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# Spatiotemporal variability in methane emission from an Arctic fen over a growing season – dynamics and driving factors

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**Abstract**. Methane emissions from Northern wetlands constitute a substantial part of the total natural emission of methane, a strong greenhouse gas. Both environmental and biotic factors influence the production, oxidation and transport of methane and hence its net flux. The methane emission from Northern wetlands is highly variable both spatially and temporally. As many factors influence the methane flux, knowledge about the interrelation and character of these factors is needed in order to comprehend how environmental changes will affect natural methane emissions. Here the small scale variability in methane emission is investigated using ten plots on a 'moist to wet' gradient, from the fringe towards the central part of a high-Arctic fen. The fluxes were measured during the growing season of 2013 and varied greatly both spatially (with up to a factor ten between the relatively dry and wet plots) and seasonally. The growing season had two peaks of comparable size. The mean growing season emission of methane was relatively low compared to previous years and other circumpolar sites and the uptake of $CO_2$ was small and turned into a loss for the most of the growing season. This was mainly ascribed the unprecedented low amount of snowfall, early snowmelt and subsequent dry growing season conditions. The seasonal development in methane emission was found to correlate very well with the environmental parameters; soil temperature, water level and active layer, although the character of the causal relationships are different. In the wetter part of the gradient the methane flux was also significantly correlated with the net ecosystem exchange. These strong correlations accentuate the autocorrelation and seasonality in these driving factors. Density of vascular plants and species composition appear to play a pivotal role in relation to the magnitude of the methane fluxes. Qualitative analysis of organic acids and dissolved organic carbon did not show any uniform pattern with regards to the location on the moisture gradient. So-called extreme emission events were investigated separately and no correlations with atmospheric variables like wind speed, air pressure, air temperature or changes within these were found. These events were found to constitute up to 25 % of the seasonal methane emission from the relatively dry plots (no extreme events were detected from the 'wettest' plots) and hence constitute a rather significant portion of annual emissions. This study qualitatively highlights the importance of studying controls on methane emission in an integrative manner, as both environmental and biotic controls are interrelated and often display the same seasonal patterns.

**Resume**. Metanudledning fra Nordlige vådområder udgør en betydelig del af den naturlige udledning af metan, en potent drivhusgas. Både fysiske og biologiske faktorer influerer produktion, oxidation og transport af metan og dermed netto udledningen. Udledningen af metan fra Nordlige vådområder viser stor rumlig og tidslig variation. Eftersom mange faktorer indvirker på udledningen af metan er viden om disses karakteristika og indbyrdes forhold nødvendig for at forstå hvordan miljømæssige ændringer vil påvirke den naturlige metanudledning. I dette studie vil den rumlige variation i metanudledningen bliver undersøgt mellem 10 plot (0.6 x 0.6 m), som er placeret på en 'fugtig til våd' gradient nær randen af et høj-Arktisk kær. Udledningen blev målt i vækstsæsonen 2013 og varierede både rumligt (med op til en faktor 10 mellem de to fjerneste plot) og sæsonmæssigt. Vækstsæsonen bestod af to 'peaks' af sammenlignelig størrelse i metanudledning. Den gennemsnitlige sæsonmæssige udledning var relativ lav sammenlignet med tidligere år og andre studier fra circumpolare regioner og netto optaget af kuldioxid var lavt, med netto udledningen i store dele af sæsonen. Dette tilskrives hovedsagligt den meget lave mængde af vinternedbør, de tidlige snefrie forhold og en efterfølgende usædvanlig tør vækstsæson. Den sæsonmæssige udvikling i metanudledningen korrelerede særdeles godt med de fysiske parametre; jordtemperatur, vandstand og aktiv lag, på trods af at karakteren af deres indvirken på metanproduktionen er forskellig. I den våde del af gradienten var metanudledningen desuden negativt korreleret med netto udledningen af kuldioxid. Det faktum at alle disse korrelationer var stærke, fremhæver den store grad af autokorrelation mellem parametrene og deres lighed i forhold til den sæsonmæssige udvikling. Densiteten og sammensætningen af karplanter har tilsyneladende en dominerende rolle i forhold til størrelsesordenen af metanudledningen. Analyser af organiske syre og opløst organisk stof viste intet ensartet mønster med hensyn til placering på gradienten. Såkaldte 'ekstreme' metanudledninger i den sidste halvdel af vækstsæsonen blev undersøgt separat, men ingen atmosfæriske parametre, såsom vindhastighed, ændring i lufttryk eller temperatur viste korrelationer med disse events. For de relativt tørre plot på gradienten udgjorde disse events op mod 25 % af udledningen og kan altså i randområderne af kær udgøre en betydelig del af den sæsonmæssige udledning. Ingen events blev målt fra de 'vådeste' plot. Dette studie belyser vigtigheden af integrerede studier af de parametre der er styrende for metanudledningen, da både de fysiske og biologiske parametre ofte er afhængige og udviser de samme sæsonmæssige mønstre.

Content

## 1 Introduction

Since preindustrial times, the concentration of the greenhouse gas methane has increased by approximately 150 % from 722 ± 25 ppb in 1750 to 1803 ± 2 ppb in 2006 (IPCC 2013). The atmospheric concentration of methane is much smaller than the concentration of carbon dioxide, however the global warming potential for each molecule of methane is approximately 20-30 times greater than for carbon dioxide (Blake and Rowland 1988; Le Mer and Roger 2001). Natural sources comprise approximately 50 % of the emission of methane annually, whereof wetlands are the largest single source with 177-284 Tg $CH_4$ $yr^{-1}$ (about 60 % of the natural sources) (IPCC 2013).

Northern latitude wetlands are estimated to account for one third to half of the methane emission from natural wetlands (Avery et al. 1999; Christensen et al. 2003; Schlesinger and Bernhardt 2013). Furthermore, future climate change is expected to be the most pronounced in these northern continental regions (IPCC 2013) and it is unclear how the emissions from northern wetlands will respond to these changes (Cao et al. 1998). Part of the large uncertainty in the emission estimate is related to an uncertainty in the areal extent of wetlands (Long et al. 2010). However, there are many factors influencing the magnitude of methane emissions from wetlands, resulting in large spatial and temporal variability (Schlesinger and Bernhardt 2013). Especially emissions from Arctic ecosystems show large variability and often range 2-3 orders of magnitude (Morrissey and Livingston 1992), not only spatially and temporally within wetlands, but also regionally (Joabsson et al. 1999b). Among the most important factors influencing methane emission in Arctic ecosystems are temperature, water table depth, active layer depth, vegetation cover, net primary production and substrate availability and quality (Bellisario et al. 1999; Bubier 1995; Grøndahl et al. 2008; Friborg et al. 2000; Long et al. 2010; Joabsson et al. 1999b; Hargreaves and Fowler 1998; Ström et al. 2003; Ström et al. 2012; Whalen and Reeburgh 1992). Furthermore ebullition (eruptive release of accumulated gases) can constitute a substantial part of the total methane emission (Tokida et al. 2007).

Environmental and biotic factors influencing the methane emission are often interrelated or even counteracting each other (Joabsson et al. 1999b). This study therefore aims at investigating and identifying small scale patterns and potential explanatory factors of the methane emission from an Arctic wetland. The emissions used in this study are measured on a moist to wet gradient on the fringe of an Arctic fen during the growing season of 2013. It is hypothesized that soil temperatures exert a direct control on the production and oxidation of methane and thereby the seasonal development in methane fluxes and their magnitude. As methane is produced by anaerobic microbes (Stams and Plugge 2010), water saturation is considered a prerequisite for methane production and hence the water table is expected to be crucial in relation to the methane emission. It is likewise hypothesized that the active layer has a conditional control on the methane emission, as the thaw depth determines how much of the soil organic carbon is available for microbial decomposition. These three environmental variables are furthermore expected to follow the same overall seasonal development as they are controlled to a large extent by the incoming solar radiation. The major biotic control on methane emissions is thought to be vegetation composition and density (Schimel 1995; Ström and Christensen 2007; Koelbener et al. 2010). Presence of vascular plants is expected to increase emission rates, by providing a plant mediated transportation pathway (Schlesinger and Bernhardt 2013). The plant productivity is also expected to increase the potential methane emission, by assimilating higher amounts of fresh labile carbon to the soil matrix (Joabsson et al. 1999b) and the vascular plant composition is expected to control the production and quality of substrate available for acetoclastic methanogenesis (Ström et al. 2005). Lastly, the emission of methane through ebullition is believed to be triggered by environmental variables like wind speed and rapidly decreasing air pressure (Tokida et al. 2007; Green and Baird 2013; Bartlett and Harriss 1993).

These hypotheses will be investigated through a) an investigation of similarities and differences in seasonal emission patterns on the moist to wet gradient. b) An analysis of the character of the control of environmental parameters such as soil temperature, water level and active layer in relation to the spatial variability of the methane emission. c) Analysis of the relationship between methane fluxes and net ecosystem exchange. d) Investigation of how the density of vascular plants varies between plots and how this affects the seasonal methane emission. e) Qualitative assessment of differences in organic acid concentrations and dissolved organic carbon for selected plots on the moist to wet gradient and f) analysis of possible atmospheric parameters controlling ebullition events.

# 2 Background

## 2.1 Methanogenesis

Methane is produced by methanogens, which are anaerobic microbes belonging to the domain of archaea (Stams and Plugge 2010). Methanogenesis is the final step in anaerobic decomposition of organic matter (Schlesinger and Bernhardt 2013). In anaerobic environments, microorganisms derive energy through electron transfer from an external donor to an external electron acceptor (Megonigal et al. 2004). Whether an electron acceptor will be reduced depends on the competition between the electron acceptors. The reduction resulting in the highest energy yield for the microbes is favored. In anaerobic environments, the order in which the electron acceptors are favored is: $NO_3^-$ reduction > Mn(IV) reduction > Fe(III) reduction > $SO_4^{2-}$ reduction > $HCO_3^-$ reduction (i.e. methanogenesis). Hence methanogenesis is thermodynamically the least favorable electron donor (Megonigal et al. 2004). In wetlands methanogenesis is often the dominant pathway for fermentation of organic matter, due to lack of oxidants like manganese, iron(III) and sulfate (Schlesinger and Bernhardt 2013).

Methanogens can use hydrogen/carbon dioxide, formate, carbon monoxide, methanol, methylated compounds and acetate to produce methane (Stams and Plugge 2010), although the acetate splitting or acetoclastic methanogenesis and $CO_2$ reduction with hydrogen acting as the electron donor are the most common (Schlesinger and Bernhardt 2013). An estimated two thirds of the biologically produced methane is derived from acetate, even though only two methanogenic genera are known to consume acetate (Stams and Plugge 2010). In acetoclastic methanogenesis both carbon dioxide and methane are end products:

$$CH_3COOH => CH_4 + CO_2 \qquad \text{(Borggaard and Elberling 2007)}$$

Most methanogens can perform carbon dioxide reduction by hydrogen gas:

$$CO_2 + 4H_2 => CH_4 + 2H_2O \qquad \text{(Borggaard and Elberling 2007)}$$

However, the energy yield from this reaction is lower and it is therefore not dominating when acetate is not available (Schlesinger and Bernhardt 2013).

Many processes are involved in the anaerobic decomposition necessary prior to methanogenesis (Fig. 2.1). Firstly, microorganisms break down polymers to simpler monomers, like simple sugar, amino acids and fatty acids. The monomers are then fermented either to carbon dioxide and hydrogen or to organic acids and alcohols. These acids and alcohols are then, through acetogenesis, broken down to acetate, from which methane and carbon dioxide is produced.  The direct formation of carbon dioxide and hydrogen is relatively complicated under anaerobic conditions and requires a rather long set of bacterial processes to occur. Secondary fermentation is therefore dominant under anaerobic conditions (Megonigal et al. 2004). Acetoclastic methanogenesis is generally favored in the upper part of the peat, whereas the hydrogenotrophic reduction of carbon dioxide dominates in deeper peat layers, where the organic material is more recalcitrant (Lai 2009). Methanogenesis is often limited by the availability of substrate (Schlesinger and Bernhardt 2013).

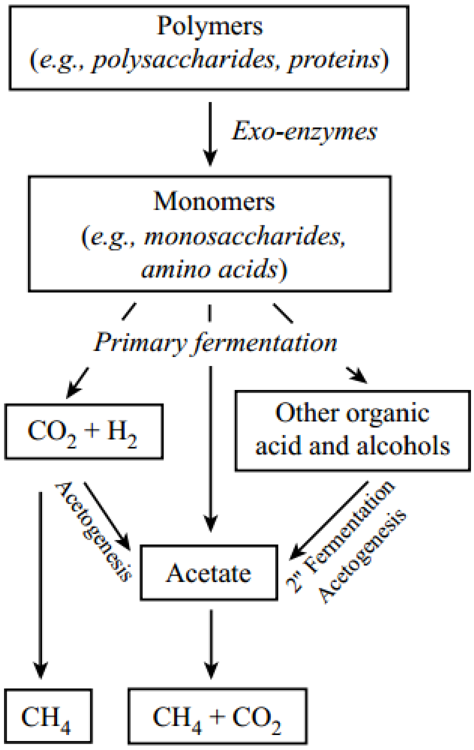


**Figure 2.1:** Scheme of the metabolic pathways in anaerobic decomposition leading to the two primary methane forming processes: reduction of carbon dioxide and fermentation of acetate (acetoclastic methanogenesis)(Megonigal et al. 2004).

## 2.2 Oxidation

Methane can be oxidized by prokaryotic methanotrophs, in parts of the soil where oxygen is present (Christensen 2010), i.e. in oxidized soil layers or in the rhizosphere of vascular plants (Fig. 2.2). Contrary to the fermentation process, the oxidation of methane by microorganisms is a high energy yield process, hence the oxidation results in low release of methane relative to the methane production (Schlesinger and Bernhardt 2013). On average, an estimated 50 % of the produced methane is oxidized in the soil matrix (Christensen 2010). Approximately 3 % of the annual carbon uptake is emitted back into the atmosphere as methane (Schlesinger and Bernhardt 2013).

## 2.3 Transport pathways

Because of the very low solubility of methane in water, combined with the large difference in the concentration of methane in the soil pore space and the atmosphere, methane escapes to the atmosphere (Joabsson et al. 1999b). There are three pathways by which methane can be transported from the soil matrix to the atmosphere (Fig. 2.2); diffusion, ebullition and plant mediated transport (Fig. 2.2). The different types of pathways represent different potential emission rates and therefore increase the temporal variability in methane emission. Diffusion has been found to constitute a minor part of the total methane emission (Christensen 2010).

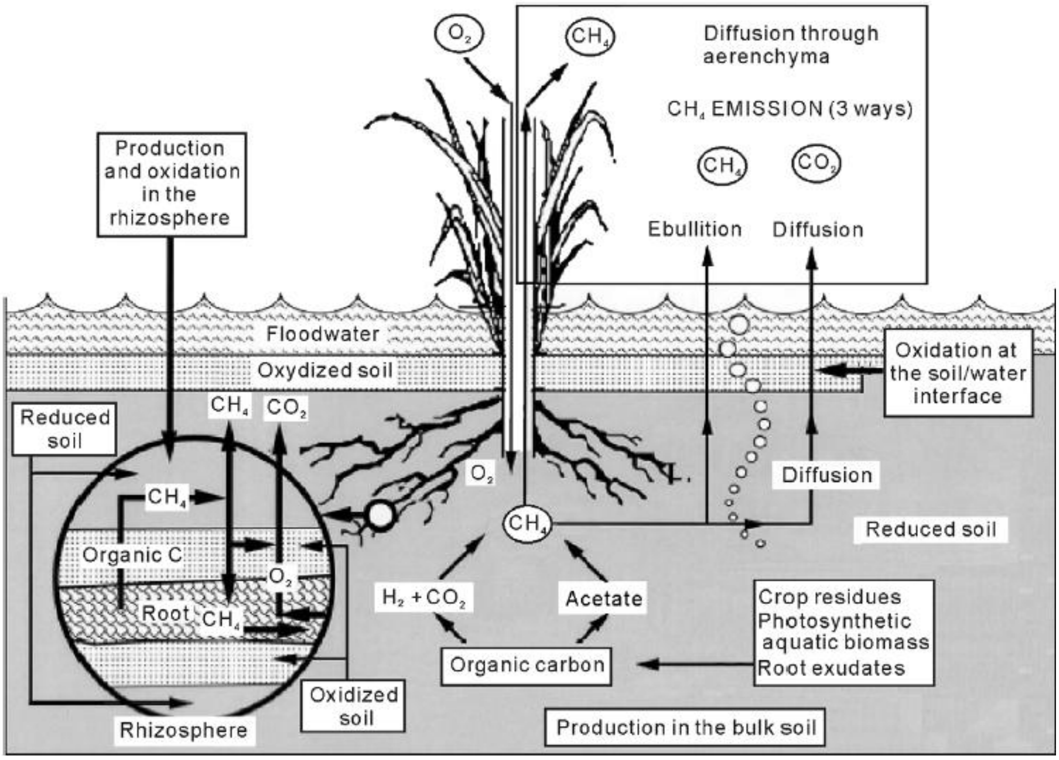


**Figure 2.2:** Schematic representation of the different transportation pathways of methane from the saturated soil matrix to the atmosphere; exchange through aerenchyma of vascular plants, ebullition and diffusion through the soil matrix. The figure also displays how a thin layer around the roots of vascular plants is oxidized, as aerenchyma facilitate a transport pathway of oxygen to the rhizosphere (Lai 2009).

Ebullition occurs when the partial pressure of gases in the soil pore water exceeds the hydrostatic pressure in the soil (Schlesinger and Bernhardt 2013; Chanton and Whiting 1995). This build up in pressure takes place when the production of methane and carbon dioxide is higher than the diffusion potential (Joabsson 2001). Ebullition is usually not the dominant pathway of methane during the growing season (Christensen 2010). However it can represent a large proportion of the total emission outside the growing season, where the production is very low and physical processes, like soil freezing, relatively more important (Christensen 2010; Mastepanov et al. 2008). Furthermore ebullition has been shown to be dominant in non-vegetated plots (Grünfeld and Brix 1999). Ebullition bubbles bypass the oxic zone without notable oxidation due to the low solubility of methane and rapid transfer from the anaerobic zone to the atmosphere (Lai 2009).

Wetland plants have adapted to the permanently waterlogged conditions by developing air filled channels within their tissue, so-called aerenchyma (Schlesinger and Bernhardt 2013). These aerenchymae allow plants to survive long periods of inundation, by facilitating transport of oxygen to the roots (Fig. 2.2). Furthermore, the addition of oxygen also facilitate higher mineralization rates in the root vicinity, stimulating the growth of the plant itself (Schlesinger and Bernhardt 2013). At the same time the aerenchyma also acts as a direct pathway for methane to escape to the atmosphere. During the growing season, the transport through vascular plants is believed to constitute the majority of the flux (Christensen 2010). Experiments with shading has shown relatively stable concentrations of dissolved methane over a whole growing season, compared to plots exposed to solar radiation. This was ascribed higher emission due to better development of roots and hence larger emission potential (Joabsson and Christensen 2001).

## 2.4 Controls on methane emission

Several previous studies have found relations between methane emission from Northern latitude, permafrost underlain wetlands and both environmental variables, like soil temperature, active layer depth and water level, as well as with biological variables like primary production, vegetation cover, vegetation composition and substrate quality (Nakano et al. 2000; Whalen and Reeburgh 1992; Joabsson et al. 1999b; Mastepanov et al. 2013; Ström et al. 2003; Ström et al. 2012; Schimel 1995; Friborg et al. 2000; Grøndahl et al. 2008). However, as many of these factors follow the same seasonal patterns and are interdependent, their individual effects on the methane emission are hard to distinguish (Christensen 1993; Nakano et al. 2000).

Soil temperature is often reported as a controlling factor in relation to the daily and seasonal variation in methane emission (Friborg et al. 2000; Long et al. 2010 ;Bellisario et al. 1999). Temperature affects the production of methane directly by increasing the productivity of the methane producing microbes (Lai 2009). Both methanogens and methanotrophs are positively related to temperature, however the methanogens are more responsive. This means, all other things being equal, that an increase in temperature will lead to an increase in methane emission, as the production will increase faster than the consumption (Christensen 2010; Long et al. 2010). Christensen (1993) found that the emission from waterlogged sites was mainly controlled by temperature. The relation between soil temperature and methane emission has been reported as linear, logarithmic, polynomial or exponential (Whalen and Reeburgh 1992). These relationships of different character suggests that the relationship with temperature is not straight forward (Whalen and Reeburgh 1992), possibly owing to the fact that the methane emission is controlled by many other factors other than the actual production.

Active layer has also been found to correlate well with both the seasonal variability in methane emission and regional differences in the magnitude of methane emissions (Whalen and Reeburgh 1992; Nakano et al. 2000). Whalen and Reeburgh (1992) found that an integrated parameter, combining soil temperature and active layer showed the largest correlation with the seasonal methane flux in Northeastern Alaska. Nakano et al. (2000) found the thermal regime of the active layer to be the controlling factor in waterlogged Siberian sites. Methane fluxes compared between two Siberian wetlands showed fluxes that were approximately 6 times higher for a site with almost 2 times greater active layer and ground temperature of the active layer. Hence active layer and the thermal regime of the active layer shows great importance in relation to the methane emission on large temporal and spatial scales.

As anaerobic conditions are a prerequisite for the production of methane, waterlogged conditions are crucial to methane emission. Other than ensuring anaerobic conditions, the position of the water table is also important for the emission of methane as it determines the thickness of the a potential overlying oxic horizon, in which methane oxidation can occur (Lai 2009; Chowdhury and Dick 2013). Whalen and Reeburgh (1992) found that the methane flux for the entire season did not correlate well with the water table, as this was high early in the season, when the methane emission had hardly started. However Bubier et al. (1993b) found strong correlation with the mean seasonal water table position between different wetlands. Daulat and Clymo (1998) found a linear response to decreased water table position in a controlled laboratory experiment, using peat cores. A mesocosm experiment by (Grünfeld and Brix 1999) showed that the methane emission decreased significantly with water levels 22 cm below the surface, whereas a water level 8 cm below the surface indicated smaller, but not significantly, methane fluxes as compared to waterlogged fluxes. This was ascribed to the high water retention capacity of the organic peat. Hence, not only the water table position, but also the saturation in the oxic zone is important for the methane emission. Micro topographic differences have also been shown to affect the methane emission, largely through the effect on the water table depth (Bubier et al. 1993a).

The density and composition of vegetation is important in relation to methane emission, not only because of the physical transportation pathway that vascular plants offer, but also due to their effects on substrate availability and quality (Joabsson et al. 1999b; Ström et al. 2005; Ström et al. 2003; Ström et al. 2012; Ström and Christensen 2007). Although peatlands hold very large amounts of organic carbon, up to 90 % of bulk soil, studies have shown that recently fixed carbon increases the production rate significantly by providing labile and easily available substrate for methanogens (Joabsson and Christensen 2001; Ström et al. 2012). Plants in peatlands can contribute to the methane substrate through root exudates, root turnover or litter fall, although studies have shown that the methane production is more closely related to the living vegetation than to litter (Chanton et al. 1995; Schimel 1995). Root exudates usually constitute less than 10 % of the dissolved organic carbon in the soil solution (Ström et al. 2012). It has also been shown that potential methane production is highest in the same depth as the maximum root density and that decreased net ecosystem exchange of $CO_2$ resulted in lower seasonal methane emission (Joabsson and Christensen 2001). Studies have shown that vegetation composition and presence of vascular plants is one of the key factors in controlling methane emission from wetlands (Joabsson et al. 1999a; Schimel 1995; Ström et al. 2012). The proportion of different vascular species is important for the magnitude of the methane emission. Schimel (1995) showed a significantly higher methane emission from *Eriophorum angustifolium* than from *Carex aquatilis*. Studies in Zackenberg have shown higher acetate formation rates in the root vicinity of *Eriophorum scheuchzeri* compared to *Dupontia psilosantha* and *Carex stans* (Ström et al. 2003; Ström et al. 2012).

Peatlands and fens also produce large amounts of dissolved organic carbon which is transported from wetlands through drainage waters (Olefeldt and Roulet 2012; Dinsmore et al. 2009). Ström et al. (2003) found a negative relationship between the potential methane emission and the concentration of DOC, indicating that the quality of the DOC decreases with increasing decomposition.

### 2.5 Controls on extreme events

Many environmental parameters have been shown to control the timing and formation of methane ebullition bubbles. Tokida et al. (2007) found ebullition events to be triggered by rapid drop in atmospheric pressure. Similarly Strack et al. (2005) found the ebullition events to relate with the seasonal hydrostatic pressure in the peat. The character of the changes might have large importance, as rapid increases in pressure or rapid decreases in temperature can halt bubble formation and emission (Fechner-Levy and Hemond 1996). Likewise wind speed has been reported to trigger emission of methane from relatively shallow peatlands (i.e. 0.5-2 m) (Bartlett and Harriss 1993). However, due to the stochastic behavior of ebullition events, quantitative relations between the emission and the mechanisms controlling the transport are not well understood (Green and Baird 2013).

## 3 Methods

### 3.1 Site description

This study was performed in the southern part of the Rylekærene (the dunlin fens, see figure 3.1) in the Zackenberg valley (74°30'N, 20°30'W), Northeast Greenland (Mastepanov 2010; Meltofte and Rasch 2008), over the majority of the growing season of 2013. Zackenberg is located in the High-Arctic zone (Walker et al. 2005), with a long-term average temperature of the warmest month just below 6 °C from 1996-2005 (Hansen *et al.,* 2008), although the 1996-2013 mean is 6.3 °C (data from Mylius (formerly Pedersen) 2013, personal communication).

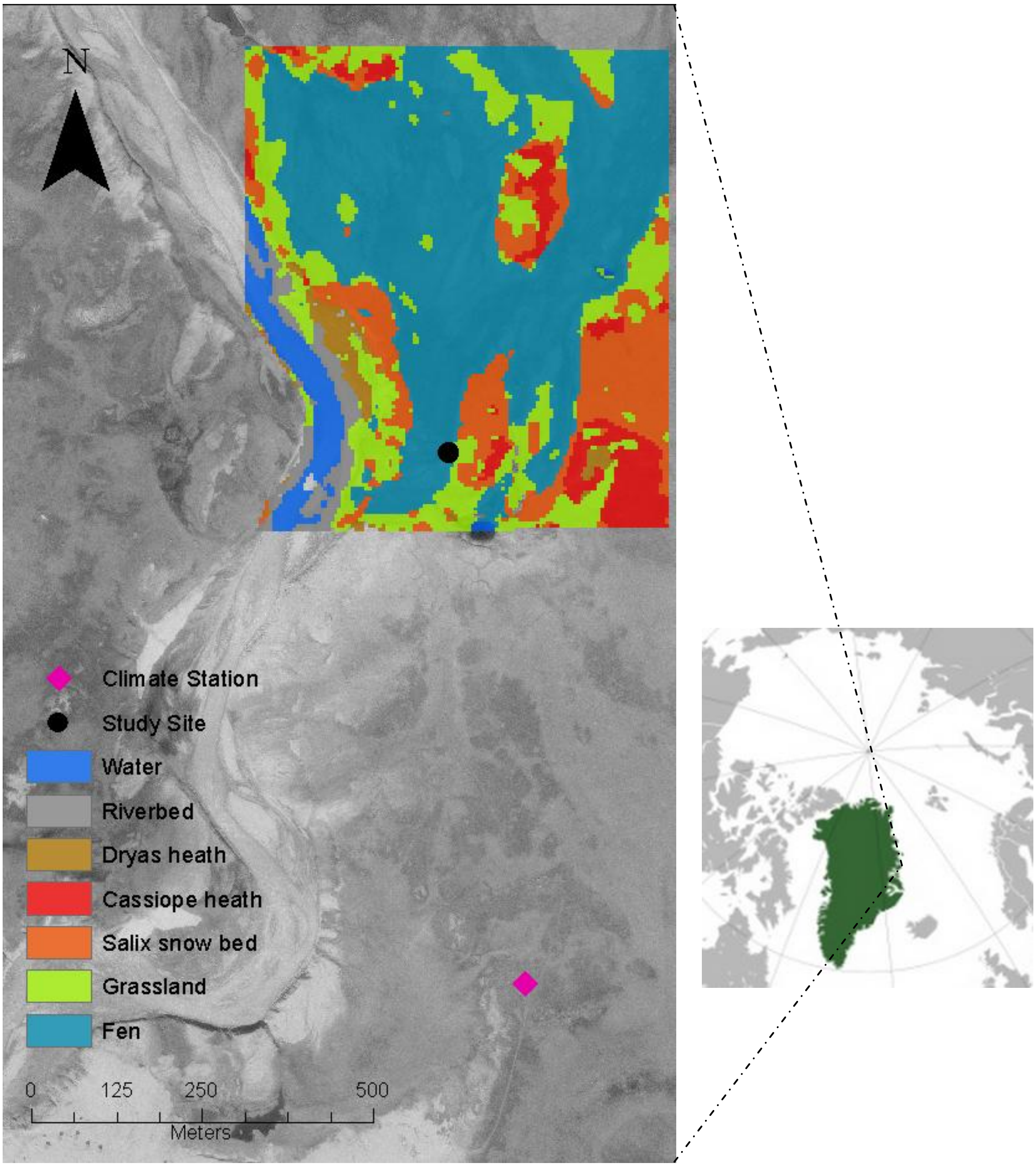


**Figure 3.1:** Location of the study site in Rylekærene, Zackenberg, Northeast Greenland. The vegetation classification (Elberling et al. 2008) is displayed with an ecw-orthophoto of the Zackenberg valley.

Rylekærene is a patterned fen, wherein elevated dry heath vegetation patches are found (Tagesson 2011). The wet part of Rylekærene consists of two different kinds of fen: 'wet continuous fen' and 'hummocky fen' (Grøndahl et al. 2008). The site studied here is located on the fringe of the continuous part of the fen. The vegetation is dominated by the sedges *Eriophorum scheuchzeri*, *Carex stans* and *Dupontia psilosantha* (Ström et al. 2003). In the drier parts of the fen *Arctagrostis latifolia* is also abundant and individuals of *Salix arctica* are present. The study site has an understory of 100 % moss cover, where the dominating genera are *Tomenthypnum*, *Scorpidium*, *Aulacomnium* and *Drepanoclaudus* (Tagesson et al. 2012). Zackenberg is underlain by continuous permafrost down to a depth of about 300 meters (Meltofte and Rasch 2008). In Rylekærene the active layer normally reaches a maximum depth of 45 to 65 cm below the surface (Mastepanov et al. 2013) and the peat is approximately 20-30 cm thick (Ström et al. 2012). During summer the prevailing wind direction is from S/SE with an almost constant breeze, due to the exchange between the land surface and the cooler fjord south of Zackenberg (Hansen et al. 2008).

### 3.2 Field sampling

The data for this study was collected from the 8$^{th}$ of June to the 20$^{th}$ of August 2013, covering almost the entire growing season.

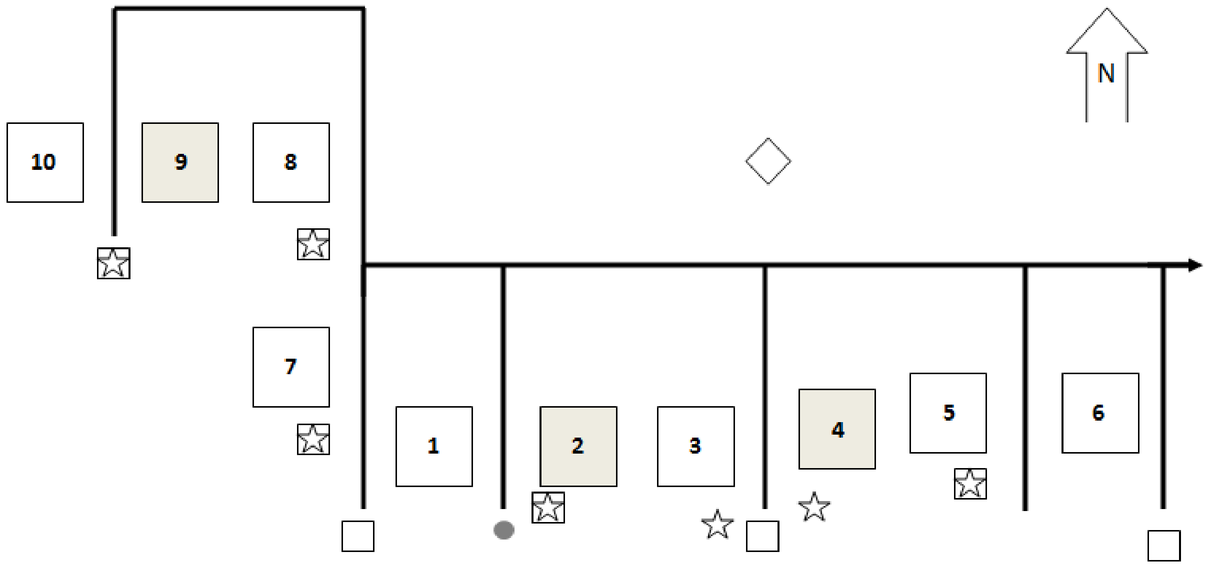


**Figure 3.2**: Overview of the automatic chamber site in the Rylekærene fen in Zackenberg. Squares resemble each of the ten chambers, the shaded chambers are the ones from which soil pore water was sampled once a week from the 8$^{th}$ of July to the 16$^{th}$ of August. The diamond shows the position of the soil temperature probes, the grey circle the hole in which the water level has been read daily since installation of a ruler in 2006. Stars show the position of newly installed water permeable PVC tubes, in which water level has been recorded daily throughout the season in 2013 and squares show the position of fix poles, to which the active layer and water level is recorded. Thick black lines represent raised boardwalks; the boardwalks continue about 25 m to the east towards a hut in which the gas analyzer is installed.

### 3.2.1 Methane flux

Methane and carbon dioxide were measured continuously using automatic chamber technique. In total 10 chambers, with a basal area of 0.6 by 0.6 m and 0.3 m high, are installed on a gradient, from the moist fringe of the fen towards progressively wetter conditions, with approximately 15 meters between the two most distant chambers (Fig. 3.2). The first 6 chambers in the gradient were installed in 2005, two additional chambers were installed in 2011 and another two in 2012 (Mastepanov et al. 2013; Pedersen et al. 2012). The concentration of methane, carbon dioxide and water vapor is measured continuously using a off-axis cavity integrated output spectroscopy (off-axis ICOS)(Gupta 2012), in 2013 with the instrument FGGA, Los Gatos Research, USA. The air is drawn from the chamber with a flow rate of approximately 0.4 L $min^{-1}$, through black high density polyethylene tubing with an inner diameter of 4 mm (Mastepanov et al. 2013). Each chamber is equipped with a small fan that is active throughout the measurement period for each chamber. First, the chamber is ventilated with open lid, the chamber is then closed for a sufficient time to record a concentration change, before the final ventilation after the measurement has ended. In the first part of the season the concentration of methane, carbon dioxide and water vapor was measured from each chamber once every second hour, for ten minutes (3 minutes ventilation, 5 minutes measurement and 2 minutes ventilation). On the 2$^{nd}$ of August the sampling regime was changed to a three hour round to allow for larger concentration increases over 8 minutes, as a C-12 and C-13 isotope instrument was installed, which required longer measurement time. This of course resulted in a lower number of measurements from the 2$^{nd}$ to the 20$^{th}$ of August, but has not disturbed the measurements themselves.

#### 3.2.2 Environmental variables

Several environmental variables are measured in addition to the methane and carbon dioxide fluxes. These are meteorological variables, soil temperature, active layer and water level in the fen.

The meteorological variables air temperature, barometric pressure, precipitation, wind speed and direction are measured at the Climate station, operated by Greenland Survey, Asiaq (data from Hangaard 2013, personal communication). The Climate station is situated approximately 500 meters south of the study site, on a homogenous white arctic bell-heather *Cassiope tretragona* heath (Hansen et al. (2008), Fig. 3.1).

Soil temperature is measured every 5$^{th}$ minute approximately midway between the least moist chamber and the wettest chamber (using Tinytag plus 2, Gemini data loggers, UK, see location in Fig. 3.2). The temperature sensors are situated in 5, 10 and 15 cm depth.

Active layer is measured in the vicinity of each chamber (Fig. 3.2), every third day throughout the season. As the soil swells throughout the season, due to differing degrees of saturation, the active layer is measured in relation to poles, installed into the permafrost and later corrected for the difference between the top of the fix pole and the vegetation surface. The distance from the top of the fix poles to the vegetation was measured in the end of August.

Manual water level measurements are conducted daily, using two different methods. 1) Between two chambers in the middle of the gradient (numbered 1 and 2) a ruler has been installed for manual water level readings (grey circle in Fig. 3.2). The vegetation and soil around the ruler has been removed in order to make readings possible. 2) In the vicinity of the other chambers, water permeable polyvinyl chloride

(PVC) tubes, with a diameter of 2 cm, were installed in the active part of the peat/soil (shown as stars in Fig. 3.2). The water level was recorded daily by detecting the water surface and measuring the distance between the water level and the top of the PVC tube. Furthermore the vertical distance between the top of the tube and the top of the fix pole (also used for active layer measurements) is recorded. These measurements are then corrected for the distance between top of fix pole and vegetation surface after the season. Comparison of the measurements made with method 1 and 2, suggest that the water level is systematically underestimated when using method 1. To what degree the underestimation is, is hard to tell, but approximately 5 cm throughout the season. Since mostly the relative water levels, rather than the absolute values, are applied in this study, the absolute water level measurements have not been corrected, but it should be kept in mind when interpreting the water level.

#### 3.2.3 Vegetation analysis

Within each chamber all tillers of grasses, half grasses and dwarf shrubs were counted within a 20 by 20 cm sub section. The species found within these subsections were *Eriophorum scheuchzeri, Dupontia psilosantha, Carex stans, Arctagrostis latifolia* and *Salix arctica*. The counts were thereafter upscaled to number of individuals per square meter. The understory is covered by 100 % mosses in all chambers, but the individual moss species were not distinguished.

#### 3.2.4 Organic acids and dissolved organic carbon

In order to measure the available substrates for methanogenesis in the form of organic acids and the amount of dissolved organic carbon, water samples were taken once a week from the 8$^{th}$ of July to the 16$^{th}$ of August. The samples were taken from three chambers, one from a chamber representing the least moist part of the gradient (chamber 4), one from the intermediate moisture regime (chamber 2) and one from the wet part of the gradient (chamber 9) (Fig. 3.2). Samples were taken by drawing pore water with a syringe through a stainless steel tube with an outer diameter of 3 mm, in the center of the chamber. Initially a sampling depth of 5 cm below the vegetation surface was desired, but as the fen progressively dried out, deeper sampling depths became necessary almost from the start of the sampling period. The driest chamber dried out completely before the 9$^{th}$ of August, hence only four samples were taken from this chamber. The other two chambers were sampled on 6 occasions. In total 14 ml of pore water was drawn from the chambers at each sampling occasion. The first 2 ml were discarded, 2 ml were filtered through a 0.45 µm (Q-Max RR 25 mm 0.45µm CA) and used to rinse the plastic vial in which the sample was stored until analysis. 10 ml of sample was filtered through a 0.45 µm filter and stored at -18 °C and brought for analysis at the University of Lund and University of Copenhagen. All syringes, vials, filters and stainless tubes were thoroughly rinsed in deionized water and dried prior to every sampling.

### 3.3 Laboratory analysis

The water samples were kept frozen from the day of sampling, until immediately prior to analysis of organic acids in the University of Lund. Before analysis, the samples were passed through sterile 0.8 µm/0.2 µm filters (Acrodisc PF Syringe Filter 0.8/0.2 µm Supor Membrane, Low Protein Binding Non-Pyrogenic). The concentration of organic acids was analyzed using a high performance liquid chromatography (HPLC) system, directly combined with a mass spectrometer (Applied Biosystems 2000 Q-Trap triple quadrupole mass spectrometer). The different components of the sample were first separated using liquid chromatography. The eluent (water and sodium hydroxide 0.1 Molar) and 50 µl of sample was passed through the precolumn (Dionex IonPac AG15 2-mm P/N 53943) and the column (Dionex IonPac

AS15, 2 X 250 mm) to separate the different components of the sample. Before these were identified in the mass spectrometer, the eluent was passed through an anion self-regenerating suppressor (Dionex ASRS 300 2 mm, P/N 064555) in order to remove the sodium hydroxide. In the mass spectrometer, the solution was ionized in an ionspray (Q Trap LC/MS/MS TurboSpray ion source). The detailed settings of the mass spectrometer are listed in Ström et al. (2012). The output from the HPLC analysis is the concentration of lactic, acetic, formic, glucolic, malic, succinic, tartaric, oxalic and citric acids. Since the pH of the soil pore water in the Rylekærene fen is above 6 (data not shown), most of the acids listed above will be on the form of their conjugate base. This is also true for acetic acid (or acetate) which is the substrate in acetoclastic methanogenesis, one of the two direct pathways in methane production (Fig. 2.1).

The samples were kept cold after thaw and analyzed for DOC the following day in University of Copenhagen. For DOC analysis, 250 µL of sample was diluted 12 times with redistilled water and mixed with 2 Molar hydrochloric acid in order to remove inorganic carbon compounds, i.e. carbonates and bicarbonates. The solution was then analyzed for dissolved organic carbon using a non-dispersive infrared gas analyzer (Shimadzu SpectraChrom, TOC5000A).

## 3.4 Data analysis

In order to compute the flux of methane from the concentration measurements, the slope of each concentration change during the closed lid period is determined using linear regression. The slopes were fitted automatically using software developed for this particular system (Mastepanov 2010) and assessed visually. Both measurements with positive and negative slopes, as well as measurements within which the gas exchange was in equilibrium (between release and uptake) were included in this study. The data was not filtered based on the correlation coefficients of the slopes larger than a certain value, as this would exclude measurements where the oxidation equaled the production and hence lead to an overestimation of the fluxes, especially in the later part of the season. In total 11.5 % or 929 out of 8046 measurements were not accepted, mainly due to leakages in the beginning of the season and system shutdown due to strong winds. The fluxes were computed using the following equation modified from the Ideal Gas law:

$$F_c = \frac{\frac{dC}{dt} \cdot V \cdot P \cdot M}{R \cdot T \cdot A}$$

Where $F_c$ is the flux, $\frac{dC}{dt}$ is the slope of regression line (concentration change over time, of either methane or carbon dioxide), V is the volume of the chamber, P is the atmospheric pressure, M the molar mass, R the universal gas constant, T the temperature in Kelvin and A the basal area of the chamber.

The 10 chambers are divided into three subgroups based on the magnitude of the fluxes and the location on the least moist to wet gradient in the fen. Therefore, chambers 3-6 (the driest) have been classified as low flux chambers. Chamber 1 and 2 (situated in the intermediate zone between the increasingly dry part and the almost constantly saturated part of the fen) are classified as medium flux chambers. The four last chambers 7-10, that were installed 5-6 years later than the others, are classified as high flux chambers.

On some occasions, large emissions of methane (in the magnitude of up to 15 times higher than the fluxes measured in the days and hours just prior to or after the measurement) have been detected. Especially from the chambers classified as low flux chambers. These fluxes have been filtered from the data used for the analysis of the seasonal changes. For the low flux chambers, fluxes higher than 0.6 mg $CH_4$ $m^{-2}$ $h^{-1}$ have been removed, if they were detected outside the peak of the growing season (i.e. after the 15th of July). Likewise values higher than 2 mg $CH_4$ $m^{-2}$ $h^{-1}$ have been filtered from the fluxes measured in the medium flux chamber and 5 mg $CH_4$ $m^{-2}$ $h^{-1}$ for the high flux chambers. In total 117, 4 and 8 were removed from the low flux, medium flux and high flux chambers, respectively. The 8 events in the high flux class are solely from chamber 7 and 66 out of the 117 events from the low flux class are from chamber 5. In about 50 % of the cases (n = 60) the concentration change resembled actual ebullition events, where the concentration increases rapidly and then flattens or even falls, within the period of closed lid. The remaining 69 events displayed linear or even slightly exponential concentration changes, suggesting a constantly high emission rate. For the remainder of this paper, these events will be collectively referred to as extreme events.

Differences between flux groups in seasonal methane flux, carbon dioxide flux and vegetation composition were tested using one-way analysis of variance (ANOVA), followed by post hoc multiple comparison Tukey HSD test. Linear relationships between averaged daily methane and the variables soil temperature, water level, active layer depth and net ecosystem exchange were investigated using Pearson's correlation coefficient and tested for statistical significance using Student's t-test. Furthermore relations between extreme events and atmospheric variables like temperature, wind speed, air pressure and wind direction were investigated with Pearson correlation. When using Pearson's correlation coefficient and Student's t-test it is a prerequisite that data is independent, random, that there is no autocorrelation and the data should be normally distributed (Rogerson 2001). The datasets used for analysis in this study do not fulfill the first three requirements and only half of the datasets fulfill the fourth requirement of normality (tested using Shapiro-Wilk normality test). This should be kept in mind when assessing the results of analyses. All statistical tests were carried out in R (R core team 2012).

## 4 Results

### 4.1 Meteorological parameters

In 2013 it was snow free in the fen around the chambers on the 3rd of June and the maximum snow depth at the climate station was 13 cm (Mylius (formerly Pedersen), personal communication). The mean air temperature of July (the warmest month) was 7.1 °C. The dominating wind direction during the summer months, June to August, was southeast, from where the wind came 65 % of the time (Fig. 4.1). The wind came from North, Northwest and Northeast 25 % of the time. However the wind speed was 6 to 16 m/s (corresponding to 4 to 7 Beaufort) almost half of the time the wind came from Northern directions.

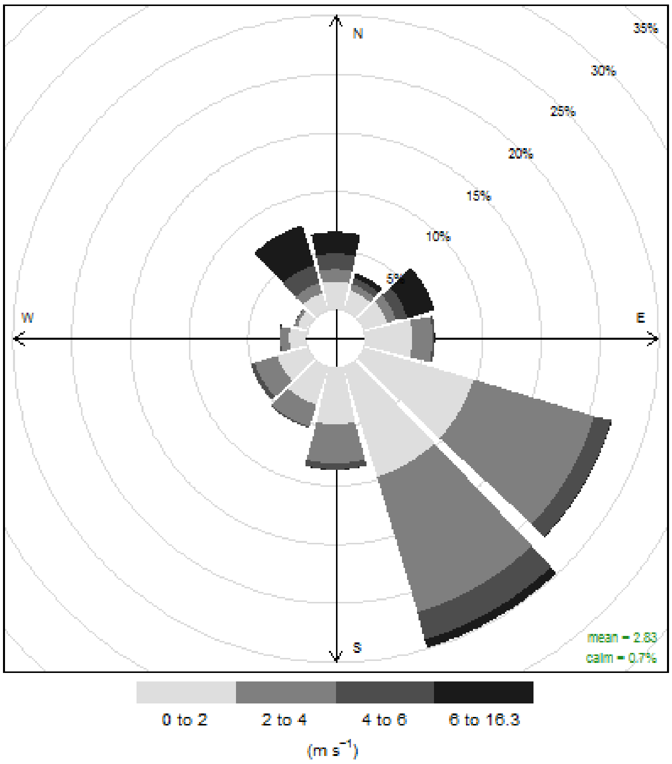


**Figure 4.1**: Wind direction and wind speed distribution during the summer 2013 (June, July and August), Zackenberg, Northeast Greenland.

### 4.2 Environmental variables

In the beginning of the season the water level in the fen was just around the vegetation surface for about two weeks, thereafter it started decreasing (Fig. 4.2d). This decreasing trend continued throughout the second half of June. After a week with low pressure and relatively large amounts of precipitation in the first week of July (Fig 4.2a), the water level increased and reached its seasonal maximum, just above the vegetation surface, around the 8th of July. Thereafter the water level decreased gradually throughout the rest of July and August, reaching a depth of approximately 30 cm below the vegetation surface (Fig. 4.2d). The soil temperature in 5 and 10 cm depths started showing a diurnal pattern within the first week after snow melt, with an increasing trend up until the 17th of June (Fig. 4.2c). The temperature in 15 cm depth reaches above zero degrees on the 17th of June, after which the diurnal fluctuations are also visible for this depth, although with considerably smaller amplitude (Fig. 4.2c). The seasonal dynamics in the soil temperature is generally following the overall trends in the air temperature (Fig.4.2b and 4.2c), especially in the first part of the season. In the second half of June there is a slightly decreasing trend in both air and soil temperatures, until the first week of July, where the soil temperature showed the highest peak of the season. In the second half of July and in August, the soil temperatures are decreasing steadily (Fig. 4.2c), while the air temperature showed the highest peaks (although with great diurnal variation) during the second half of July and start of August. The active layer was first measured on the 4th of June, the day after the day of complete snowmelt. The thawed part of the soil was only a couple of cm on this day and from here the active layer continued to decrease, almost linearly, throughout the season, reaching a maximum thaw depth of approximately 35 cm in the end of August (Fig. 4.2d).

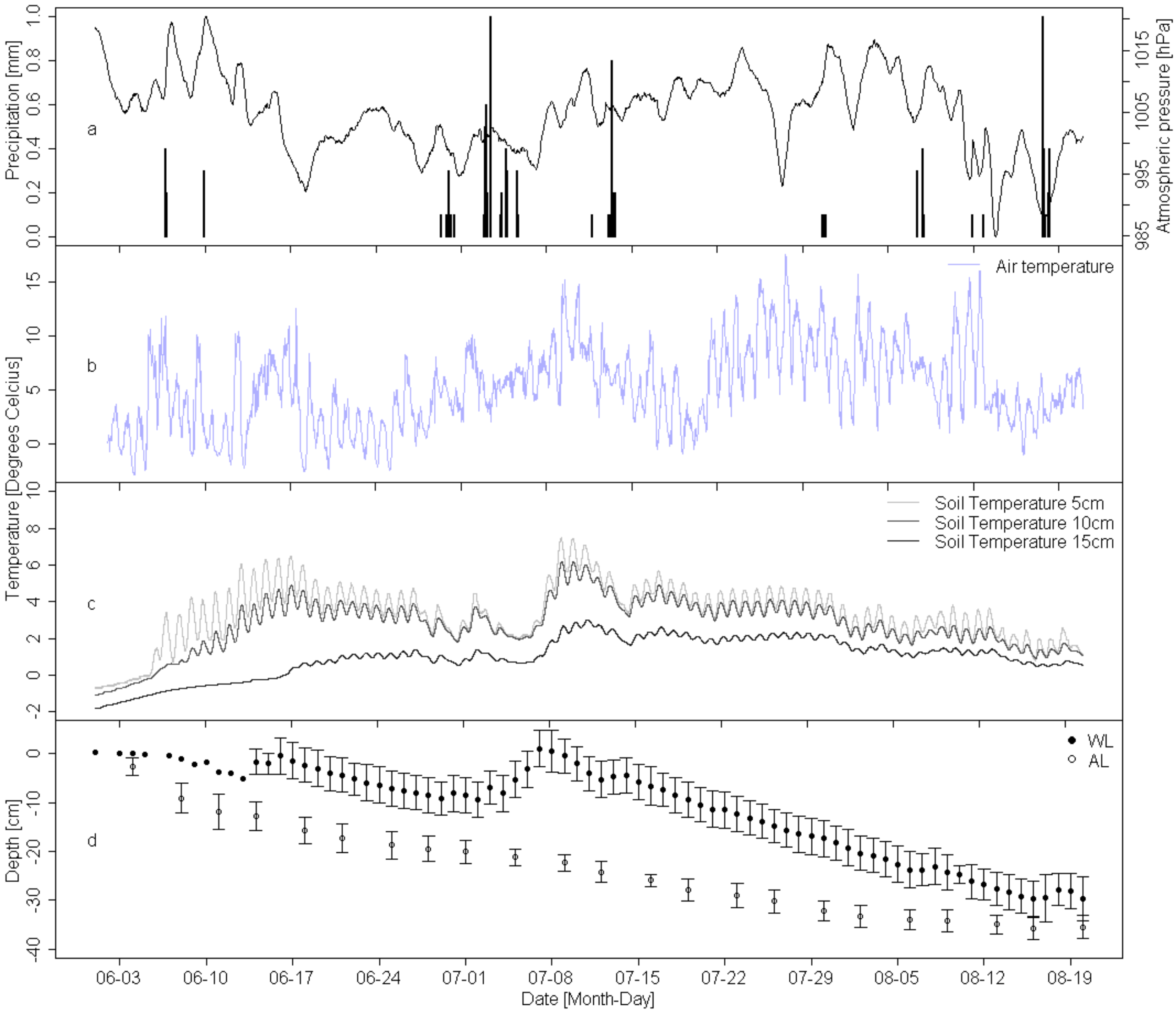


**Figure 4.2**: Selected environmental variables, shown for the period 1st of June to 20th of August. a) Black bars: precipitation, black line: air pressure, b) air temperature, c) soil temperature in the fen in three different depths; 5, 10 and 15 cm, d) active layer (AL) and water level (WL) in relation to the surface of vegetation.

## 4.3 Seasonal fluxes

The average and total seasonal flux (here from 8th of June to 20th of August) of methane and carbon dioxide for the whole study period is shown in table 4.1. The fluxes are depicted both for all 10 chambers and for the 6 original chambers, in order to make comparison with results prior to the installation of the 4 new chambers possible. When the methane emission from all ten chambers is considered the mean emission is almost three times bigger than for the 6 original chambers. For the total methane emission, the total from the ten chambers is about four times higher than the emission from the original six chambers. With regards to the $CO_2$ flux, there is a small average and total uptake over the season, when considering all ten chambers, whereas the average and total from the original six chambers, shows a relatively large net release of $CO_2$.

From late July onwards episodic events of very high fluxes were observed from chamber 1-7. When these 'extreme events' are included in the total and mean seasonal methane emission, the rates increase notably. The methane emission when excluding the extreme events from the 10 chambers constitute 95 % of the total methane emission, while it is 76 % when considering only the 6 original chambers (shaded columns in table 4.1).

**Table 4.1**: Mean (± one standard deviation) and total growing season fluxes of methane ($CH_4$) and carbon dioxide ($CO_2$). First two columns are means and total for all ten chambers, whereas column 3 and 4 is based on the six original chambers, in order to make comparison with studies prior to 2011. The 2006-2010 range is adapted from Mastepanov et al. (2013) and is based on the 6 original chambers (classified as low and medium flux chambers in this study). The two shaded columns show the methane flux from all ten chambers and the six original, including ebullition and extreme emission events.

| | CH4 (10) | CO2 (10) | CH4 (6) | CO2 (6) | 2006-2010 range CH4 | 2006-2010 range CO2 | CH4 (10) | CH4 (6) |
|---|---|---|---|---|---|---|---|---|
| Mean [mg m$^{-2}$ h$^{-1}$] | 0.90 ± 0.85 | -7.2 ± 196.87 | 0.35 ± 0.29 | 46.16 ± 161.54 | 0.85-2.61 | -58.7 - -316.9 | 1.02 ± 1.17 | 0.49 ± 0.95 |
| Total [g C m$^{-2}$] | 1.2 | -3.5 | 0.5 | 22.4 | 1.42-4.09 | -36.5 - -192.5 | 1.4 | 0.7 |

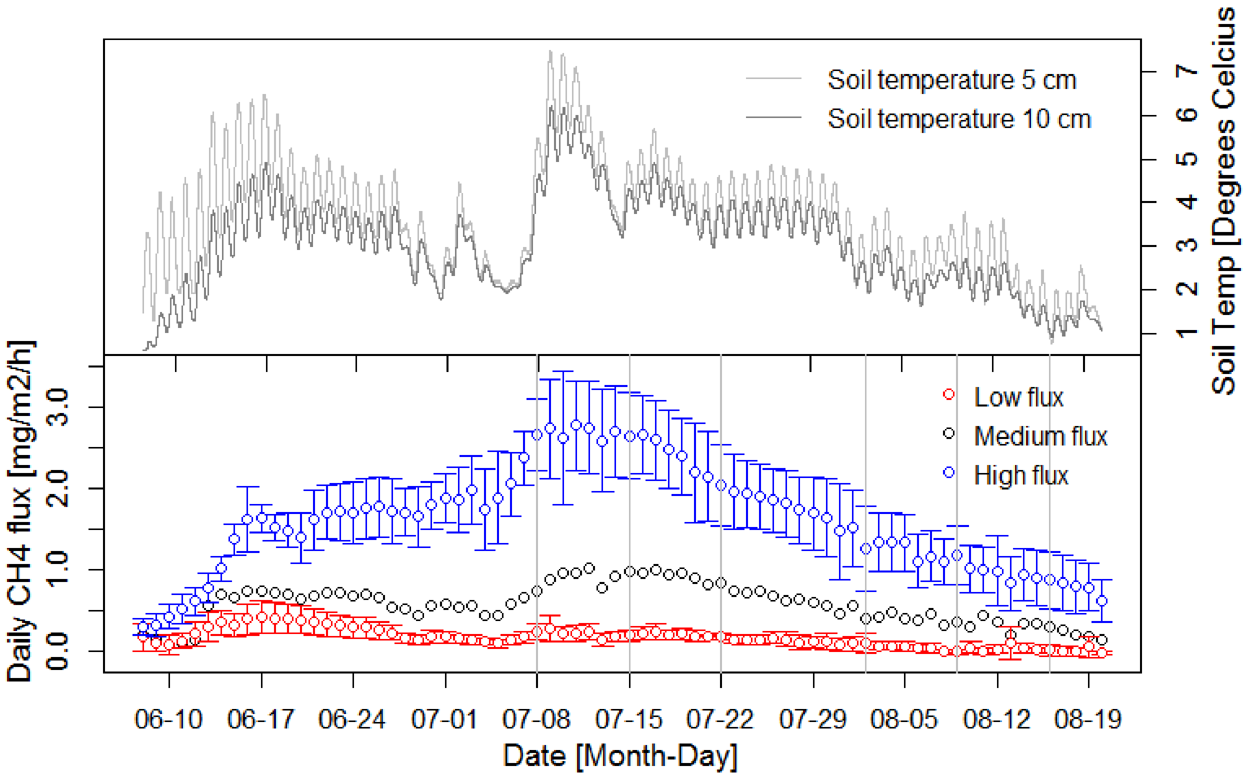


**Figure 4.3**: Top: soil temperature from 5 and 10 cm depth. Bottom: Mean daily flux of methane from the three different flux groups; low, medium and high. Bars depict one standard deviation. Vertical grey lines indicate the dates on which water samples were taken from chamber 2, 4 and 9.

The seasonal patterns in methane flux from the three emission groups (the low, medium and high flux group) follow the overall development in the soil temperature at 5 and 10 cm depth (Fig. 4.3). The chamber measurements started on the 8$^{th}$ of June, where after the emission immediately starts increasing following the trend of the soil temperature, reaching a peak around the 17$^{th}$ of June. Immediately after the air temperature decreases in the third week of June, both the soil temperature and the methane flux decrease. The emission from the medium flux group is approximately a factor of 1.5 larger than the emission from the low flux group, during the peak around the 17$^{th}$ of June. Whereas, the emission from the high flux group is approximately double the emission from the medium flux group (Fig. 4.3). After this initial peak, the flux from the low flux group starts to decrease gradually. The same is more or less true for the medium flux group, whereas the flux from the high flux group starts increasing again, but with a smaller gradient than during the initial peak. From the 7$^{th}$ of July, a second peak occurs. This peak is very small for the low flux group, larger for the medium flux group and very clear for the high flux group. From the middle of July the fluxes from all three groups decrease gradually until the end of August.

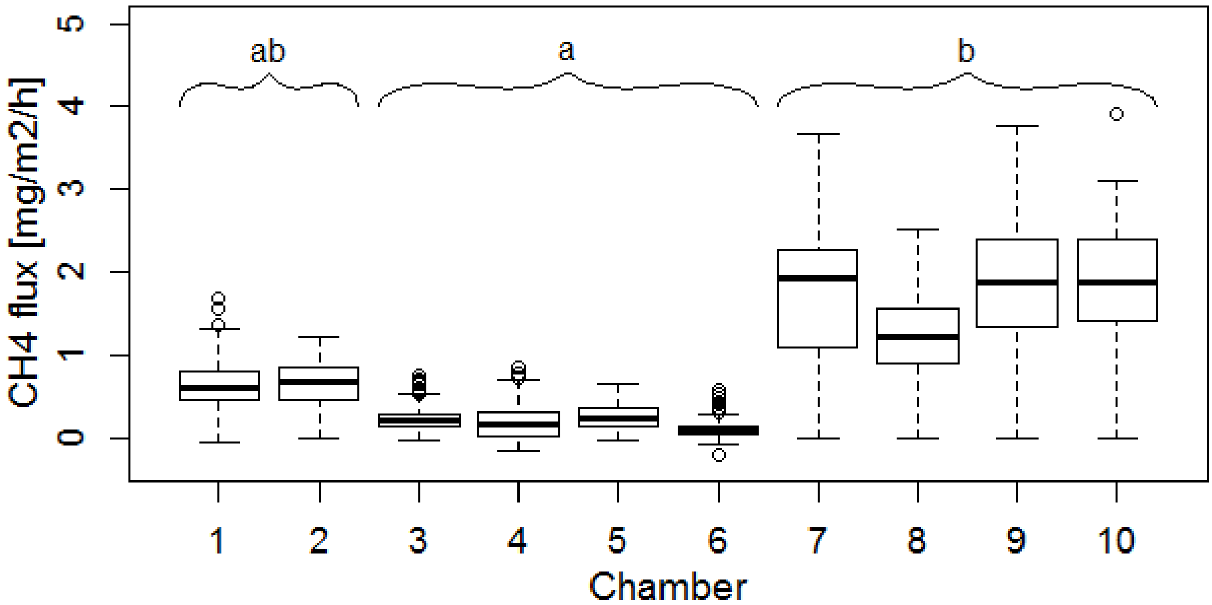

**Figure 4.4:** Seasonal methane ($CH_4$) fluxes (mean of measurements from the 8$^{th}$ of June to the 20$^{th}$ of August) from each of the ten chambers. The mean of flux groups differed significantly (ANOVA, $F(2, 7) = 53.2$, $p < 0.001$). Different letters indicate significant differences between the flux groups: medium (chamber 1 and 2), low (chamber 3, 4, 5 and 6) and high (chamber 7, 8, 9, and 10), post-hoc Tukey HSD test ($p < 0.001$).

The seasonal mean methane fluxes from the low and high flux group are significantly different (Fig. 4.4). The medium flux group is not significant different from neither the low nor the high flux group. It should be noted that the mean methane emission from chamber 7 is overestimated, as the first two weeks of measurements were discarded due to leakages.

The second peak of methane emission coincides with the peak $CO_2$ uptake of the growing season (Fig. 4.5). The $CO_2$ uptake is largest for the high methane flux chambers. For large parts of the growing season, the $CO_2$ flux for the medium and low flux chambers is positive. Over the season there is no statistically significant difference in the $CO_2$ flux between the low and medium flux groups, whereas the $CO_2$ flux from the high flux group is significantly different from the other two groups (Fig. 4.5).

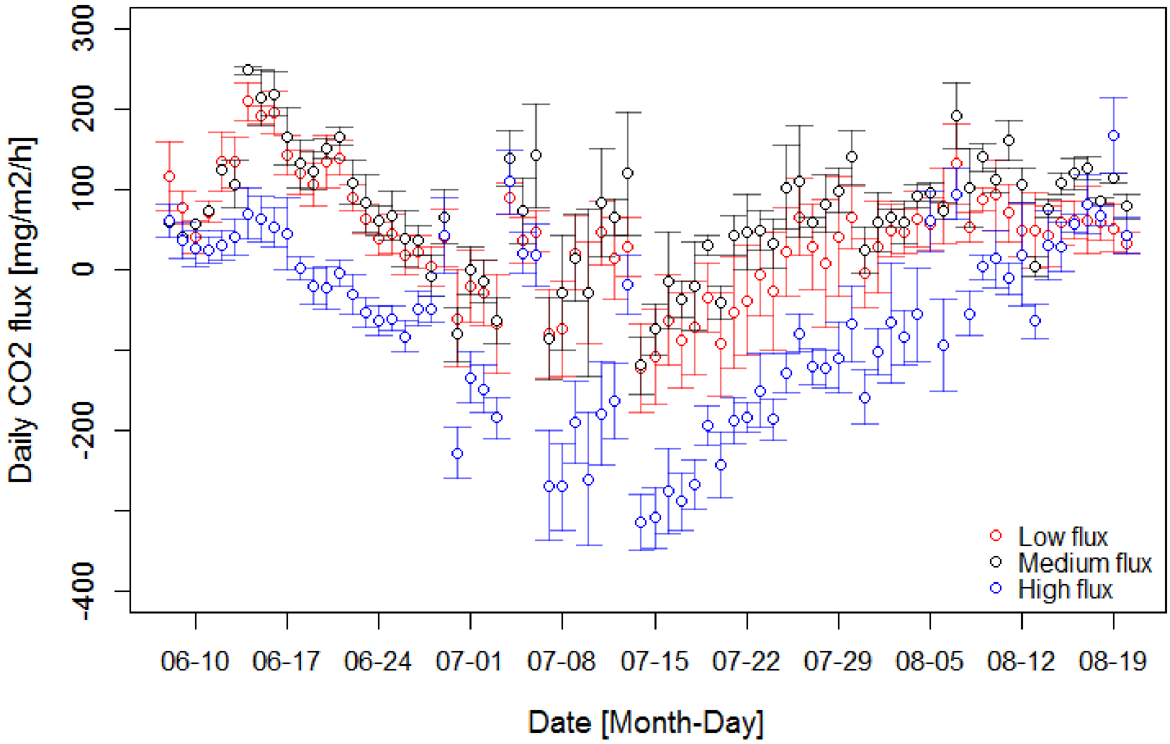


**Figure 4.5**: Mean daily net ecosystem exchange (NEE) for the three flux groups; low, medium and high flux. There is significant separation with regards to the seasonal NEE (ANOVA, F (2, 7) = 31.2, p <0.001). The high flux group is significantly different from the low and medium groups (Tukey HSD test, p < 0.001),whereas there is no significant separation between the low and medium flux groups.

4.4 Trends from individual chambers

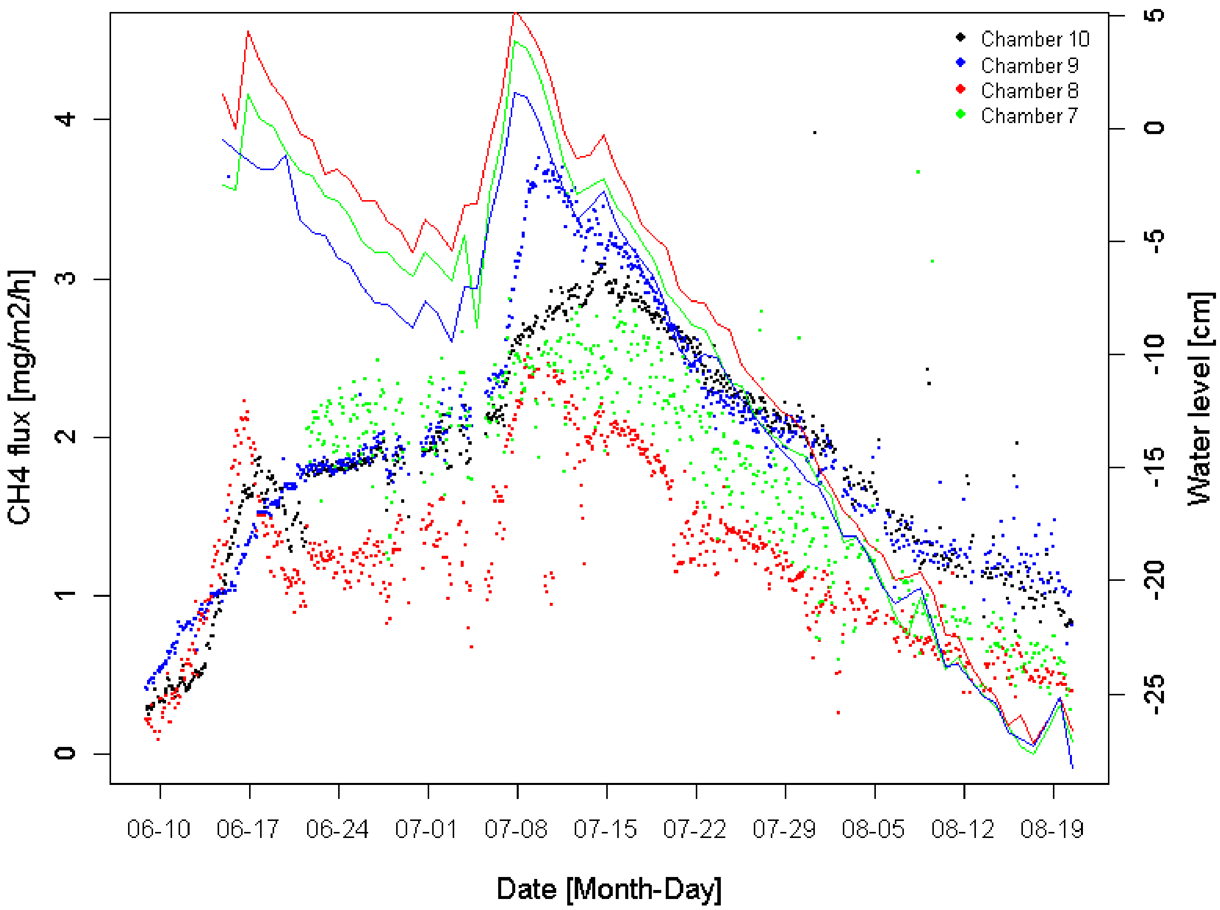


**Figure 4.6**: Dots: All measured methane ($CH_4$) fluxes from the four high flux chambers; 7, 8, 9 and 10, excluding extreme emission events. Lines: Water level as measured in the vicinity of each chamber, lines are assigned color according to which chamber it was measured in the vicinity of. The water level for chamber 9 is measured just between chamber 9 and 10.

The general pattern in the seasonal methane dynamics of the high flux chambers is relatively uniform (Fig. 4.6). However there are remarkable differences, especially within the two peak periods. The first peak, around the 17$^{th}$ to 21$^{st}$ of June (two weeks after complete snowmelt), is only apparent from chamber 8 and 10. The flux from chamber 9 doesn't decrease after the 17$^{th}$ of June, like for the other two chambers, but continues to increase with a less steep slope than initially. Already within the first week after the flux in chamber 10 has started to decrease, it starts increasing again, apparently with the same gradient as the flux from chamber 9. Contrary to this pattern, the flux from chamber 8 stabilizes on a lower level, however with relatively large diurnal fluctuations. Unfortunately there was a leakage from chamber 7 up until the 21$^{st}$ of June, hence the first peak has not been documented from this chamber. From the 21$^{st}$ of June and until the first week of July, the emission from chamber 7 appears to be at the same level or even a little higher than the emission from chamber 9 and 10, although the diurnal fluctuation is greater for chamber 7. From the beginning of the second peak period on the 8$^{th}$ of July the emission from chamber 9 starts showing the same pattern as chamber 8 with steep increasing emission, whereas chamber 10 and 7 show more moderate increases and peak in the middle of July, after the emission from chamber 8 and 9 has started declining. From the middle of July onwards, the emission is gradually decreasing from all four high flux chambers.

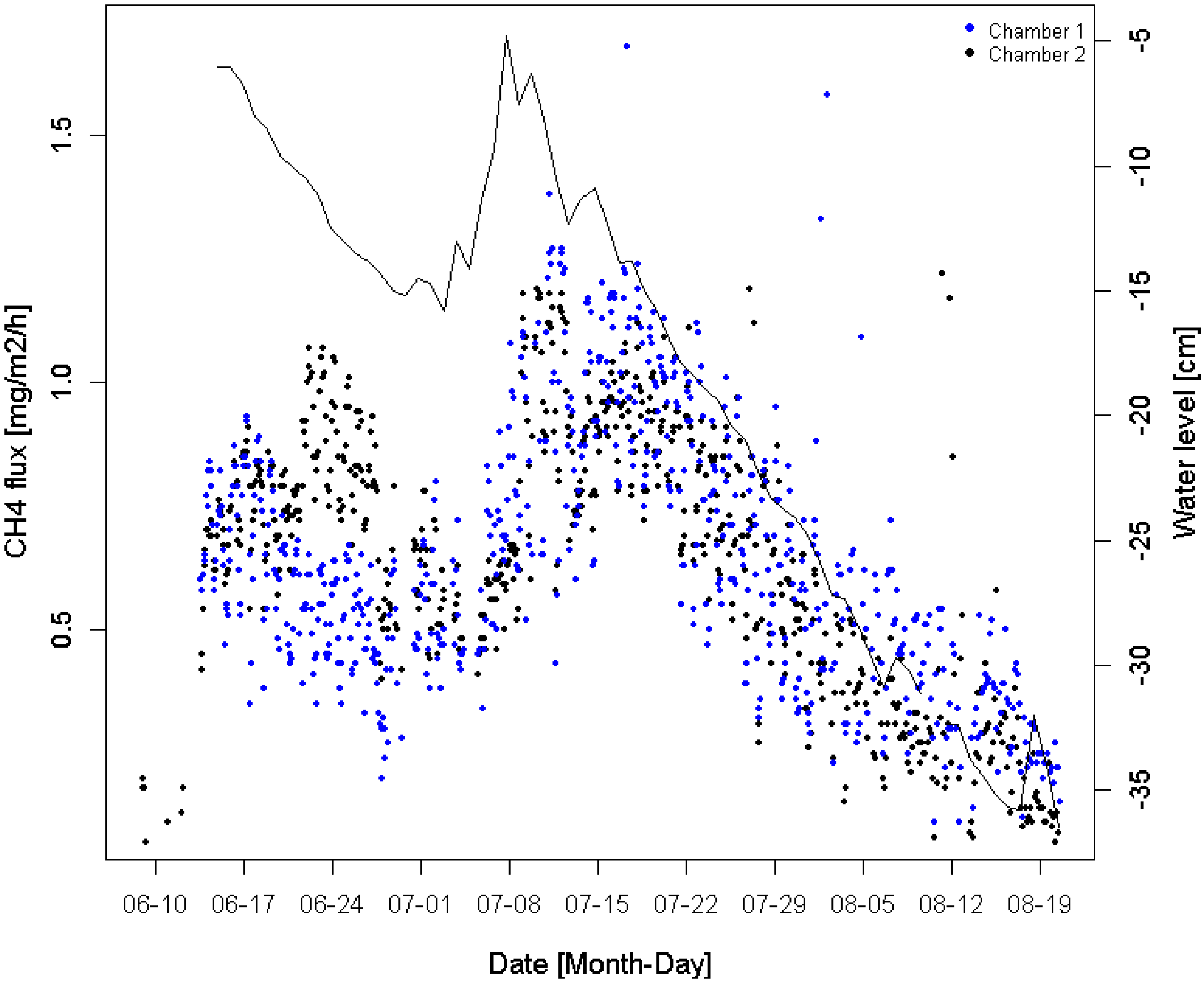


**Figure 4.7**: Dots: All measured methane ($CH_4$) fluxes from chamber 1 and 2, the medium flux chambers, excluding extreme emission events. Line: Water level measured between the two chambers.

The emission from the two medium flux chambers is generally following the same pattern over the summer season (Fig. 4.7). However, the flux for chamber 2 has a higher peak than chamber 1 in June. The peak is also occurring about one week later than for chamber 1. As for the high flux chambers the emission is larger for the second peak in July, than the initial peak in the middle of June. Although for chamber two where the peak is larger in the beginning of the season, the second peak is only slightly larger than the first.

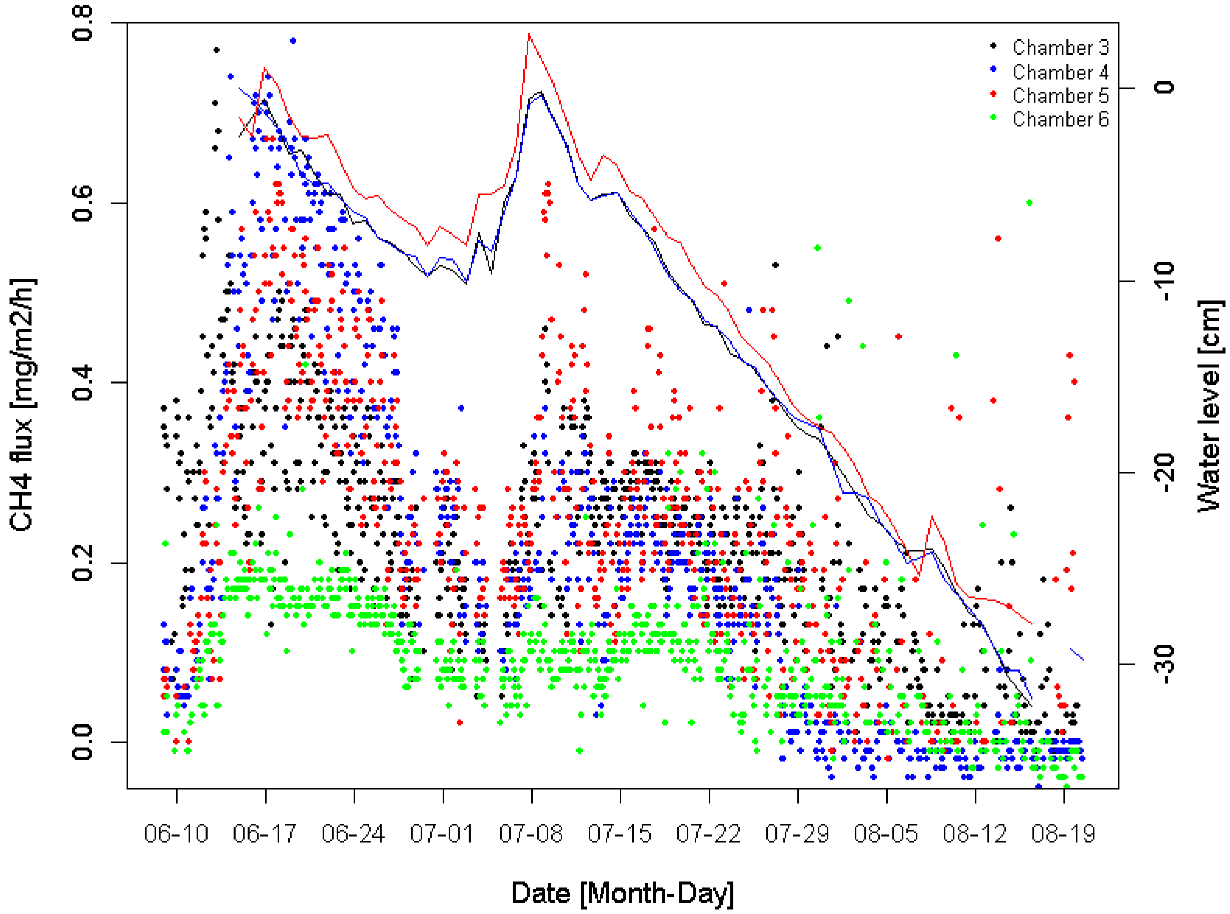


**Figure 4.8**: Dots: All measured methane ($CH_4$) fluxes from the low flux group: chamber 3, 4, 5 and 6, excluding extreme emission events. Lines: Water level measured in the vicinity of chamber 3, 4 and 5, the water level measurement from chamber 5 is also representative of chamber 6.

The methane emission from the low flux chambers also display a seasonal pattern with two peaks. However, for all the low flux chambers the first peak is larger than the second peak. The average seasonal flux from chamber 6 is significantly different than the fluxes from chamber 3-5 (Fig. 4.4).

## 4.5 Relations with environmental variables and net ecosystem exchange

Methane emissions from all chambers are positively correlated with the water level (table 4.2). All chambers are also positively correlated with the soil temperature in 5, 10 and 15 cm depth. Only the four low flux chambers do not show a significant correlation with the temperature in 15 cm depth. The shaded values indicate the depth at which the soil temperature results in the highest correlation with the methane emission.

The relation between the $CO_2$ exchange and the methane emission is negatively correlated for the five chambers the furthest from the fringe of the fen (all four high flux chambers and the one medium flux chamber, chamber 1, table 4.2). For the remaining five chambers there is either no relation or a weak positive correlation (i.e. increasing methane emission with $CO_2$ release).

**Table 4.2**: Correlation coefficients between seasonal methane flux from the individual chambers and the environmental variables; active layer (AL), water level (WL) and soil temperature (SoilT) in 5, 10 and 15 cm depths. Correlation coefficient between seasonal methane emission and net ecosystem exchange (NEE) is given in the last column. Correlations are also shown for the mean values for each flux group (low, medium and high). Correlations with active layer are shown both before and after the second growing season peak on the 8th of July. Shaded cells indicate at which depth the correlation with seasonal temperature is strongest. The chambers are listed with the least moist first and wettest last, hence the mixed ordering of numbers. Stars represent statistical significance; * $p < 0.05$ and ** $p < 0.005$.

| Chamber | AL | AL (> 8.7.2013) | AL (<8.7.2013) | WL | SoilT5 | SoilT10 | SoilT15 | NEE |
|---|---|---|---|---|---|---|---|---|
| Low | | | | | | | | |
| 6 | 0.25 | 0.13 | 0.17 | **0.56**** | **0.58**** | **0.56**** | 0.06 | 0.07 |
| 5 | 0.26 | -0.06 | 0.59 | **0.75**** | **0.64**** | **0.64**** | 0.06 | 0.08 |
| 4 | **0.71**** | -0.01 | **0.96**** | **0.79**** | **0.62**** | **0.55**** | -0.16 | **0.35**** |
| 3 | **0.78**** | **0.76*** | **0.92**** | **0.82**** | **0.73**** | **0.58**** | -0.11 | **0.34**** |
| Mean | **0.69**** | 0.19 | **0.94**** | **0.89**** | **0.73**** | **0.65**** | -0.06 | 0.19 |
| Medium | | | | | | | | |
| 2 | 0.23 | -0.57 | **0.96**** | **0.79**** | **0.78**** | **0.88**** | **0.56**** | -0.16 |
| 1 | 0.36 | **0.83*** | **0.92**** | **0.63**** | **0.77**** | **0.83**** | **0.58**** | **-0.42**** |
| Mean | 0.13 | -0.52 | **0.92**** | **0.75**** | **0.78**** | **0.88**** | **0.64**** | **-0.29*** |
| High | | | | | | | | |
| 7 | **0.78**** | -0.56 | **0.87**** | **0.95**** | **0.75**** | **0.79**** | **0.59**** | **-0.68**** |
| 8 | 0.17 | **-0.81*** | **0.99**** | **0.83**** | **0.77**** | **0.87**** | **0.59**** | **-0.65**** |
| 9 | **0.46*** | **-0.92*** | **0.98**** | **0.63**** | **0.59**** | **0.74**** | **0.82**** | **-0.82**** |
| 10 | 0.44 | **-0.83*** | **0.94**** | **0.61**** | **0.53**** | **0.75**** | **0.76**** | **-0.79**** |
| Mean | -0.02 | **-0.98**** | **0.98**** | **0.76**** | **0.64**** | **0.82**** | **0.77**** | **-0.78**** |

The relation between mean daily methane emission and active layer is only statistically significant for four out of the ten chambers (for chamber 3, 4, 7 and 9, table 4.2). However, if the relation is considered in two periods, one before the peak methane emission around the 8th of July and one after, significant positive relationship for the medium and high flux chambers are found, whereas the relation before the peak is negative for these chambers (although not significant in all cases, table 4.2). The negative relation represents an increase in methane emission with increasing active layer depth, due to the sign convention adapted here, where the active layer is negative as it is measured as the depth from the vegetation surface. The different relations between active layer and methane emission from low and high flux chambers are also depicted visually in Fig. 4.9. Here it's clear that the relation is negative in the beginning of the season in the example of the high flux chamber and positive in the last part of the season, whereas the relation is positive throughout the season in the low flux chamber (i.e. decreasing emission with increasing thaw depth).

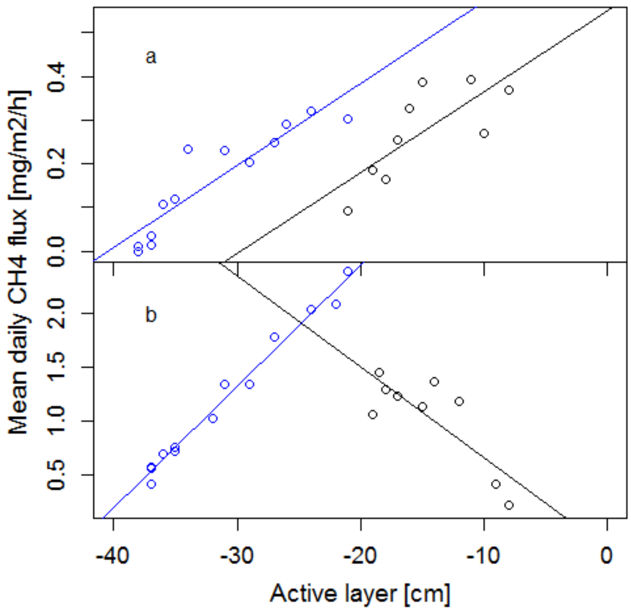


**Figure 4.9**: Visualization of relations with active layer for a low flux and a high flux chamber. a) Active layer in relation to daily methane emission from chamber 3, belonging to the low flux category. b) Active layer in relation to daily methane emission from chamber 8, belonging to the high flux category. Black lines and dots represent relations before the 8$^{th}$ of July, whereas blue lines and dots represent relations after the 8$^{th}$ of July.

4.6 Vegetation

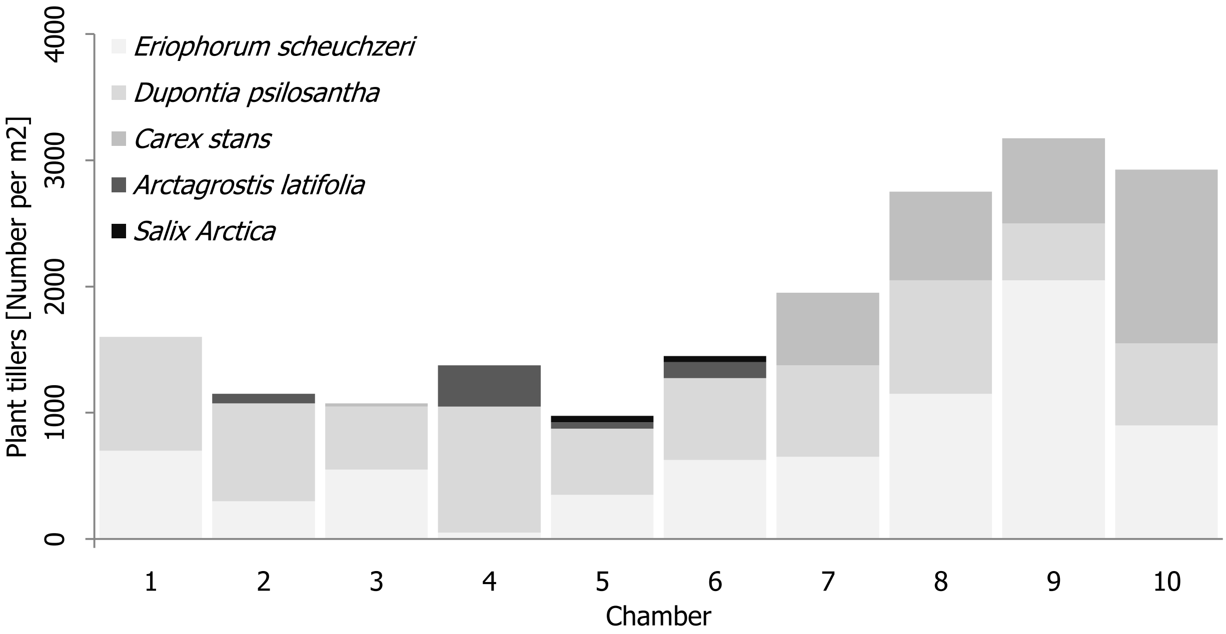


**Figure 4.10**: Count of different plant tillers within a subsection of 20 by 20 in each chamber and upscaled to number per square meter.

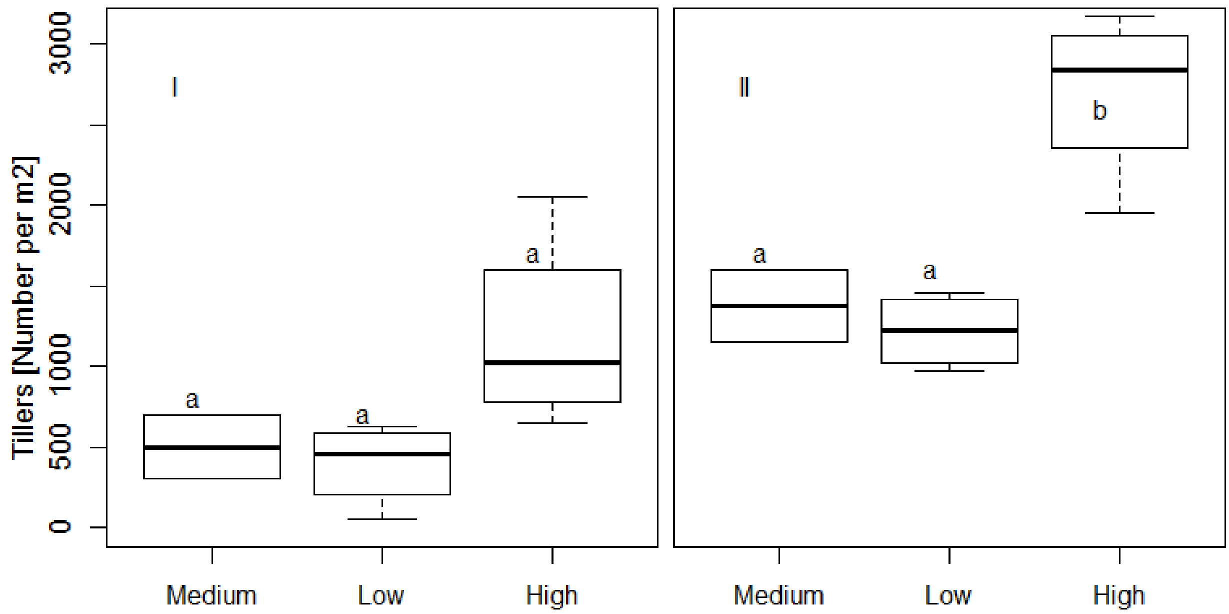


**Figure 4.11**: Binned count of tillers for the three different flux groups, different letters indicate significant differences. I) Count of *Eriophorum scheuchzeri* tillers in each group, there is no significant difference between the groups (ANOVA, F (2, 7) = 3.5, p = 0.09). II) Count of all plant tillers within each flux group. There is significant separation between the groups (ANOVA, F (2, 7) = 15.7, p = 0.003), with significantly more tillers in the high flux chambers (Tukey HSD test, p < 0.005) as compared to the low and medium chambers, which are not significantly different.

The vegetation analysis of each chamber revealed that the species composition is generally more diverse in the relatively dry chambers compared to the wetter high flux chambers (Fig. 4.9). *Eriophorum scheuchzeri* and *Dupontia psilosantha* are found in all chambers, although only very few individuals of *E. scheuchzeri* are found in chamber 4. *Arctagrostis latifolia* is only found in the relatively dry medium and low flux chambers, whereas *Carex stans* is only found in the wetter high flux chambers. Although there are less species in the wetter part of the fen, the number of plant tillers is significantly higher for the high flux chambers, than for the low and medium flux chambers, where there is no significant difference (Fig. 4.11). There is also a higher number of *E. scheuchzeri* tillers in the wetter part, although there is no significant difference between the classes (Fig. 4.11). The relation between the mean seasonal methane flux and both the number of *E. Scheuchzeri* and total number of tillers is positive, with a Pearson's correlation coefficient of 0.7 ($p < 0.05$) and 0.87 ($p < 0.005$), respectively (Fig. 4.12).

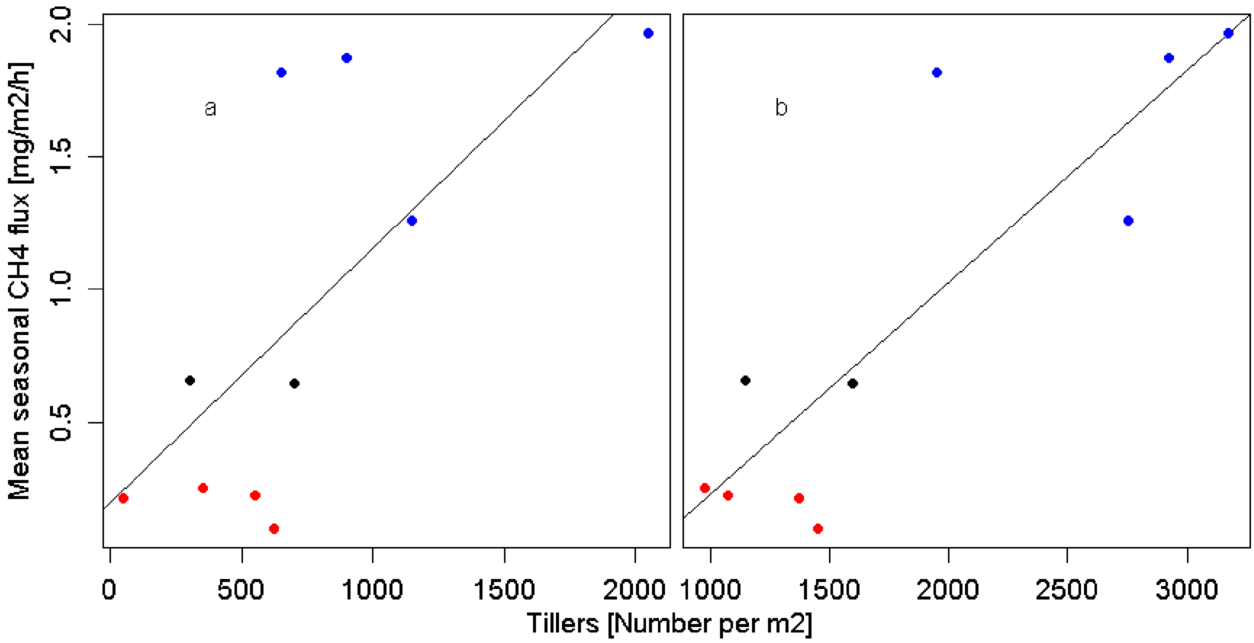


**Figure 4.12**: Relation between average seasonal methane ($CH_4$) flux and a) number of *E. scheuchzeri* tillers in each chamber ($R = 0.7$, $p < 0.05$) and b) all plant tillers in each chamber ($R = 0.87$, $p < 0.005$). Colors indicate to which flux group the points belong; red = low flux group, black = medium flux group and blue = high flux group.

## 4.7 Organic acids and dissolved organic carbon

Pore water samples were taken from the chambers from the 7th of July and weekly until the middle of August. In total 6 samples were taken from chamber 2 and 9 (representing the medium and high flux groups) and 4 samples from chamber 4 (representing the low flux group). About 90 % of the organic acids are comprised by lactic, acetic, formic and malic acids. Tartaric and citric acids were below detection limit for all samples. Acetic acid constitutes the majority of the organic acids from chamber 4 and 9 (55 and 41.5 % respectively). In chamber 2, 49 % of the organic acid is in the form of lactic acid.

**Table 4.3**: Seasonal mean pore water concentration (µg C $l^{-1}$) of organic acids and dissolved organic carbon (DOC) (± one standard deviation), measured in the period 7th of July to 16th of August in three of the 10 chambers (chamber 2, 4 and 9). The mean of the organic acids and DOC is based on 6 samples for chamber 2 and 9, and 4 samples from chamber 4.

| | 2 | 4 | 9 |
|---|---|---|---|
| Lactic | 100.5 ±148.6 | 22.2 ± 4.7 | 55.4 ± 68 |
| Acetic | 58.6 ± 29.8 | 101.6 ± 40 | 72.4 ± 39.6 |
| Formic | 20.6 ± 21.8 | 10.5 ± 8.8 | 23.7 ± 22.8 |
| Glycolic | 4.3 ± 1.3 | 5.3 ± 1.5 | 8.5 ± 3.8 |
| Malic | 10 ± 17.6 | 35.4 ± 36.6 | 4 ± 3.9 |
| Succinic | 3.6 ± 1.4 | 5.2 ± 4.2 | 3.7 ± 1.1 |
| Oxalic | 8.5 ± 4.2 | 4.5 ± 2.2 | 6.7 ± 2.5 |
| Total | 206.1 ± 36.8 | 184.6 ± 35.1 | 174.3 ± 27.9 |
| DOC | 65280 ± 24295 | 54360 ± 9493 | 46420 ± 21086 |

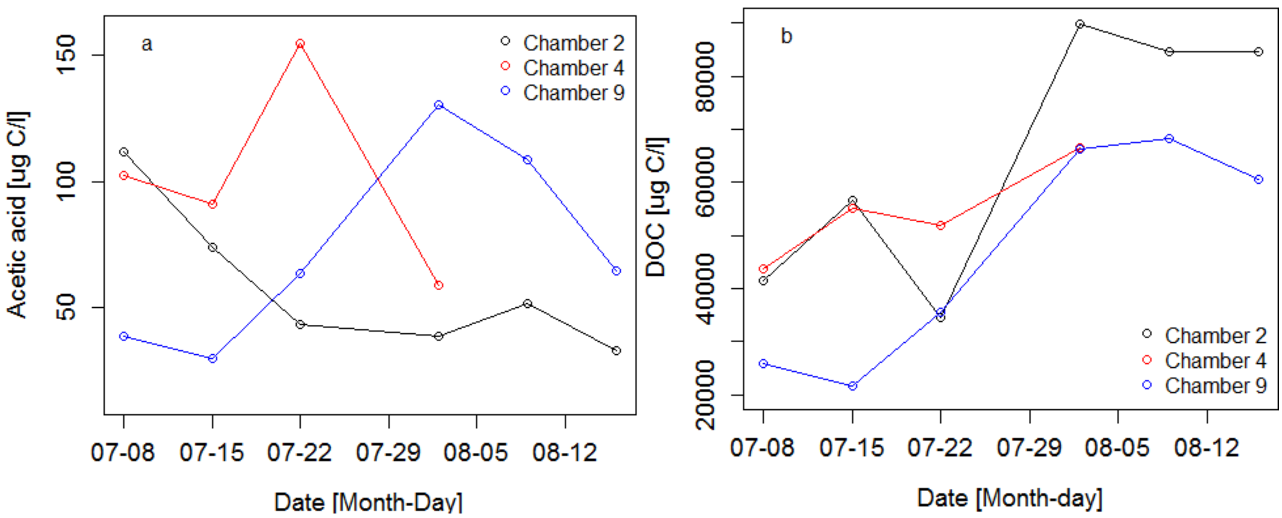


**Figure 4.13**: Development in a) acetic acid and b) DOC (µg C $l^{-1}$), from the 8th of July to 16th of August. The concentrations are measured from three of the ten chambers, namely chamber 4, 2 and 9, representing the low, medium and high flux chambers, respectively.

The seasonal patterns in the concentration of the acetic acids in the pore water are quite different between the three chambers that were sampled (Fig. 4.11a). The development from chamber 2, with initial high concentration and then gradual decrease, is almost the opposite of chamber 9, where the concentration is low during the peak growing season and then peaking in the beginning of August. The concentration of acetic acid in chamber 4 is in the same range as in the two other chambers. Unlike the pattern of acetic acid the seasonal development in DOC concentration seems to be more uniform over the different classes. In all three chambers the concentration of DOC is relatively low during the peak growing season and increases until the beginning of August.

## 4.8 Extreme events

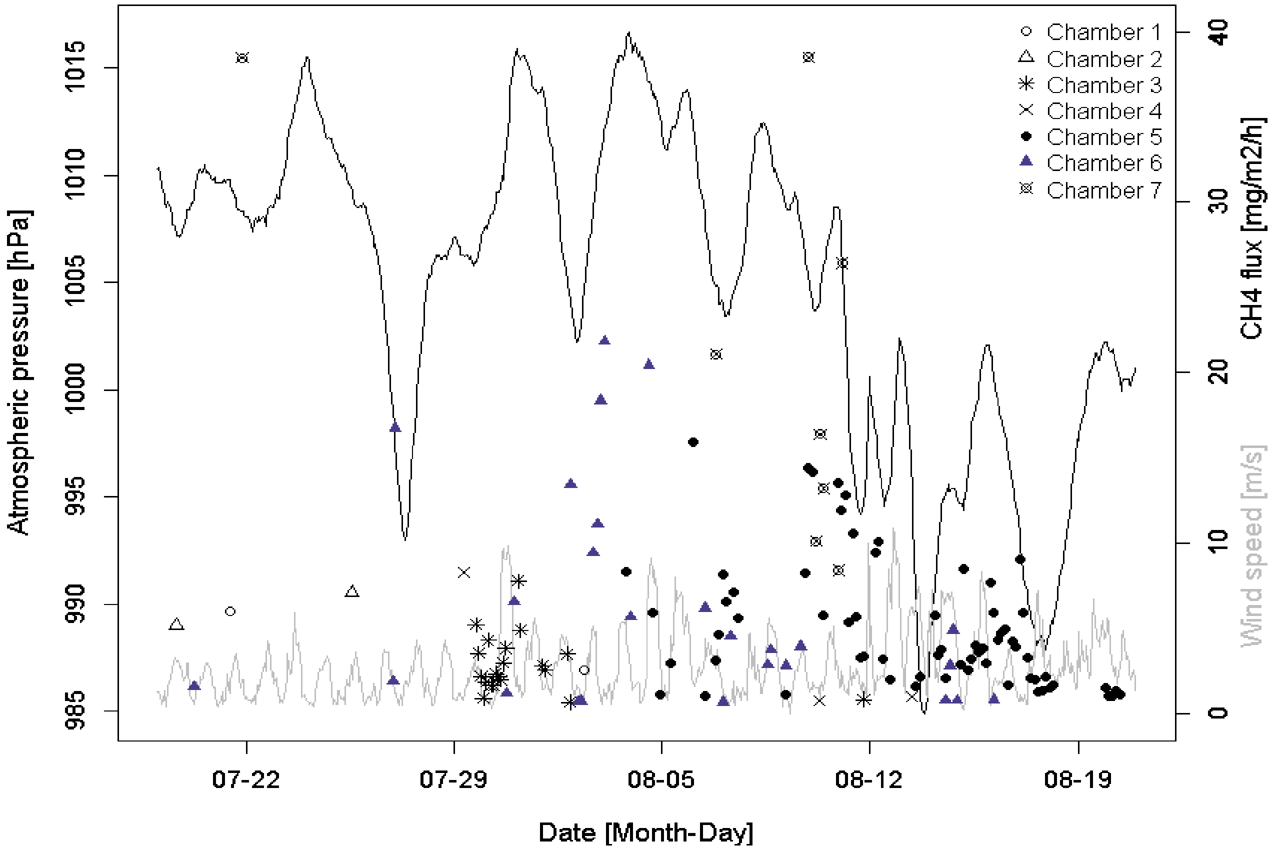


**Figure 4.14**: All extreme methane emissions from the seven chambers that displayed such events (1-7), depicted together with air pressure (black line) and wind speed (grey line). The correlation between extreme events and air pressure is $R^2$ = 0.25 (p = 0.005) and for wind speed $R^2$ = -0.18 (p = 0.04).

Analysis of relations between extreme methane emission events and air pressure, showed a weak positive relation ($R^2$ = 0.25, p = 0.005, Fig. 4.14). With regards to wind speed, a weak negative correlation was found ($R^2$ = -0.18, p = 0.04). No correlation was found between extreme events and air temperature, precipitation and wind direction. Furthermore, relations between change in air pressure and wind speed did not show any significant relationships, neither when considering change 10 hours prior to an extreme event (data not shown).

## 5 Discussion

### 5.1 Auxiliary data

#### 5.1.1 Atmospheric variables

The maximum snow depth of 0.13 m at the climate station in 2013 was extremely low compared to the 1997-2011 mean of 0.79 m ± 0.35 m (Pedersen et al. 2012). Likewise the early timing of snowmelt, on the 3rd of June, corresponds to 13 days earlier than the mean day of snowmelt since monitoring started in 2006 and has only occurred once before, in 2009 (data not shown) (Mastepanov et al. (2013), Mylius (formerly Pedersen), personal communication). As 72 - 92 % of the precipitation in Zackenberg falls as snow (Hansen et al. 2008), the amount of winter precipitation and the timing of the snowmelt exerts a strong control on the fen moisture regime the following growing season (Mastepanov et al. 2013).

Alongside snow cover dynamics, the mean temperature of July has been found to correlate well with the land-atmosphere $CO_2$ exchange on high Arctic heath tundra (Lund et al. 2012). The mean July temperature of 7.1 °C in 2013 was 0.8 °C higher than the 1996-2013 mean (data not shown, Pedersen et al. (2012) and Mylius (formerly Pedersen), personal communication).

The prevailing wind direction was southeastern in 2013 as was the dominating wind directions during summer from 1996-2005 (Hansen et al. 2008). However, the frequency of strong northerly winds (25 %) was higher than the long-term mean during summer months of 17 % (data not shown, Hangaard, personal communication). In general the atmospheric variables in 2013 differed substantially from the long term mean with extremely low winter precipitation, warmer than average summer temperatures and higher frequency of summer storms.

#### 5.1.2 Soil environmental characteristics

The fen was only completely water saturated for one week after the day of snowmelt in 2013 and the water level reached a maximum depth of 30 cm below the surface in the end of August (Fig. 4.2d). Such low water level has also only been observed once before since monitoring started at the site, namely in 2010 (Mastepanov et al. 2013). The active layer increased gradually from the day of snow melt and reached a maximum depth of ~35 cm (Fig. 4.2d), which is substantially more shallow than the 45-55 cm range from 2006-2010 (Mastepanov et al. 2013). As the soil temperatures haven't dropped below zero within the period studied here, the active layer measurements from the third week of August might not be the maximum thaw depth of 2013. Nevertheless, there is no change between the last five measurements, i.e. for fifteen days, hence it is assumed that the active layer would not increase to within the 2006-2010 range during the last part of the growing season. The reason for the shallow active layer is probably the low heat conductivity of the unsaturated peat, due to the relatively dry conditions (Tokida et al. 2007).

The seasonal maximum in soil temperature in 5 cm depth from 2007-2010 in the fen was 8-11 °C (Mastepanov et al. 2013). In 2013 the seasonal maximum in 5 cm depth was approximately 7 °C (Fig. 4.2c). This corresponds well with the relatively shallow active layer and low heat conductivity due to low water saturation. Furthermore the seasonal development in the soil temperature is following the pattern in the air temperature more closely in the beginning of the season, when the water table is high (Fig. 4.2c and d). The seasonal peak in the soil temperature in 5, 10 and 15 cm depth is around the 8th of July, which coincides with the seasonal peak in water level (due to precipitation events in the previous week) and a peak in the air temperature (Fig. 4.2).

5.1.3 Vegetation Characteristics

The vegetation analysis depicted in Fig. 4.10 and 4.11 clearly shows that the density of vascular plant tillers is significantly higher for the high flux chambers compared to the low and medium flux chambers, within which there is no significant difference. There is no significant difference between the three groups with regards to the number of *E. scheuchzeri* tillers (Fig. 4.11 I). However, the mean density of *E. scheuchzeri* tillers is clearly higher for the high flux chambers than for the other two groups, but the variation within the high flux group is so large that it is not significantly different from the other groups. Both with regards to the amount of total plant tillers and *E. scheuchzeri* tillers, the mean of the medium flux group is marginally higher than for the low flux group, although not significantly. It is however evident that the number of different species is larger within the low flux group, where i.e. *S. arctica* is represented in the two 'driest' chambers, 5 and 6 (Fig. 4.10). The poor separation between groups with regards to plant density is probably largely an artifact of the low number of replicates (10), but also the sampling strategy introduces uncertainty, that could be eliminated with a total count of all tillers within each 0.6 x 0.6 m chamber.

5.1.4 Soil water chemistry

The pore water sampling started during the seasonal peak in water level and soil temperature, namely on the 8$^{th}$ of July. The late growing season mean concentrations of organic acids from chamber 2, 4 and 9 (table 4.3) are generally lower than values previously reported from the Zackenberg fen (Ström et al. 2012). In Ström et al. (2012) acetic acid constituted the majority of the organic acids (> 80 %) and the total concentration of organic acids was 4 to 8 times larger than the concentrations found in this study. In Ström et al. (2001), the concentration of lactic acid was higher than the concentration of acetic acid at a site very close to the site studied here. The results found here are not unambiguous with regards to the main constituent of the organic acids, but acetic acid constitutes maximum 55 % of the organic acids (table 4.3). A possible explanation for the low absolute amount and proportion of acetic acid could be a smaller supply of root exudates to the soil pore water this year, compared to previous studies. This is in good agreement with the largely positive net ecosystem exchange reported here (table 4.1). These relations should however be considered preliminary as the very few data points and lack of replication inhibit any statistical testing.

Contrary to the seasonal mean of organic acid concentrations, DOC concentrations are approximately double the values reported in Ström et al. (2003) (table 4.3). The relatively low amount of organic acids and high concentration of DOC can be an effect of the timing of the sampling. All samples are taken during or after the growing season peak, where the concentrations of organic acids are usually lower. However the DOC values reported in Ström et al. (2003) were also sampled in August. Ström et al. (2003) found a negative relation between the potential methane production and DOC concentration and suggested that the relation expresses a decreasing quality of the DOC with increasing decomposition. Hence the relatively high concentrations of DOC measured in this study are probably consistent with the low concentrations of organic acids (table 4.3).

## 5.2 Seasonal $CH_4$ and $CO_2$ dynamics

### 5.2.1 Growing season flux of $CH_4$

The period with soil temperatures above zero degrees has previously been defined as the 'growing season' in order to compare fluxes between years, where the development in water level, active layer and snowmelt doesn't occur on the same calendar days (Mastepanov et al. 2013). In this sense, this study does not cover the full growing season. The temperatures usually drop below zero degrees around day of year (DOY) 250-270 in Zackenberg (Mastepanov et al. 2013), which is 20-40 days after the measurements ended in this study. Although this last period is not included in the seasonal mean and total fluxes (table 4.1), the fluxes in the end of the growing season (particularly the fluxes from the 6 original chambers, Fig. 4.3) are so small, that a comparison to earlier years is considered acceptable here. The fluxes published in (Mastepanov et al. 2013, table 4.1) are based on measurements from the 6 original chambers (i.e. the low and medium flux chambers). Although the mean seasonal fluxes reported here are slightly underestimated, it is clear that the mean flux of 2013 from the 6 original chambers is substantially smaller than the previously reported range (table 4.1). Even the mean from the 10 chambers (both excluding and including the extreme methane emission events) is in the low part of this range. With regards to the total growing season emission (table 4.1), this is also considerably below the 2006-2010 range.

The 2013 methane emission is also low when compared to other northern, permafrost underlain wetlands. In Siberia, Nakano et al. (2000) found emission rates of 15.9 - 76.3 mg $CH_4$ $m^{-2}$ $d^{-1}$ (at Tiksi, 71.5 °N) and 117 - 520.4 mg $CH_4$ $m^{-2}$ $d^{-1}$ (at Chersky, 68.5 °N). At Toolik Lake (68 °N) Schimel (1995) and Torn and Chapin (1993) found rates of 10.5 – 200.4 mg $CH_4$ $m^{-2}$ $d^{-1}$ and 5 – 60 mg $CH_4$ $m^{-2}$ $d^{-1}$, respectively. On the Northern coast of Alaska, in Barrow (71 °N) Harazono et al. (2006) found daily emission rates from 10 mg $CH_4$ $m^{-2}$ $d^{-1}$ during spring and up to 150 mg $CH_4$ $m^{-2}$ $d^{-1}$ during peak emission in July. Compared to these ranges it is clear that the magnitude of the fluxes in 2013 were unusually low. Most probably as a result of the low snow fall, early snowmelt in combination with warmer than average July temperatures and consequently favorable conditions for methanotrophic microbes.

### 5.2.2 Growing season flux of $CO_2$

The mean and total net uptake of $CO_2$ was also unusually low from the 10 chambers in 2013, actually 12 and 2.5 times smaller than the lowest reported values from 2006-2010, respectively (table 4.1). When considering only the low and medium flux chambers the net ecosystem exchange is even positive, representing a net release of $CO_2$ from the ecosystem over the growing season. This has been unprecedented in the record from this site which has previously been a net sink of $CO_2$ (Mastepanov et al. 2013). Arctic peatlands are generally considered net sinks of carbon dioxide and net sources of methane (Dinsmore et al. 2009; Blodau et al. 2004). The extremely dry conditions in 2013 thus seem to have shifted the balance of this particular wetland. It should however be noted that the 6 original chambers are the ones closest to the fringe of the fen. It is therefore not suggested that the carbon balance for the whole fen, Rylekærene, constitutes a net source of carbon dioxide. However the 2013 growing season is definitely not as great a sink of carbon as it has previously been considered, especially when including methane in the balance.

5.2.3 Seasonal development in $CH_4$ flux

2013 was the first year, since automatic measurements started in 2006, that the growing season methane flux showed two peaks with comparable size, one around the 17th of June and one around the 8th of July (Fig. 4.3). The main reason the fluxes from all the chambers start declining around the 17th of June (Fig. 4.3), is probably the combined effect of changes in water level and soil temperature. The water level is more or less falling gradually from the last day of snow melt until the beginning of July, where it reaches a depth of approximately 10 cm (Fig. 4.2). The soil temperatures are however increasing until around the 17th of June, where the air temperature starts showing a negative trend (Fig. 4.2). The water table position is not only important as it determines the relative proportions of the anaerobic and aerobic horizons in the soil, it also performs a control on the effect of the soil temperature (Kutzbach et al. 2004). When the water table has fallen below a depth of 10 cm, temperature fluctuations aren't as important for the methane production, due to lower fluctuations in this depth (Tokida et al. 2007). It is therefore likely that the decrease in methane fluxes from the 17th of June, when the water level was around the surface of the vegetation (Fig. 4.2), is directly caused by the observed drop in temperature. The substrate for methanogenesis in this initial peak period is probably not originating from recently fixed carbon (i.e. from the same year). The net ecosystem exchange is positive for the three different flux groups up until the 17th of June, representing a larger release of $CO_2$ than uptake (Fig. 4.5). It is therefore hypothesized that the majority of the substrate originates from fine roots and cells that have been broken during freeze-in the previous autumn (Mastepanov et al. 2013). Hence, it is suggested that the development during this peak is highly controlled through the combined effect of the water level and soil temperature.

Shortly after the first peak, the methane emission again starts increasing from the high flux chambers, with a slower rate than initially, while the soil temperature and water level continue to decrease (Fig. 4.3). The fluxes from the medium flux chambers are stagnating and the fluxes from the low flux chambers continue to decrease (Fig. 4.3). This increase from the high flux chambers coincides with the first days of negative net ecosystem exchange from this flux group (Fig. 4.5). Several studies have shown a positive relationship between the methane emission and net primary production (Joabsson and Christensen 2001; Whiting and Chanton 1993). This suggests that the substrate for methanogenesis during the 'between peak' period could originate increasingly from freshly assimilated carbon. Both from table 4.1 and Fig. 4.5 it is obvious that the seasonal $CO_2$ uptake is larger for the high flux chamber group, whereas there is no significant difference in the seasonal carbon dioxide flux from the low and medium flux chambers.

The second growing season peak around the 8th of July occurred in all chambers (Fig. 4.6, 4.7 and 4.8), again coinciding with a high water table and increasing soil temperatures (Fig. 4.2). However, the magnitude in relation to the first peak differed between the flux groups. Where the flux is approximately double the first peak for the high flux chambers, in the same order of magnitude as the first peak from the medium flux chambers, it is lower than the initial peak from the low flux chambers. As the changes in environmental parameters are largely similar for all the chambers and as the water level increases to the vegetation surface in all chambers (Fig. 4.6, 4.7 and 4.8), the reason for the differences in emission magnitude is probably mainly related to easily available substrate resulting from increased plant productivity. The second growing season methane peak coincides with the growing season peak in $CO_2$ uptake (Fig. 4.5), which was clearly larger for the high flux chambers. This is probably a direct effect of the higher plant density in these chambers (Fig. 4.10 and 4.11).

## 5.3 Spatial variation in $CH_4$ fluxes and character of controlling factors

Even within the small confined spatial extent of this study (a ~ 15 meter gradient), the methane emission varies up to a factor of 10 from the plot with the lowest emission to the highest emissions (Fig. 4.6, 4.7 and 4.8). This is in line with previous observations of strong spatial variability in many northern wetlands (Schimel 1995; Nakano et al. 2000; Torn and Chapin 1993; Reeburgh and Whalen 1992; Bellisario et al. 1999). The large variation within and between these studies have been explained through differences in soil temperature, water saturation, active layer depth and vegetation cover. Here the qualitative role of these factors will be assessed.

Most of the chambers on the moist to wet gradient display significant relationships with the environmental parameters active layer, water level and soil temperature (table 4.2). The seemingly large explanatory power of each variable underlines the interdependency and seasonality in both the environmental variables and the methane emission (Fig. 4.2). While they all seem to correlate exceptionally well with the seasonal methane emission, the character of the control they exert on the methane emission is quite different from one variable to another, both temporally (as touched upon in the previous section) and spatially.

The correlation coefficient between the methane emission and the soil temperature is generally larger for the medium and high flux chambers than for the low flux chambers (table 4.3). Although the correlations are stronger for soil temperatures in 10 and 15 cm depth for the medium and high flux chambers, they are also stronger with 5 cm than the correlations with emissions from the low flux chambers. This indicates that the emission is to a larger degree following the seasonal pattern of the temperature in the high and medium flux chambers. As described several studies have found strong relations between methane emission and temperature, however these relationships appear to only be applicable for the particular season studied. Mastepanov et al. (2013) showed large variation in correlation coefficients and regression slopes between years, independent of whether the relations studied were linear or exponential. This suggests that the temperature dependence of the methane emission is strong in relation to the seasonal development, rather than the actual magnitude and emission potential at the site. This also corresponds well with the seasonal pattern of two growing season emission peaks discussed previously.

Two of the low flux chambers, 3 and 4, are significantly correlated with the active layer throughout the season, hence the flux is declining with increasing active layer. For the medium and high flux chambers there is generally a tendency to increased methane flux with increasing active layer up until the second emission peak and then decreasing fluxes with increasing active layer (Table 4.2 and Fig. 4.9). Hence the active layer is not in itself an explanatory factor, it is rather a conditional factor, since methane will only be produced if the soil thaws, but the seasonal dynamics are not controlled by the depth directly. The relations in Fig. 4.9 are adding to illustrate that the high positive correlation between the two low flux chambers 3 and 4 is mainly an artifact of the low seasonal variability in the methane flux, rather than expressing an actual causal relationship. The large correlation coefficient for chamber 7 can probably for a large part be ascribed the lack of measurements from this chamber up until the 21$^{st}$ of June, hence the first growing season peak is not included in the analysis of the relationship (Fig. 4.6). Other studies have suggested that deepening of the active layer (i.e. due to climate warming) could lead to an increased methane emission due to increased temperatures of the thawed horizon (Nakano et al. 2000; Whalen and Reeburgh 1992). It is however not possible to register these changes within one site and one growing season, as the changes are occurring on regional or inter annual scales. The relatively shallow thaw depth compared to previous years, can hypothetically have been a limiting factor for the methane production. Both because less of the soil organic carbon has been available for decomposition, but also as the saturated zone (i.e. the difference between the water level and the active layer) has been relatively thin (Fig. 4.2d), especially in the later part of the season. It is however questionable whether these conditions are sufficient to significantly decrease the magnitude of the fluxes, as the carbon in deeper layers is probably more recalcitrant (Christensen et al. 1999) and the emission rates in the late part of the season are usually low due to seasonality in fluxes (Fig. 4.3 and Mastepanov et al. 2013).

For all the chambers there is a strong correlation between the methane emission and the water level (table 4.2). As has been discussed the water level controls not only the demarcation between the anaerobic and aerobic zone (Chowdhury and Dick 2013), but also influences the amplitude of the temperature variation. However in the study with annual comparison between emissions and environmental parameters by Mastepanov et al. (2013), the water level was only significantly related to the emission in 2010, which was exceptionally dry compared to the years 2006-2009. In this study it was suggested that the control of the water level was only important for the seasonal development when the water table drops below a certain threshold. This is in line with a study by Grünfeld and Brix (1999) showing no significant difference between completely saturated control mesocosms and mesocosms with water level lowered to 8 cm below the surface. When the water level doesn’t drop drastically below the vegetation surface the capillary forces in the peat apparently maintain sufficiently high moisture for methanogenesis to continue, without notable oxidation. Similarly Treat et al. (2007) found that the methane emission only decreased in the driest plot they investigated with falling water table. Schimel (1995) likewise concluded that relatively small variations in water level were a less important control on methane fluxes as compared to plant composition. On larger scales the water level/water saturation of an area is important for the species composition, which in turn affects the methane emission and magnitude of fluxes (Tagesson 2011). Hence the long term effect of the hydrological regime can indirectly (through changing vegetation composition) influence the emission. Water saturation is obviously crucial for the anaerobic production of methane, but the strong seasonal correlation that was found for all chambers (table 4.2) is probably to a higher degree a result of similar seasonal development in methane emission and water level, than due to a direct causal relationship. This statement is supported by the fact that the growing season methane peak has been skewed towards the beginning of the season in several years, while the seasonal development in water level has differed (Mastepanov et al. 2013).

The growing season methane emission is only negatively correlated to the net ecosystem exchange for the high flux chambers and chamber 1, i.e. the 5 chambers most distant from the fringe of the fen (table 4.2), which are also the chambers with the highest plant density (Fig. 4.10). For the low flux chambers 3 and 4 there is even a significant positive relation between the emission of methane and carbon dioxide, representing higher methane emission with higher net carbon dioxide release. These can be related as both methane and carbon dioxide are end products of decomposition and controlled by the same soil environmental factors (Treat et al. 2007). However, the absence of negative correlation between methane emission and net ecosystem exchange for the low flux chambers is probably related to the very low uptake during the peak growing season (Fig. 4.5) and resulting low assimilation of labile carbon to the soil. This pattern confirms the hypothesis that the production of methane is limited by availability of substrate (Schlesinger and Bernhardt 2013). Ström et al. (2012) showed that the concentration of acetic acid carbon in the Zackenberg fen area could sustain about 2-2.5 hours of methane production by acetoclastic methanogenesis, implying the need for a continuous input of acetic acid to sustain methane production. The low productivity of the plants in the low and medium flux chambers is probably highly related to the dry conditions of the 2013 growing season. However, the productivity of the vegetation from the 6 original chambers might also be affected by the longer exposure to the greenhouse effect from the permanently installed chamber walls themselves. Although, the significance of this effect is unknown.

The positive relation between the number of plant tillers and the methane emission (Fig. 4.12b), indirectly shows the importance of production of substrate through photosynthetic activity. As previously touched upon the, several studies have shown *Eriophorum* species to have a more stimulating effect on the availability of substrate than other vascular species (Ström et al. 2003; Ström et al. 2005; Ström et al. 2012; Schimel 1995; Moore et al. 2011). The relationship between methane emission and *E. scheuchzeri* is not stronger than the relation to the total number of tillers (Fig. 4.12a and b). However, it should be stressed that the relations in Fig. 4.12 are only based on 10 replicates and there is large variation within the high flux emission group both with regard to the presence of *E. scheuchzeri* and the seasonal methane emission (Fig. 4.4 and Fig. 4.11 I). As mentioned previously a total count of plant tillers could aid in reducing the uncertainty, as well as the determination of the different mosses and their effect on substrate availability. Another factor with potential importance in relation to the emission rate is the phenology of the vascular plants, as studies from rice paddies have shown the plant mediated transport to be low when plants are small (Le Mer and Roger 2001). Chambers 7 and 10 have the lowest density of *E. Scheuchzeri* within the high flux group, although chamber 10 has a high number of total tillers (Fig. 4.10). These two chambers are also exhibiting a different pattern than chamber 8 and 9 during the second growing season peak (Fig. 4.6), where the emission increase is smaller and the emission peak is 5 - 7 days later. The emission from chamber 8 during this peak is not larger than the emission from chamber 7 and 10, but different incremental patterns as response to methanogenesis stimulating environmental conditions could be an artifact of species specific substrate production, although it cannot be shown here.

The low concentration of acetic acid in chamber 9 during the second growing season peak (Fig. 4.13a) could support the theory that the acetic acid carbon is decomposed almost immediately, when environmental variables aren't limiting (Schlesinger and Bernhardt 2013). This together with the higher density of vascular plants, in particular *E. scheuchzeri* (Fig. 4.10 and 4.11) and the higher productivity of the high flux chambers (Fig. 4.5) is probably the main reason for the larger magnitude of emissions from these chambers. Contrary, the concentration of acetic acid in chamber 2 and 4 is larger (Fig. 4.13a), suggesting a slower methane production rate in these chambers, potentially caused by other factors than substrate availability. However, with the lack of replicates, caution should be taken in interpreting these patterns. The seasonal development in the DOC concentration is similar for all the chambers, with relatively low concentrations during peak growing season and then increasing during the late growing season (Fig. 4.13b), indicating that less and less of the organic carbon is fully decomposed as the season progresses. Although these patterns should only be viewed as preliminary results, the low seasonal ratio between organic acids and DOC is consistent with the low plant productivity (Fig. 4.5) and hence low magnitude of methane emissions in 2013.

## 5.4 Extreme events

Extreme emission events were only recorded from 7 out of the 10 chambers and almost 80 % of these events were recorded in the two chambers closest to the fringe of the fen (chamber 5 and 6 in Fig. 3.2 and Fig. 4.14). Due to the stochastic nature of ebullition timing there is a risk that events are not captured when using automatic chamber technique, as the chambers naturally cannot measure 100 % of the time (Green and Baird 2013). However, the spatial variability in ebullition fluxes is strong and the presence of hotspots has been suggested (Green and Baird 2013). The results presented in table 4.1 and Fig. 4.14 show that the extreme emission events constitute a considerable seasonal proportion (25 %) of the emission from the low and medium flux sites, whereas the contribution is approximately 5 % when considering all 10 chambers. The extreme events mainly originated from the low flux chambers and the far majority was recorded after the water level had dropped under 10 cm below the vegetation surface (Fig. 4.2). The timing and frequency of these events is unprecedented in the 7 year record of continuous measurements at the site (Mastepanov, personal communication).

The summer of 2013 had a higher frequency of strong northern winds than the 1996-2006 long term mean (Fig. 4.1 and Hansen 2008), which hypothetically can trigger ebullition events (Bartlett and Harriss 1993). However the relation between wind speed and the timing of the high emission events shows a very weak negative correlation. Furthermore, the fluxes observed here are measured using the closed chamber technique, which could theoretically be an obstacle to measuring wind induced fluxes. This however depends on whether the effect of wind speed on ebullition rate is a strictly local phenomenon or whether disturbance of the surrounding peat is the trigger of ebullition. Hypothetically the later is more probable, as the very high fluxes were mainly registered in August, when the water table was well below the vegetation surface. Hence the shear stress needed to impact the horizons in which the methane is situated, would probably have to be great enough to impact larger areas. Nevertheless, these observations cannot confirm the hypothesis that ebullition events are triggered by wind speed.

The weak positive correlation with air pressure found here (Fig. 4.14) does not support the current paradigm that rapid drop in air pressure is a dominant trigger of ebullition (Tokida et al. 2007). In general, the lack of correlation with atmospheric variables, including temperature and wind direction, suggests that the mechanism responsible for triggering the extreme events has to be found within the soil matrix. Furthermore the timing late in the season does not correspond to other studies that found almost no ebullition in the late growing season, presumably because of better developed roots, increasing the potential gas transport through vascular plants (Joabsson 2001). The fact that almost half of the extreme events showed constantly high emission rates, could indicate that these fluxes were plant mediated and not typical eruptive bubbles escaping through the saturated zone. Previous studies have observed the accumulation of bubbles in certain layers (Rothfuss and Conrad 1998). The dry conditions in 2013 and resulting water stress for the plants can potentially have forced the plants to invest in more and deeper rooting systems than previous years, thereby reaching potentially large and previously undisturbed methane pools.

With regards to the 50 % extreme events that showed eruptive characteristics, these could be related to the vegetation density of the chambers. The ebullition events were observed in the seven chambers with the lowest vegetation density (Fig. 4.10). In the chambers with well developed root density, the potential for plant mediated transport is higher, hence the potential buildup of methane in the saturated soil is smaller. These explanations for both the ebullitive and constantly high fluxes are however speculative and studies of the rooting depth and density is needed to determine their importance. However, the main differences registered here between the high flux and the low flux chambers is their position on the moist to wet gradient and the different density of vascular plants.

## 6 Conclusion

The magnitude of the methane fluxes measured in the Zackenberg fen during the growing season of 2013 were unusually low compared to previous years and comparable sites from the circumpolar Arctic. The carbon dioxide uptake of 2013 was equally small and several plots showed positive seasonal mean net ecosystem exchange. The low productivity of plants and methanogens was mainly ascribed the unprecedented dry conditions, due to low winter precipitation and early snowmelt.

Despite the large differences in emission magnitude between chambers (up to a factor of 10), the seasonal emission pattern was similar for all the chambers. The temporal variability of emissions was largely controlled through environmental factors, although the character of the control differed among factors. Soil temperature exerted a direct control on the actual production of the methane, especially in the beginning of the season, when the water level was at the vegetation surface. Whereas active layer and water level generally displayed a more conditional character in relation to the emission, as frozen and oxidized soils inhibited the production and thereby the emission of methane. The water level correlated well with the emission from all the chambers, however this strong relation is probably a result of the dry conditions of 2013. Soil temperature, water level and active layer were found to follow the same general seasonal development and consequently the separate effects are difficult to quantify.

The spatial variability appears to be largely controlled through the net primary productivity and hence through the vegetation density and species composition. Especially the presence of vascular species and in particular *Eriophorum Scheuchzeri* appeared to exert great control, not only on ‘interplot’ scale, but also in relation to magnitudes of growing season fluxes. Low emissions from the least moist chambers during peak growing season are primarily ascribed lack of substrate availability and low quality, as a result of low plant productivity. Relatively low concentrations were found of organic acids and relatively high concentrations of DOC during the late growing season of 2013, compared to previous studies. This is again probably directly linked to the low plant productivity due to the dry conditions of 2013.

In the late growing season of 2013, 129 extreme emission events were measured, half of which displayed ebullition like characteristics in the concentration increase. The extreme events were mainly observed in the medium and low flux chambers, with a far majority from the two driest plots. No explanation for the timing of these extreme emissions was found in atmospheric variables like drop in air pressure, temperature or increase in wind speed. It is therefore suggested that the timing of these events is related to processes in the soil matrix, like deeper rooting depth in these relatively dry plots. This hypothesis could however not be tested in this study, but the mechanisms behind the events can potentially be very important for the annual emissions, especially from the fringe of the fen.

This study underlines the importance of studying factors controlling methane emission from wetlands in an integrative manner. The importance of the controlling factors varies temporally, as shown here seasonally, and spatially, even within small distances. Furthermore, the factors are interdependent and the relative importance of single or combinations of factors can change if boundary conditions change.

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