0.01 µmol l^{-1}) in July and on TP 1 in August (0.04 µmol l^{-1}). No dissolved CH_4 was detected in the surface water on TP 11 on any of the measurement times. No statistically significant difference was seen between dissolved CH_4 concentration on the RP 0 and TP 1 (U=20.000, p=0.355). Methane concentrations were significantly higher on the RP 0 than on TP 11 (U=3.500, p=0.002) and 8 (U=5.000, p=0.001).

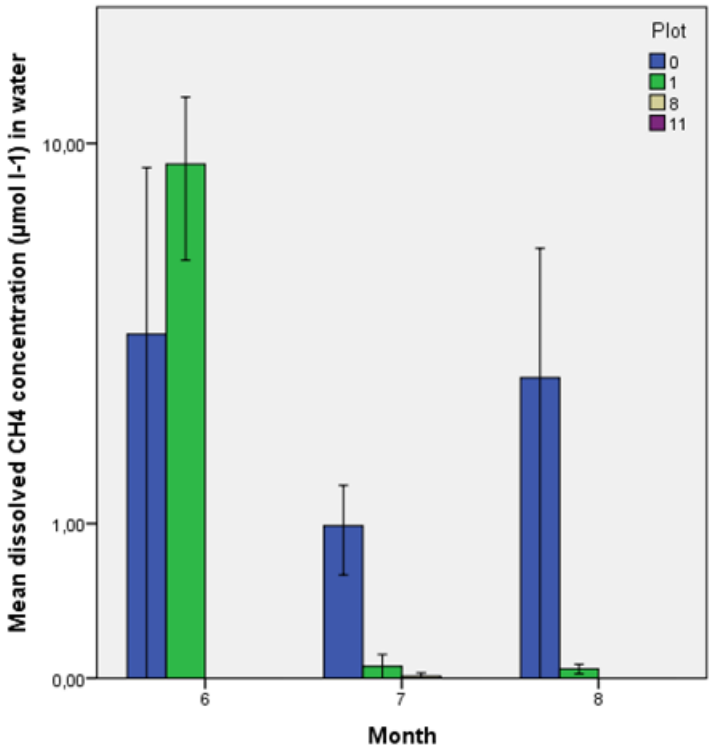

Figure 18. Mean dissolved methane (CH_4) concentrations of three replicates in surface water in June (6), July (7) and August (8). Results from the RP (0) and TPs (1, 8 and 11) (Error Bars: +/- 1 SD). Note the logarithmic scale.

6.5.2 Nitrous oxide concentration in surface water

Throughout the summer, highest dissolved N_2O concentrations were measured from TP 8 (Fig. 19). In June mean N_2O concentration on TP 8 was 12 700 µmol l^{-1}, in July is was 2170 µmol l^{-1} and in August 646 µmol l^{-1}. The concentration from the RP 0 were similar to ones measured from TPs 1 and 11 and these were all generally low (both < 400 µmol l^{-1}). The N_2O concentrations on TP 8 were significantly higher (U=5.000, p=0.002) than on the RP 0. Nitrous oxide concentrations on TP 8 were also significantly higher than on TP 11 (U=7.000, p=0.010) and 1 (U=4.000, p=0.004).

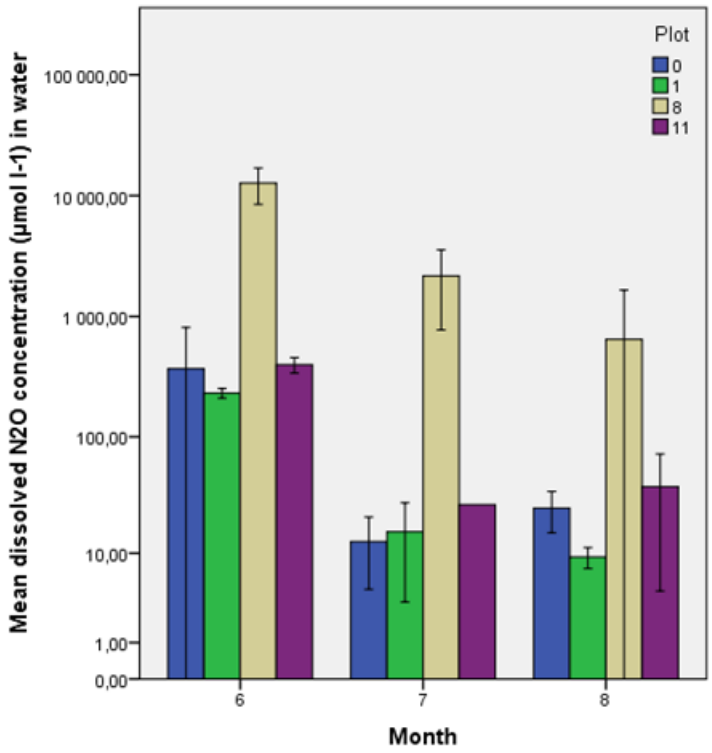

Figure 19. Mean dissolved nitrous oxide (N_2O) concentrations of three replicates in surface water in June (6), July (7) and August (8). Results from the RP (0) and TPs (1, 8 and 11) (Error Bars: +/- 1 SD, could not be calculated if under three samples per plot). Note the logarithmic scale.

6.5.3 Carbon dioxide concentration in surface water

Overall measured dissolved CO_2 concentrations during summer (Fig. 20) were generally highest in June and lowest in August. The measured mean CO_2 concentrations on TP 8 were highest in June (4760 µmol l^{-1}), but lower in July (254 µmol l^{-1}) and August (439 µmol l^{-1}). The similar pattern was seen with concentrations on TP 11 though these were a lot lower (154 – 1 460 µmol l^{-1}) than on TP 8. CO_2 concentrations on RP 0 and TP 1 were generally low every month (230 – 833 µmol l^{-1} and 479 – 732 µmol l^{-1} respectively).

There was no statistically significant difference ER rates between the TPs: 8 and 11 (U=26.000, p=0.560), 8 and 1 (U=29.00, p=0.791) or 1 and 11 (U=21.000, p=0.655). No statistically significant difference was found between the RP 0 and the TPs 11 (U=29.000, p=0.791), 1 (U=21.000, p=0.266) and 8 (U=30.000. p=0.354) either.

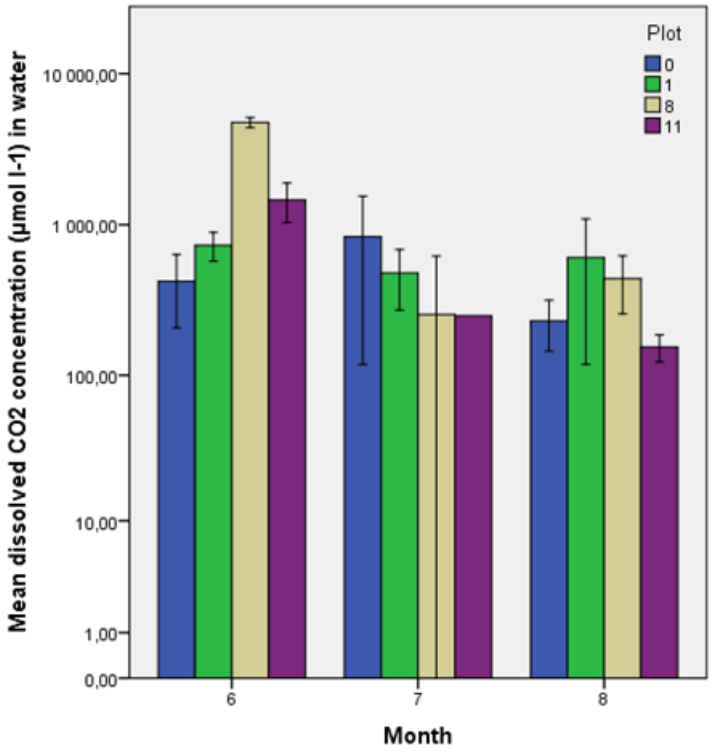

Figure 20. Mean dissolved carbon dioxide (CO_2) concentrations of three replicates in surface water in June (6), July (7) and August (8). Results from the RP (0) and TPs (1, 8 and 11) (Error Bars: +/- 1 SD, could not be calculated if under three samples per plot). Note the logarithmic scale.

6.6 Correlations between measured gas fluxes, environmental variables and chemical properties

6.6.1 Methane

Correlations between CH_4 fluxes, measured environmental variables and chemical properties were assessed with Spearman's correlation coefficient (Appendix 1). Methane fluxes decreased with increased SO_4^{2-} concentrations ($r_s(29)=-0.479$, $p=0.009$) in surface water (Fig. 21). Methane fluxes also decreased with increased surface water NO_3^- concentrations ($r_s(29)= -0.463$, $p=0.011$). Results show an decrease in CH_4 fluxes with increased surface water Cl^- concentrations ($r_s(29)=-0.561$, $p=0.002$) and EC values ($r_s(29)=-0.506$, $p=0.005$) as well. Methane emissions increased with increased TOC ($r_s(29)=0.443$, $p=0.016$) values (Fig. 22).

Methane fluxes decreased with increased dissolved N_2O concentrations in surface water ($r_s(28)=-0.418$, $p=0.010$) and showed to decrease with increased N_2O fluxes ($r_s(31)=-0.558$, $p=0.001$) as well. Methane fluxes decreased with increased concentrations of N_2O measured of soil air samples from silicone gas collectors at 5 cm depth ($r_s(17)=-0.512$, $p=0.036$). Methane fluxes did not correlate with measured dissolved CH_4 concentrations in surface water samples or with CH_4 concentrations measured from soil air samples from silicone gas collectors. Other correlations between different sampling techniques results can be seen in Appendix 2.

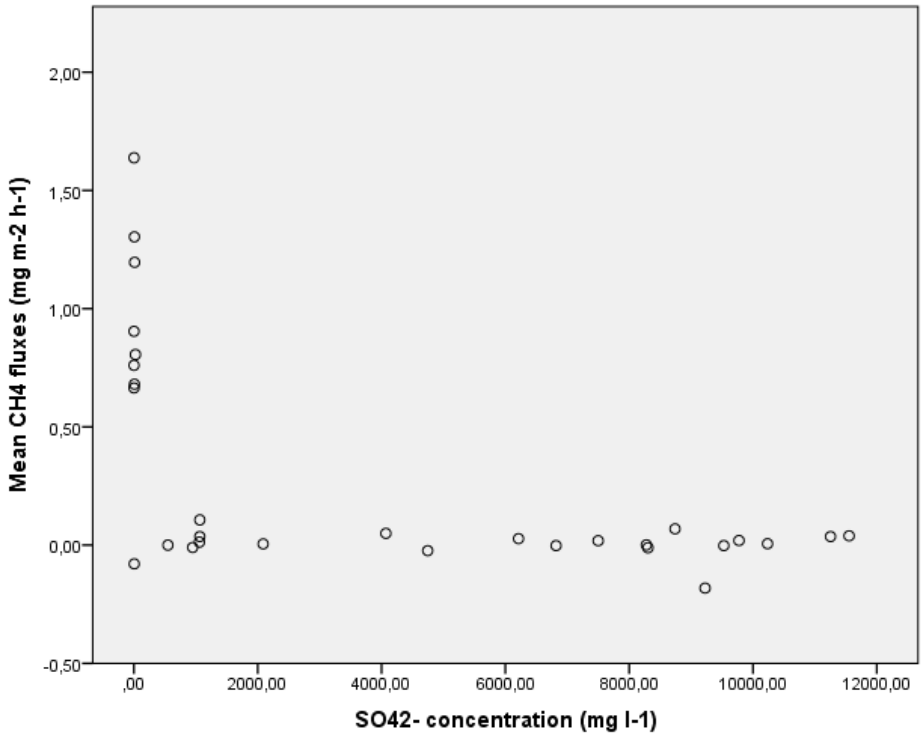

Figure 21. Methane (CH_4) fluxes from chamber measurements plotted with sulfate (SO_4) concentration in the surface water including both RP and TPs and sampling times.

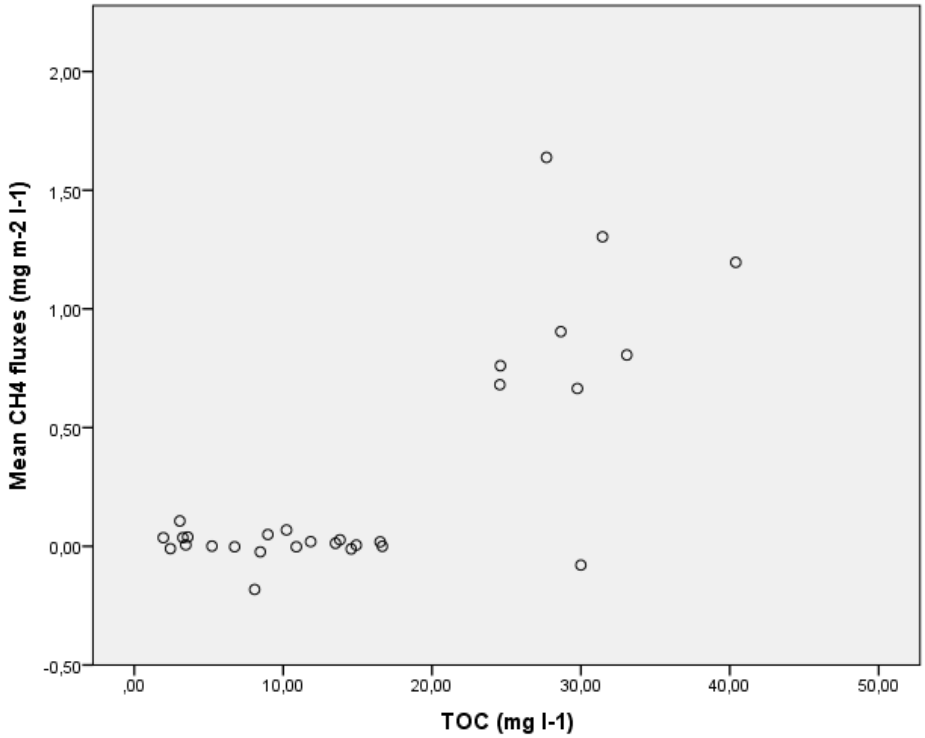

Figure 22. Methane (CH_4) fluxes from chamber measurements plotted with total organic carbon (TOC) including both RP and TPs and sampling times.

6.6.2 Nitrous oxide

Correlations between N_2O fluxes, measured environmental variables and chemical properties were assessed with Spearman's correlation coefficient (Appendix 1). Nitrous oxide fluxes increased with increased NO_3^- ($r_s(29)=0.691$, $p=0.000$) (Fig. 23) and NH_4^+ ($r_s=0.506$, $p=0.005$) (Fig. 24) concentrations in surface water. Nitrous oxide fluxes also showed to increase with increased surface water SO_4^{2-} ($r_s(29)=0.533$, $p=0.003$) and Cl^- ($r_s=29)=0.575$, $p=0.001$). Nitrous oxide fluxes increased with increasing EC values ($r_s(29)=0.539$, $p=0.003$), but decreased with increased CH_4 fluxes ($r_s(31)=-0.558$, $p=0.001$) and increased dissolved CH_4 concentrations measured from surface water samples ($r_s(27)=-0.451$, $p=0.018$).

Measured N_2O fluxes showed to increase ($r_s(28)=0.621$, $p=0.000$) with dissolved N_2O concentrations in surface water samples. Nitrous oxide fluxes also increased with measured N_2O concentrations in soil air samples from silicone gas collectors at 20 cm depth ($r_s(19)=0.537$, $p=0.018$), but not at 5 cm depth ($r_s(17)=0.463$, $p=0.061$). Other correlations between different sampling techniques results can be seen in Appendix 2.

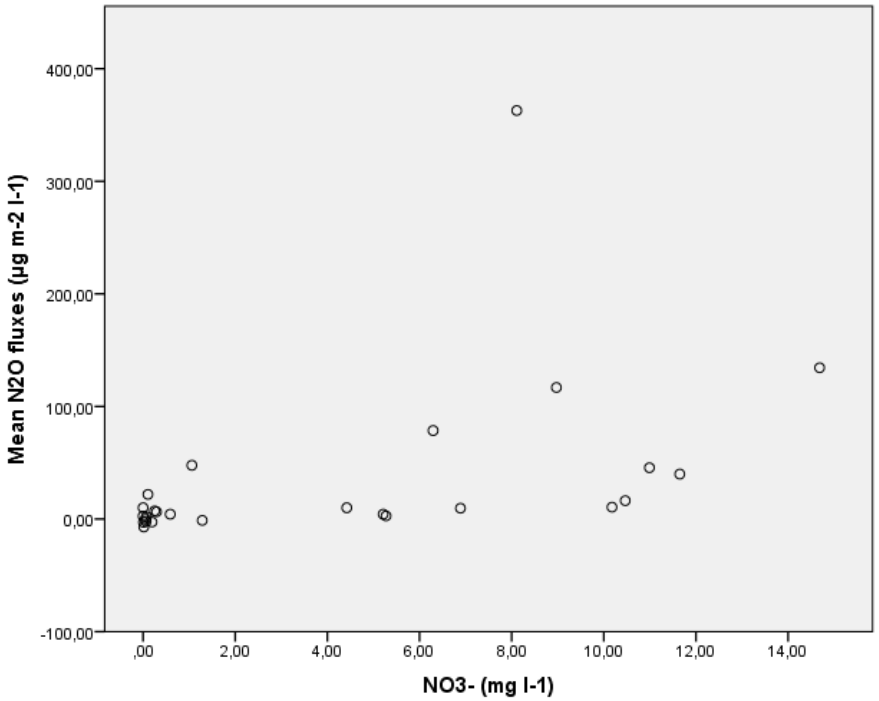

Figure 23. Nitrous oxide (N_2O) fluxes from chamber measurements plotted with and nitrate (NO_3^-) concentration measured from surface water samples including both RP and TPs and sampling times.

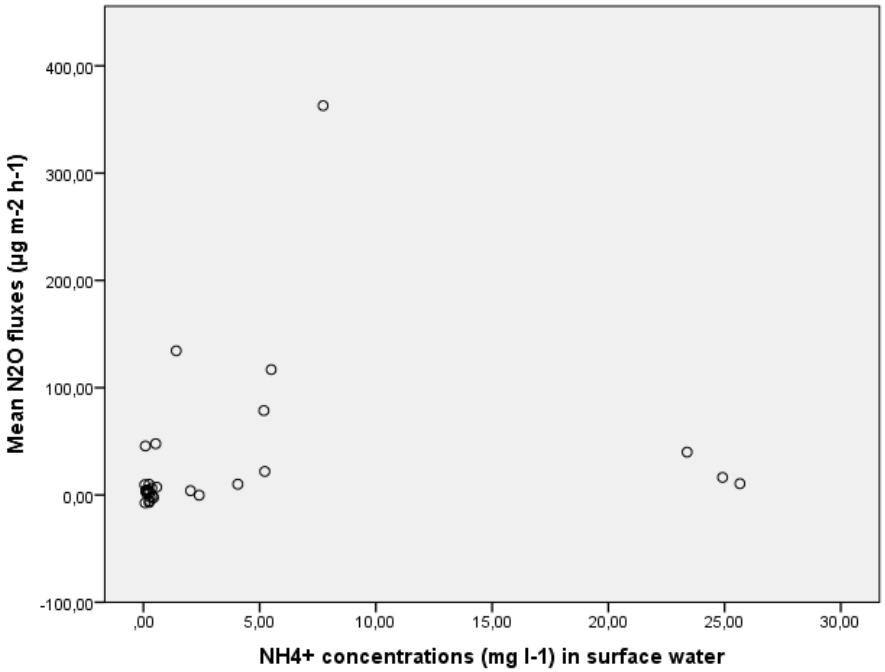

Figure 24. Nitrous oxide (N_2O) fluxes from chamber measurements plotted with ammonium (NH_4^+) concentration measured from surface water samples including both RP and TPs and sampling times.

6.6.3 Ecosystem respiration

Ecosystem respiration rates increased with increasing air temperature ($r_s(30)=0.372$, $p=0.43$). Ecosystem respiration rates also increased with increased ground temperature at depths of 5 cm ($r_s(30)=0.418$, $p=0.022$) (Fig. 25), 10 cm ($r_s(30)=0.379$, $p=0.039$) and 20 cm ($r_s(30)=0.491$, $p=0.006$). Fluxes of CO_2 increased with increased NO_3^- concentrations in surface water ($r_s(28)=0.432$, $p=0.022$) samples (Fig. 26). No statistically significant correlations were found between ER rates and other measured environmental variables or chemical properties assessed with Spearman's correlation coefficient (Appendix 1).

Ecosystem respiration rates decreased with increased CO_2 concentrations measured from soil air samples at 5 cm depth ($r_s(16)=-0.553$, $p=0.026$), but not at 20 cm depth ($r_s(19)=-0.046$, $p=0.853$). Ecosystem respiration rates also decreased with increasing dissolved CH_4 concentrations measured from surface water samples ($r_s(26)=-0.396$, $p=0.045$). Other correlations between different sampling techniques results can be seen in Appendix 2.

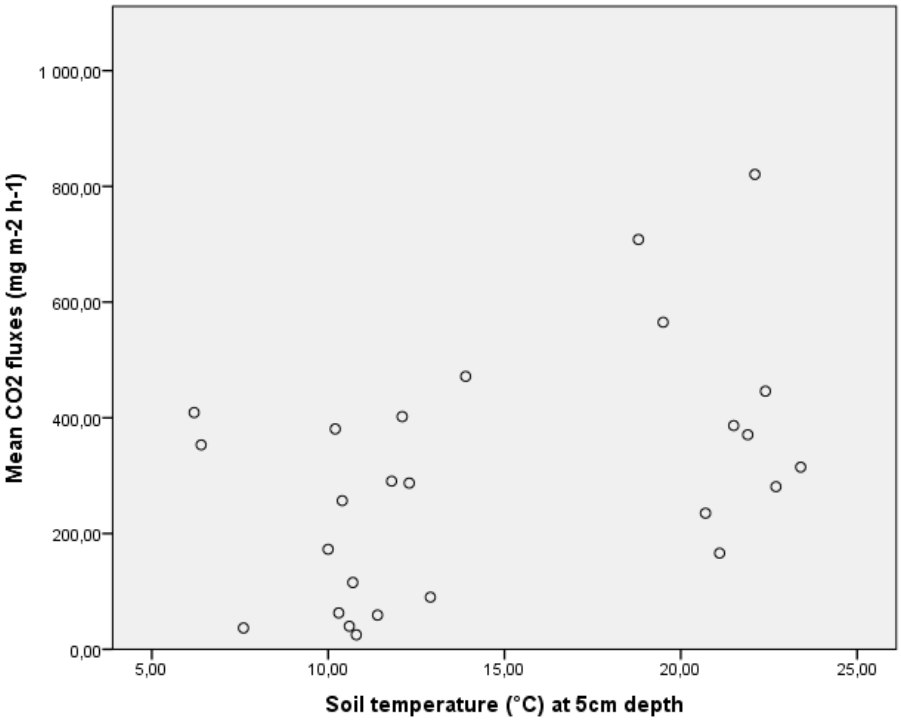

Figure 25. Ecosystem respiration rates (CO_2 fluxes) from chamber measurements plotted with soil temperature (ºC) measured at 5 cm depth including both RP and TPs and sampling times.

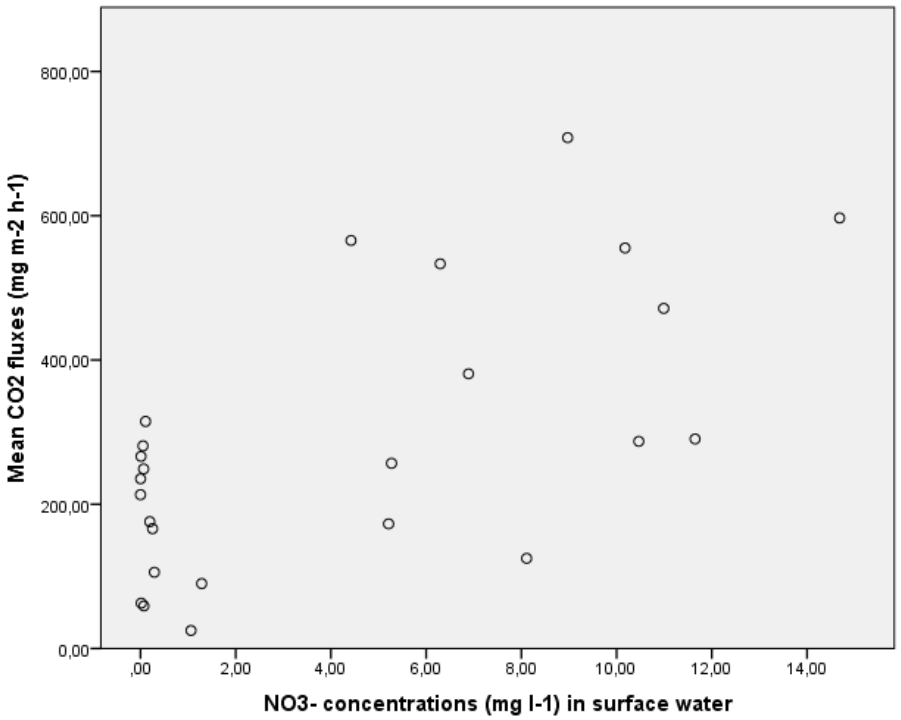

Figure 26. Ecosystem respiration rates (CO_2 fluxes) from chamber measurements plotted with nitrate (NO_{3-}) concentration measured from surface water samples including both RP and TPs and sampling times.

7 DISCUSSION

7.1 The effect of metal mine waste water on chemical properties of peat

Mining produces vast amounts of metals and anions from mining ores and processes (Wood 2012, Lottermoser 2010, Pöyry 2010, McLemore 2008, Kauppila et al. 2011). Electrical conductivity represents the total (available) ion concentration in surface water. This study showed substantial differences in e.g. measured EC values from treatment peatlands (1690 - 10 610 µS cm^{-1}) compared to reference peatland not affected by mining waste water (< 130 µS cm^{-1}). EC values were especially high on TP A effected by the process waste water and somewhat lower on TP B effected by mine drainage water. Measurements, conducted by the Geological Survey of Finland and the University of Oulu, found sulfate and metalloids e.g. magnesium, sodium, calcium and potassium, in the lower water bodies of the studied metal mine. These compounds increase EC and have known to be retained poorly in these treatment peatlands (Hämäläinen 2015).

The highest concentrations of anions (NO_3^-, SO_4^{2-}, Cl^-), were generally measured in surface water samples taken closest to the waste water inlet in treatment peatland A (TP 8), and slightly further away from another waste water inlet in treatment peatland B (TP 11). Levels of all anions were lower further away from the inlets on TP 1 on treatment peatland A, and lowest on the reference peatland (RP 0). High NO_3^- concentrations where measured on both treatment peatlands closest to process- and drainage water inlets, on TPs 8 and 11 (Fig. 5). Especially high amounts of NH_4^+ were measured closest to the process water inlet, on TP 8 (Fig. 8). Nitrate and NH_4^+ are common components of mining explosives where they can dissolve to mine drainage and process waters (McLemore 2008, Hämäläinen 2015). Significantly lower concentrations of NO_3^- and NH_4^+ were measured on TP 1 further away from inlets, suggesting quick turnover times, absorption and/or plant uptake rates in these treatment peatlands.

High concentrations of sulfate were measured on all TPs, but concentrations in the reference peatland were clearly lower (Fig. 6). Similar pattern was seen with Cl^- (Fig. 7). Mining of sulphurous mining ores can release SO_4^{2-} (Lottermoser 2010, McLemore 2008, Wood 2012) and Cl^- into mine waste water. Sulfates and sulfuric acid are also widely used chemicals in metallurgical processes (Lottermoser 2010, Pöyry 2010, McLemore 2008). Significantly higher concentrations of SO_4^{2-} in surface water were measured from TP 8 closer to process water inlet in treatment peatland A used for process water treatment, compared to TP 11 on treatment peatland B that is used for treating mining drainage waters. Highest concentrations of Cl^- were also measured on TP 8 (Fig. 7)

The surface water on reference peatland had higher levels of TOC (> 27.3 mg C l^{-1}*)* than the treatment peatlands (< 15.7 mg C l^{-1}). Of the treatment plots, the highest TOC concentrations were measured on TP 1 furthest from the waste water inlets. TOC concentrations were generally lowest on TP 11 effected by mining drainage waters in June and July, but slightly higher in August (Table 8). These findings suggest that mining effluents contain substances that might enhance microbial and/or vegetation dominated processes that use carbon from the soil in peatlands that naturally accumulate it well (Frolking et al. 2013, Laine et al. 2013, Winde 2011).

Mining waste water can be a source of acidification of soil, but this is usually not the case with treatment peatlands, as industry practice is to treat mining drainage and process waters with pH adjusting compounds to prevent acidification of lower water bodies (Pöyry 2010). This alkaline (pH > 7) waste water elevates pH on treatment peatlands, especially closer to waste water inlets. Measured pH on treatment peatlands was highest on TP 11 (7.26 - 7.54), affected by mining drainage water. pH was also relatively high in TP 8, closest to the process water inlet (6.53 - 7.34), but always below 7 further away from it (on TP 1). Results from adjacent reference peatland (6.43-6.76) were constantly lower than results from TPs and closer to those of pristine peatlands, though still higher than commonly recorded on them.

7.2 The effect of metal mine waste water on methane emissions from peatlands

Natural peatlands are great sources of atmospheric CH_4 (Walter et al. 2001, Mikaloff Fletcher et al. 2004, Strack et al. 2008). Methane is generally produced by methanogenic archaea (i.e. methanogens) (Hynninen 2011, Strack et al. 2008), released through soil in diffusion or through vascular plants (Bubier et al. 1995) and consumed by methanotrophs, the CH_4 oxidizing microbes (Kip et al. 2010). Mining effluents clearly seem to affect these microbial processes and lead to reduced CH_4 emissions. Study plots on treatment peatlands influenced by mining waste water had very low CH_4 emissions while the adjacent, unaffected reference plot showed higher emissions, more typical to pristine peatlands (Fig. 9).

Sulfate reducing microbes have been shown to limit CH_4 production in conditions where high amount of SO_4^{2-} is present (Oremland & Polcin 1982, Pester et al. 2012, van Hulzen et al. 1999) as is the case in treatment peatlands affected by mining waste water (Table 1) (Kauppila et al. 2011, Palmer et al. 2015). Methane production demands carbon sources, such as CO_2, formate or acetate, as electron acceptors (Pester et al. 2012). It is suggested that, in conditions with high SO_4^{2-} concentrations, sulfate reducing microbes dominate over methanogens by outcompeting methanogens for available electron acceptors, which can lead to very low or even nonexistent levels of CH_4 being produced (Oremland & Polcin 1982, Pester et al. 2012). In this study, TPs produced very low amounts of CH_4 (max. 0.05 mg $m^{-2}h^{-1}$) or were even sources of uptake (down to -0.18 mg $m^{-2}h^{-1}$). Reference peatland 0 did not receive any SO_4^{2-} from mining waste waters and significant CH_4 emissions (min. 0.50 mg $m^{-2}h^{-1}$), from the reference peatland were measured. It is shown that measured surface water SO_4^{2-} concentrations significantly decreased CH_4 emissions from peatlands (Fig. 21), in this study. These findings are supported by measured CH_4 concentrations from the silicone gas collectors and surface water samples. Methane concentrations from soil air samples (Fig. 12 & 13) were always higher on the reference peatland compared to the treatment peatlands. Peatland surface water samples in July and August showed also higher dissolved CH_4 concentrations on the reference peatland than on the TPs, except in June (Fig. 18).

Methanogenesis is also controlled by soil composition, pH, temperature and water table level (Pester et al. 2012, Bubier et al. 1995, Yu et al. 2013). High CH_4 peaks were discovered after snow melt in June. Such peaks have been previously recorded under conditions of snow melt and thawing (Hynninen 2011, also Bubier et al. 1995). Observed water table levels were also clearly highest in June, compared to other months studied. This probably had a significant effect on measured CH_4 emissions, due to more prevalent anoxic conditions in the peat layers. In this study, CH_4 emissions were shown to increase with increasing amount of total organic carbon (TOC) (Fig 22). Highest TOC concentrations were measured in RP 0, where highest CH_4 emissions were measured. Also, pH was lower on the RP 0 than most of the treatment plots (Table 6).

Vegetation assessment showed a distinctively different vegetation composition, featuring more vascular plants and a smaller plant land coverage, on the area affected by mining waste waters compared to pristine reference plot (Table 5). Lower levels of primary production can decrease CH_4 emissions. On the other hand, sedges such as *Carex lasiocarpa* that are adapted to wet and high pH conditions, as well as mosses (like *Sphagnum and Warnsdorfia*) have known to produce high CH_4 emissions on poor and intermediate fens (Bubier et al. 1995).

7.3 The effect of metal mine waste water on nitrous oxide emissions from peatlands

Nitrous oxide can be released to the atmosphere in case of incomplete denitrification-nitrification process (Robertson & Groffman 2007, Nieminen 1998). Pristine peatlands tend to be sinks or small sources of N_2O (Kolb & Horn. 2012; Strack et al. 2008). Nitrous oxide production is dependent on available NO_3^- (Silvan et al. 2005) and N fertilization seen to result in higher N_2O emissions on forested and agricultural peatlands (Nieminen 1998, Strack et al. 2008). In this study, N_2O fluxes from the reference peatland were small (< 10.6 µg $m^{-2}h^{-1}$), and even some uptake (down to -2.87 µg $m^{-2}h^{-1}$) was measured. Treatment peatlands presented significantly higher N_2O emissions (max. 363 µg $m^{-2}h^{-1}$) compared to the reference site (Fig. 10).

Nitrous oxide in soils is mainly produced by denitrifying and nitrifying microbes from N sources such as NO_3^-, NO_2^- and NH_4^+ (Robertson & Groffman 2007, Winde 2011). Ammonium and NO_3^- which are abundant in mine waste waters feed nitrification and denitrification processes (Kauppila et al. 2011, Palmer et al. 2015). Also, ammonia-oxidizing microbes, that oxidize NH_4^+ to NO_3^-, work best in high NH_4^+ and high C environments (Huang et al. 2014). Thus, is it likely that introducing mining waste water, increases peatland's N_2O emissions. This is supported by measured highest N_2O emissions of all study plots on TP 8 closest to process waste water inlet in treatment peatland A. Nitrous oxide emissions were also measured on TP 11 in treatment peatland B, close to the mining drainage water inlet. Treatment peatland B experienced higher loads of total N and NO_3^- than treatment peatland A, but NH_4^+ loads were higher on peatland A (Table 1). Nitrate and NH_4^+ are removed from the peatlands by oxidation, nitrification-denitrification and vegetation uptake or with absorption to the peat. Therefore, concentration can decline rather rapidly moving further from the waste water inlets (Palmer et al. 2015). In this study, N_2O fluxes were low or even negative on TP 1 in treatment peatland A, furthest away from the waste water inlets.

Nitrous oxide fluxes increased with increased NO_3^- (Fig. 23) and NH_4^+ (Fig. 24) concentrations measured from surface water samples and also with increased concentrations of dissolved N_2O measured from surface water samples. Nitrous oxide fluxes showed to increase with increased N_2O concentrations in soil air samples in the deeper peat layers (20 cm), but not with concentrations measured at the upper layers of peat (5 cm). Part of the N_2O formed in the deeper layers could also be reduced to N_2 on its way up (Nieminen 1998). Nitrous oxide fluxes showed to increase with increased dissolved N_2O concentrations measured from surface water samples and it is suggested that these could be used to estimate N_2O fluxes of peatlands.

Measured concentrations of N_2O suggest that high amount of N is used by microbial reactions. Measured NH_4^+ concentrations in surface layers might be lower due to ongoing oxygen-demanding nitrification process and possibly due to NH_4^+ accumulation in deeper layers. This on the other hand suggests higher levels of NO_3^- by nitrification in addition to waste water loadings. Denitrification processes that convert NO_3^- to gaseous forms take place in deeper, anoxic layers. These processes are known to produce N_2O and N_2 in peatlands. Plants also contribute by uptake of NH_4^+ and NO_3^- and can act as a NO_3^- sink (Silvan et al. 2005, Nichols

1983). Observed plant growth in the study sites suggests that N has also been taken up by plants. Highest N_2O emissions were also measured in July (Fig. 10). N_2O emissions in peatlands have shown to increase with temperature and decrease with low soil pH in study by Strack et al. (2008). In this study, temperature or soil pH did not show to significantly affect N_2O flux rates.

7.4 The effect of metal mine waste water on ecosystem respiration from peatlands

Pristine peatlands allocate efficiently carbon to their biomass and are significant sinks of atmospheric CO_2. Ecosystem respiration (ER) i.e. combined autotrophic (plant dominated) and heterotrophic (microbial and fungal dominated) respiration also releases quantities of CO_2 back to the atmosphere. This process is highly dependent on soil moisture and temperature (Malmer et al. 2005, Gorham 1991), limited by low oxygen and high and low pH conditions (Yu et al. 2013). A dependence to soil and air temperatures was shown in this study as ER rates increased with increased temperature (Fig. 25). It is suggested that temperature is one of the most dominating factors controlling ER in studied peatlands. Belyea (2013) also suggested that CO_2 emission on wetlands are directly controlled by temperature and indirectly by water table level. Treatment peatlands are often waterlogged soils and high water tables can act as a limiting factor to gas exchange and ER in this study as well. Also, ER rates decreased with increased CO_2 concentrations measured from soil air samples at 5 cm depth (Fig. 25), but not with 20 cm depth. It is possible that high amounts of water limit the oxygen supply to upper peat layers and therefore inhibit ER as suggested by Yu et al. (2013).

Since ER is determined also by plant productivity, it is greatly affected by the soil nutrient status (Strack et al. 2008, Yu et al. 2013). Mining waste water contain high amounts of nutrients, such as NO_3^- and NH_4^+ (Table 1). Rates of ER on TPs closest to the waste water inlets (TPs 11 and 8) were significantly higher from measured ER rates on the adjacent RP 0 (Fig. 11), except in June where RP 0 showed higher fluxes than TP 8, but not higher than TP 11. Ecosystem respiration rates on TP 1, further away from the waste water inlets, were not significantly higher than ones on the RP 0. Best retention of substances, such as nutrients, in treatment peatlands has been discovered on areas closest to the waste water distribution ditch (Palmer et al. 2015). In this study, significantly increased ecosystem respiration rates were

measured with increased concentrations of NO_3^- in surface water (Fig. 26). It can be concluded that mining effluents that contain nutrients could in some cases enhance ecosystem respiration of treatment peatlands. As CO_2 is also allocated to vegetation biomass, the net CO_2 exchange including photosynthesis, might not be enhanced, or could even be reduced, in TPs compared to pristine peatlands.

Nutrient addition is shown to possibly affect the vegetation composition of wetlands (Liikanen et al. 2006). In this study, the reference plot was dominated by *Warnsdorfia*, a type of moss, while the treatment plots had higher amounts of vascular plants and generally higher variation of plants. TP 11 on treatment peatland B showed clearly different vegetation compared to treatment peatland A and had distinctively high levels of vascular plants *Carex lasiocarpa* and *Menyanthes trifoliata* which were seen in treatment peatland A only in lower amounts. The growth of vascular plants is usually quickly promoted by nutrient additions (Frolking et al. 2013). In TPs 8 and 1 different amounts of plant surface coverage were seen (Table 5). TP 8 had plant species (like *Eriophorum angustifolium* and *Menyanthes trifoliata*) adapted well to wet environments while TP 1 had especially *Carex* species found typically on bogs. There was also slightly less vegetation on TP 1 than 8. Increased levels of ER can be seen with increased vegetation coverage. As ER is highly dependent on vegetation type, these differences may explain the variations of ER rates between the study plots.

7.5 Effects of metal mine waste water on the global warming potential of treatment peatlands

Methane and nitrous oxide are considerable greenhouse gases and contributes to global warming. The global warming potential of CH_4 is 21 times and of N_2O, 310 times that of CO_2 (in CO_2 equivalents) (Table 2) (IPCC (2013 & 2007). In this study, net CH_4 emissions were highly lower on the treatment peatlands (24.6 mg CO_2 eq. d^{-1}) than on the reference peatland (441 mg CO_2 eq. d^{-1}) in given measurement period. Net N_2O emissions were higher (310 mg CO_2 eq. d^{-1}) on the treatment peatlands and lower (22.2 mg CO_2 eq. d^{-1}) on the reference peatland. As to these results, a slightly negative (-128 CO_2 eq. mg d^{-1}) global warming potential was seen on treatment peatlands compared to pristine peatlands in the scope of this study. Mining waste water effects the greenhouse gas balances of peatlands, but calculated only by

their CO_2 equivalents, and assuming no major changes happen in the net CO_2 exchange, the global warming potential of peatlands has not seen to drastically change due to mining waste water release. In the future, warming climate will most likely cause higher mean temperatures and less snow coverage that can highly influence the conditions, and greenhouse gas emissions, on northern boreal peatlands.

7.6 Critical assessment of study

Gas sampling in the field, especially in a peatland, is a laborious and demanding process. In this study, samples were collected in June, July and August. Some samples from June had to be omitted because high amounts of vegetation compromised the chamber airtightness. Some samples were also omitted throughout the measurement period because of syringe malfunctions. Originally, samples were also collected in September, but because of weather conditions in the field, most of the study plots were either completely or partly frozen. Ice inhibited sample collection in some study plots and impacted results, e.g. by preventing soil gas exchange, in others. Therefore, samples from September were not comparable and were omitted as well.

One of the main controlling factors with peatland gas emissions, is the water table level. This is a controlling factor, especially with methane emissions, due to microbial processes being profoundly influenced by oxygen exchange. Water table levels were not measured in this study and such measurements would benefit further studies in this area. Based on physical observation, water table levels were very high in June as most of the study fields were submerged after vast loads of waste water were discharged from the mine, according to the mining company. In June water table levels were also most likely affected by relatively resent snow melt and low air temperatures. In July and August temperatures were considerably higher, causing higher evaporation rates. Studied peatlands are almost treeless environments, exposed to constant sunshine in the summer period, but quickly colder and darker conditions throughout the rest of the year. It is noteworthy, that measurements were conducted and samples were collected only in the Boreal summer season, and do not represent the year-round results. In further studies, annual measurements would benefit the knowledge of Boreal greenhouse gas emissions.

8 CONCLUSIONS

Mining waste waters contain vast amounts of nutrients and other substances that could influence peatlands microbial processes. In this study, it is seen that metal mining waste water clearly affect the greenhouse gas fluxes of the peatlands used for waste water treatment. Differences in gas flux rates, as well as gas concentrations in soil air and surface water samples were seen.

Studied boreal peatlands, used for metal mine waste water treatment, showed highly elevated N_2O fluxes as well as highly lowered CH_4 fluxes. The obtained results indicate that the cause of low CH_4 emissions is most likely, the competition for electrons between methanogens and sulfate reducing microbes, that thrive and outcompete methanogens under high SO_4^{2-} conditions. The high N_2O fluxes on treatment peatlands are most likely caused by high mineral N loadings in the waste waters. The effect of the drastically higher N_2O emissions to global warming potential is counterbalanced by the effect of the lower CH_4 emissions. In the scope of this study, it is also seen possible that mining waste waters can alter the ecosystem respiration rates of treatment peatlands, especially on surface areas close to mine waste water inlets.

Peatlands are very heterogenic environments that are affected by various different processes and ever changing weather conditions. Only a small part of these factors was possible to be included in this study. The water table level, an important controlling factor of GHG emissions, was also excluded from the measurements of this study. Also, this research was only conducted in the northern summer season and does not represent the year-round conditions. Nevertheless, this study gives valuable new insight of the effects that mining waste water have on the treatment peatlands greenhouse gas balance that has been scarcely studied so far.

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APPENDICES

Appendix 1. Spearman's correlation coefficients between measured methane, nitrous oxide and ecosystem respiration rates, environmental variables and chemical properties.

Air temp. = Air temperature from ambient air samples (ºC); Peat temp. = Peat soil temperature (ºC) measured at 5, 10 or 20 cm depth; NO3- = Nitrate (NO_{3-}) concentration (mg l^{-1}) measured from surface water samples; SO42- = Sulfate (SO_4^{2-}) concentration (mg l^{-1}) measured from surface water samples; Cl = Chloride (Cl^-) concentration (mg l^{-1}) measured from surface water samples; NH4+ = Ammonium (NH_4^+) concentration (mg l^{-1}) measured from surface water samples; pH = pH value measured from surface water samples; EC = Electrical conductivity (µS cm^{-1}) measured from surface water samples; TOC = Total organic carbon concentration (mg C l^{-1}) measured from surface water samples; CH4 flux = Methane (CH_4) flux (mg $m^{-2}h^{-1}$) from the peat soil measured by gas chamber measurements; N2O flux = Nitrous oxide (N_2O) flux (µg $m^{-2}h^{-1}$) from the peat soil measured by gas chamber measurements; CO2 flux = Ecosystem respiration rate (mg $m^{-2}h^{-1}$) from the peat soil measured by gas chamber measurements; p-value = statistical significance (< 0.05 significant correlation, < 0.01 very significant correlation); N = number of samples

	Air temp.	Peat temp. (5cm)	Peat temp. (10cm)	Peat temp. (20 cm)	NO3-	SO42-	Cl-	NH4+	pH	EC	TOC	CH4 flux	N2O flux	CO2 flux
Air temp.	1,000	0,873**	0,862**	0,815**	0,006	0,347	0,111	0,585**	-0,256	0,418*	0,128	-0,093	0,212	0,372*
p-value		0,000	0,000	0,000	0,976	0,060	0,559	0,001	0,173	0,022	0,501	0,620	0,251	0,043
N	33	32	32	32	30	30	30	31	30	30	30	31	31	30
Peat temp. (5 cm)	0,873**	1,000	0,910**	0,848**	0,022	0,367*	0,126	0,546**	-0,321	0,412*	0,082	-0,129	0,223	0,418*
p-value	0,000		0,000	0,000	0,908	0,046	0,507	0,002	0,084	0,024	0,668	0,488	0,227	0,022
N	32	32	32	32	30	30	30	30	30	30	30	31	31	30
Peat temp (10 cm)	0,862**	0,910**	1,000	0,955**	-0,013	0,413*	0,092	0,556**	-0,274	0,419*	0,109	-0,100	0,113	0,379*
p-value	0,000	0,000		0,000	0,944	0,023	0,631	0,001	0,142	0,021	0,567	0,594	0,544	0,039
N	32	32	32	32	30	30	30	30	30	30	30	31	31	30
Peat temp. (20 cm)	0,815**	0,848**	0,955**	1,000	0,120	0,452*	0,243	0,526**	-0,179	0,454*	-0,008	-0,146	0,251	0,491**
p-value	0,000	0,000	0,000		0,529	0,012	0,195	0,003	0,343	0,012	0,966	0,434	0,174	0,006
N	32	32	32	32	30	30	30	30	30	30	30	31	31	30
NO3-	0,006	0,022	-0,013	0,120	1,000	0,602**	0,744**	0,260	0,459**	0,604**	-0,725**	-0,463*	0,691**	0,432*
p-value	0,976	0,908	0,944	0,529		0,000	0,000	0,144	0,007	0,000	0,000	0,011	0,000	0,022
N	30	30	30	30	33	33	33	33	33	33	33	29	29	28
SO42-	0,347	0,367*	0,413*	0,452*	0,602**	1,000	0,503**	0,622**	0,205	0,938**	-0,618**	-0,479**	0,533**	0,331
p-value	0,060	0,046	0,023	0,012	0,000		0,003	0,000	0,251	0,000	0,000	0,009	0,003	0,086
N	30	30	30	30	33	33	33	33	33	33	33	29	29	28
Cl-	0,111	0,126	0,092	0,243	0,744**	0,503**	1,000	0,005	0,698**	0,471**	-0,736**	-0,561**	0,575**	0,323
p-value	0,559	0,507	0,631	0,195	0,000	0,003		0,979	0,000	0,006	0,000	0,002	0,001	0,093
N	30	30	30	30	33	33	33	33	33	33	33	29	29	28
NH4+	0,585**	0,546**	0,556**	0,526**	0,260	0,622**	0,005	1,000	-0,257	0,685**	-0,010	-0,111	0,506**	0,236
p-value	0,001	0,002	0,001	0,003	0,144	0,000	0,979		0,148	0,000	0,956	0,567	0,005	0,227
N	31	30	30	30	33	33	33	34	33	33	33	29	29	28
pH	-0,256	-0,321	-0,274	-0,179	0,459**	0,205	0,698**	-0,257	1,000	0,143	-0,696**	-0,233	0,004	-0,006
p-value	0,173	0,084	0,142	0,343	0,007	0,251	0,000	0,148		0,429	0,000	0,223	0,982	0,977
N	30	30	30	30	33	33	33	33	33	33	33	29	29	28
EC	0,418*	0,412*	0,419*	0,454*	0,604**	0,938**	0,471**	0,685**	0,143	1,000	-0,558**	-0,506**	0,539**	0,255
p-value	0,022	0,024	0,021	0,012	0,000	0,000	0,006	0,000	0,429		0,001	0,005	0,003	0,191
N	30	30	30	30	33	33	33	33	33	33	33	29	29	28
TOC	0,128	0,082	0,109	-0,008	-0,725**	-0,618**	-0,736**	-0,010	-0,696**	-0,558**	1,000	0,443*	-0,361	-0,264
p-value	0,501	0,668	0,567	0,966	0,000	0,000	0,000	0,956	0,000	0,001		0,016	0,055	0,174
N	30	30	30	30	33	33	33	33	33	33	33	29	29	28
CH4 flux	-0,093	-0,129	-0,100	-0,146	-0,463*	-0,479**	-0,561**	-0,111	-0,233	-0,506**	0,443*	1,000	-0,558**	-0,015
p-value	0,620	0,488	0,594	0,434	0,011	0,009	0,002	0,567	0,223	0,005	0,016		0,001	0,938
N	31	31	31	31	29	29	29	29	29	29	29	31	31	30
N2O flux	0,212	0,223	0,113	0,251	0,691**	0,533**	0,575**	0,506**	0,004	0,539**	-0,361	-0,558**	1,000	0,320
p-value	0,251	0,227	0,544	0,174	0,000	0,003	0,001	0,005	0,982	0,003	0,055	0,001		0,085
N	31	31	31	31	29	29	29	29	29	29	29	31	31	30
CO2 flux	0,372*	0,418*	0,379*	0,491**	0,432*	0,331	0,323	0,236	-0,006	0,255	-0,264	-0,015	0,320	1,000
Sig. (2-tailed)	0,043	0,022	0,039	0,006	0,022	0,086	0,093	0,227	0,977	0,191	0,174	0,938	0,085	
N	30	30	30	30	28	28	28	28	28	28	28	30	30	30

*Statistically significant correlation; ** Statistically very significant correlation

Appendix 2. Spearman's correlation coefficients between measured gas fluxes, gas concentrations from silicone gas collectors at 5 and 20 cm and dissolved gases from water samples.

N2O flux = Nitrous oxide (N_2O) flux (µg $m^{-2}h^{-1}$) from the peat soil measured by gas chamber measurements; CO2 flux = Ecosystem respiration rate (mg $m^{-2}h^{-1}$)) from the peat soil measured by gas chamber measurements; CH4 flux = Methane (CH_4) flux (mg $m^{-2}h^{-1}$)) from the peat soil measured by gas chamber measurements; CH4 5 cm = Methane (CH_4) concentration (µl l^{-1}) measured from soil air at 5 cm depth by silicone gas collectors; CH4 20 cm = Methane (CH_4) concentration (µl l^{-1}) measured from soil air at 20 cm depth by silicone gas collectors; N2O 5 cm = Nitrous oxide (N_2O) concentration (µl l^{-1}) measured from soil air at 5 cm depth by silicone gas collectors; N2O 20 cm = Nitrous oxide (N_2O) concentration (µl l^{-1}) measured from soil air at 20 cm depth by silicone gas collectors; CO2 5 cm = Carbon dioxide (CO_2) concentration (µl l^{-1}) measured from soil air at 5 cm depth by silicone gas collectors; CO2 20 cm = Carbon dioxide (CO_2) concentration (µl l^{-1}) measured from soil air at 20 cm depth by silicone gas collectors; CH4W = Dissolved methane (CH_4) concentration (µmol l^{-1}) measured from surface water samples; CO2W = Dissolved carbon dioxide (CO_2) concentration (µmol l^{-1}) measured from surface water samples; N2OW = Dissolved nitrous oxide (N_2O) concentration (µmol l^{-1}) measured from surface water samples; p-value = statistical significance (< 0.05 significant correlation, < 0.01 very significant correlation); N = number of samples

	N2O flux	CO2 flux	CH4 flux	CH4 5cm	CH4 20cm	N2O 5cm	N2O 20cm	CO2 5cm	CO2 20cm	CH4 water	CO2 water	N2O water
NO2 flux	1,000	0,320	-0,558**	-0,225	0,186	0,463	0,537*	-0,150	-0,075	-0,451*	0,237	0,621**
p-value		0,085	0,001	0,384	0,431	0,061	0,018	0,567	0,753	0,018	0,225	0,000
N	31	30	31	17	20	17	19	17	20	27	28	28
CO2 flux	0,320	1,000	-0,015	-0,241	-0,354	0,224	0,377	-0,553*	-0,046	-0,396*	-0,208	0,217
p-value	0,085		0,938	0,368	0,137	0,405	0,123	0,026	0,853	0,045	0,299	0,276
N	30	30	30	16	19	16	18	16	19	26	27	27
CH4 flux	-0,558**	-0,015	1,000	0,284	0,062	-0,512*	-0,296	-0,066	-0,099	0,345	-0,169	-0,481**
p-value	0,001	0,938		0,269	0,796	0,036	0,218	0,801	0,677	0,078	0,390	0,010
N	31	30	31	17	20	17	19	17	20	27	28	28
CH4 5cm	-0,225	-0,241	0,284	1,000	0,425	-0,455*	-0,600**	0,406	0,116	0,142	-0,135	-0,208
p-value	0,384	0,368	0,269		0,055	,038	0,005	0,067	0,618	0,561	0,569	0,380
N	17	16	17	21	21	21	20	21	21	19	20	20
CH4 20cm	0,186	-0,354	0,062	0,425	1,000	-0,332	-0,452*	0,204	0,220	0,470*	-0,136	-0,018
p-value	0,431	0,137	0,796	0,055		0,141	0,031	0,375	0,302	0,027	0,535	0,936
N	20	19	20	21	24	21	23	21	24	22	23	23
N2O 5cm	0,463	0,224	-0,512*	-0,455*	-0,332	1,000	0,777**	0,008	-0,217	-0,142	0,543*	0,611**
p-value	0,061	0,405	0,036	0,038	0,141		0,000	0,991	0,345	0,561	0,013	0,004
N	17	16	17	21	21	21	20	21	21	19	20	20
N2O 20cm	0,537*	0,377	-0,296	-0,600**	-0,452*	0,777**	1,000	-0,081	-0,093	-0,506*	0,321	0,683**
p-value	0,018	0,123	0,218	0,005	0,031	0,000		0,734	0,673	0,019	0,145	0,000
N	19	18	19	20	23	20	23	20	23	21	22	22
CO2 5cm	-0,150	-0,553*	-0,066	0,406	0,204	0,008	-0,081	1,000	0,373	0,145	0,373	0,137
p-value	0,567	0,026	0,801	0,067	0,375	0,991	0,734		0,096	0,554	0,105	0,565
N	17	16	17	21	21	21	20	21	21	19	20	20
CO2 20 cm	-0,075	-0,046	-0,099	0,116	0,220	-0,217	-0,093	0,373	1,000	-0,059	0,006	0,335
p-value	0,753	0,853	0,677	0,618	0,302	0,345	0,673	0,096		0,796	0,979	0,118
N	20	19	20	21	24	21	23	21	24	22	23	23
CH4 water	-0,451*	-0,396*	0,345	0,142	0,470*	-0,142	-0,506*	0,145	-0,059	1,000	-0,140	-0,516**
p-value	0,018	0,045	0,078	0,561	0,027	0,561	0,019	0,554	0,796		0,453	0,003
N	27	26	27	19	22	19	21	19	22	31	31	31
CO2 water	0,237	-0,208	-0,169	-0,135	-0,136	0,543*	0,321	0,373	0,006	-0,140	1,000	0,339
p-value	0,225	0,299	0,390	0,569	0,535	0,013	0,145	0,105	0,979	0,453		0,068
N	28	27	28	20	23	20	22	20	23	31	32	32
N2O water	0,621**	0,217	-0,481**	-0,208	-0,018	0,611**	0,683**	0,137	0,335	-0,516**	0,339	1,000
p-value	0,000	0,276	0,010	0,380	0,936	0,004	0,000	0,565	0,118	0,003	0,058	
N	28	27	28	20	23	20	22	20	23	31	32	32

*Statistically significant correlation; ** Statistically very significant correlation