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Presence of *Eriophorum scheuchzeri* enhances substrate availability and methane emission in an Arctic wetland

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ABSTRACT

Here we present results from a field experiment in an Arctic wetland situated in Zackenberg, NE Greenland. During one growing season we investigated how dominance of the sedge *Eriophorum scheuchzeri* affected the below-ground concentrations of low molecular weight carbon compounds (LMWOC) and the fluxes of CO_2 and CH_4 in comparison to dominance of other sedges (*Carex stans* and *Dupontia psilosantha*). Three groups of LMWOC were analysed using liquid chromatography-ionspray tandem mass spectrometry, i.e., organic acids (OAs), amino acids (AAs) and simple carbohydrates (CHs). To identify the effect of plant composition the experiments were carried out in a continuous fen area with very little between species variation in environmental conditions, e.g., water-table and active layer thickness and soil temperature. The pool of labile LMWOC in this Arctic fen was dominated by OAs, constituting between 75 and 83% of the total pore water pool of OAs, CHs and AAs. The dominant OA was acetic acid, an easily available substrate for methanogens, which constituted ≥85% of the OA pool. We estimated that the concentration of acetic acid found in pore water would support 2–2.5 h of CH_4 flux and an additional continuous input of acetic acid through root exudation that would support 1.3–1.5 h of CH_4 flux. Thus, the results clearly points to the importance of a continuous input for acetoclastic methanogenesis to be sustainable. Additionally, *Eriophorum* had a very strong effect on parts of the carbon cycle in the Arctic fen. The mean seasonal CH_4 flux was twice as high in *Eriophorum* dominated plots, most likely due to a 1.7 times higher concentration of OAs in these plots. Further, the ecosystem respiration was 1.3 times higher in *Eriophorum* dominated plots. In conclusion, the results offer further support to the importance of certain vascular plant species for the carbon cycle of wetland ecosystems.

1. Introduction

Terrestrial ecosystems of the Arctic currently store large amounts of carbon. Although, the northern permafrost region cover only about 16% of the global soil area it holds approximately 50% of the global below-ground organic carbon pool (McGuire et al., 2009; Tarnocai, 2006). Arctic wetlands are characterized by waterlogged, anoxic and cool conditions, which effectively reduce decomposition rates and favour the formation of peat. The anoxic conditions at the same time favour anaerobic decomposition and methanogenesis. Consequently, natural and agricultural wetlands together contribute with over 40% of the annual atmospheric emissions of CH_4 and are considered the largest single contributor of this gas to the troposphere (Mikaloff Fletcher et al., 2004; Cicerone and Oremland, 1988).

Several environmental variables have been identified as controls of methane production and ultimately of net CH_4 emission. These include soil temperature, depth of water table (Waddington et al., 1996; Torn and Chapin, 1993) and substrate type and quality (Ström et al., 2003; Bellisario et al., 1999; Joabsson et al., 1999a). The organic carbon in soil is preliminary plant derived and originates from two main sources, i.e., 1) root and shoot residues and 2) root exudates and other root-borne organic substances released to the rhizosphere during plant growth (Kuzyakov and Domanski, 2000). Root exudates mainly consist of low molecular weight organic compounds (LMWOCs) such as organic acids, amino acids and carbohydrates. These compounds account for less than 10% of the dissolved organic matter in soil but are highly bioavailable and therefore play an important role in carbon and nutrient cycling in soils (Fischer et al., 2007). Organic acids commonly found in root exudates of a range of cultivated plants include acetic, citric, glycolic, lactic, malic, oxalic and succinic acid (Ohwaki and Hirata, 1992; Smith, 1976; Vancura and Hanzlikova, 1972; Kovacs, 1971; Vancura and Hovadik, 1965; Vancura, 1964). Microbial

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decomposition of organic matter can also lead to the production of several monocarboxylic acids. This tends to primarily occur under wet, anaerobic conditions when fermentative microbes in the soil produce a range of organic acids, including acetic, lactic, formic, and propionic acid, from plant residues (Killham, 1994). In wetlands an organic acid of particular interests is acetic acid which is often found to be a substrate of major importance for the methanogens (Ström and Christensen, 2007; Ström et al., 2003, 2005; Avery et al., 1999; Bellisario et al., 1999; Ferry, 1997; Boone, 1991; Oremland, 1988). In addition, we have in previous studies shown that species composition of vascular plants can affect CH_4 emissions and substrate availability for methanogens and pointed to the importance of *Eriophorum* species (*Eriophorum scheuchzeri*, *Eriophorum angustifolium* and *Eriophorum vaginatum*) in this respect (Ström and Christensen, 2007; Ström et al., 2003, 2005). Few studies have, however, been performed in-situ with minimal between species differences in environmental conditions.

To get a more detailed picture of the availability of labile carbon in the pore water of an Arctic fen, the primary aim of this study was to investigate A) the concentrations of LMWOCs, i.e., organic acids (OAs), amino acids (AAs) and simple carbohydrates (CHs), and B) how the concentration of LMWOC was affected by species composition and environmental variables and relates to fluxes of CH_4 and CO_2; gross primary production (GPP), net ecosystem exchange (NEE) and ecosystem dark respiration (R_{eco}). In addition a second aim of this study was to investigate how species composition and in particular the presence of *E. scheuchzeri* affected substrate availability and the fluxes of CO_2 and CH_4 under in-situ conditions. As study site we selected an Arctic continuous fen, dominated by three sedges (*Carex stans*, *Dupontia psilosantha* and *E. scheuchzeri*), with very little between species variation in water-table and active layer thickness or soil temperature.

In accordance with previous studies we hypothesize that a high-*Eriophorum* coverage leads to higher CH_4 emissions, higher CO_2 assimilation through photosynthesis (GPP) and R_{eco}. Further, we hypothesize that the effect of *Eriophorum* on CH_4 emission primarily is due to a higher concentration of labile LMWOC in the root vicinity of this species.

2. Materials and methods

2.1. Site description and set-up

The study took place in Rylekaerene an Arctic fen situated in the Zackenberg research area (74°28′N 20°34′W), located in the National park of North Eastern Greenland. The area is located in the high Arctic zone with a local climate in the Zackenberg valley that deviates slightly from the definition of the high Arctic climate. Average temperature of the warmest month is 5.8 °C, and mean annual temperature is −9 °C (Hansen et al., 2008). The Zackenberg valley is underlain by continuous permafrost and the active layer thickness (the layer that thaws and refreezes on a seasonal basis) ranges between 0.5 and 1.0 m. The peat layer in the fen is 20–30 cm thick, typical of high Arctic fen ecosystems (Meltofte et al., 2008) and in a neighbouring fen area the onset of peat accumulation has been ^{14}C-dated to AD 1290–1390 (Christiansen et al., 2002). The pH of the continuous fen pore water at 10 cm peat depth was 6.9 ± 0.2 ($n = 50$, Ström unpublished results). The dominant wind direction is N to NNW, except during summer when the prevailing winds are S to SE. Average wind speeds during summer are less than 4 m s^{-1} (Hansen et al., 2008). The dominant vegetation types identified in the Zackenberg valley are continuous and hummocky fen, grass-land and heath; which are distributed spatially based on topography, hydrology and soil type (Elberling et al., 2008). To enable a clear focus on the effect of vascular plant species composition on below-ground processes and CO_2 and CH_4 fluxes we chose to

position the study site in the minerotrophic continuous fen part of the mire, with very little between species variation in active layer thickness, water-table depth and soil temperature. The vascular plant vegetation in the site was completely dominated by three sedge species, *C. stans*, *D. psilosantha* and *E. scheuchzeri*. The moss species in the site was dominated by true mosses, e.g., *Tomenthypnum*, *Scorpidium*, *Aulacomnium* and *Drepanoclaudus*.

Two different set-ups were installed in the site. The aim of set-up[1] was to study the effects of species composition on pore-water chemistry and CO_2 and CH_4 emission. The aim of set-up[2] was to determine if the vascular plant composition noticeably affected CO_2 and CH_4 emission at community level. Set-up[1] consisted of 15 plot replicates of permanently installed circular 12.5 cm diameter aluminium bases inserted 15 cm into the ground and enclosing 0.0123 m^2 of vegetation. The Al-bases was used to create an airtight seal during gas flux measurements, see detailed description below. The plots were distributed to cover a range of the dominant vascular plant species, i.e., *Carex*, *Dupontia* and *Eriophorum*. To enable non-destructive sampling of the pore water a stainless steel tube (3 mm in diameter) was permanently installed into the soil profile at 10 cm depth within each Al-base. The tube protruded 5 cm above the peat surface giving it a total length of 15 cm and was closed at the top by a three-way valve that enabled sampling without air penetration into the soil. After the final measurement of the season (2 August) the total green above ground biomass in the plots was harvested. The harvested material was separated into *Carex*, *Dupontia* and *Eriophorum*, dried at 70 °C until stable weight was reached, and weighted to determine dry weight of the respective species in every plot.

Set-up[2] consisted of 15 larger plots (0.336 m^2) enclosing mixed continuous fen vegetation, which were randomly placed within the study area. In these mixed fen plots the percentages of basal cover of *Carex*, *Dupontia*, *Eriophorum* and any additional vascular plant species and mosses were estimated (on the 2–5 August). To simplify the estimation we used a frame with 16 subdivisions and determined the basal cover of the species in each of these subdivisions.

As a measure of the environmental conditions we, simultaneous to each flux measurement and in close proximity to each plot replicate, determined the water-table depth (WtD, cm below moss surface) and the active layer thickness (AL, cm below moss surface), soil temperature at 10 cm (T_s) and photosynthetically active radiation (PAR). PAR was continuously measured with a hemispherical JYP-1000 sensor (10 min averages).

2.2. Pore water sampling and LMWOC analysis

The pore water concentration of labile LMWOCs, i.e., OAs, AAs and CHs, was determined immediately after gas flux measurements in set-up[1]. Pore water samples were drawn from the permanently installed stainless steel tubes, situated within the circular Al-bases, using a syringe. At every sampling occasion 2 ml of pore water was gently drawn from the tube and discarded. Subsequently 5 ml of sample was drawn and immediately filtered through a sterile pre-rinsed filter (Acrodisc PF 0.8 μm/0.2 μm) into vials and frozen to await analysis.

The water was analysed for OAs, AAs and CHs using liquid chromatography-ionspray tandem mass spectrometry. The instrumental set-up consisted of a Dionex ICS-2500 liquid chromatography (LC) system directly coupled to an Applied Biosystems 2000 Q-Trap triple quadrupole mass spectrometer (MS).

The LC system was especially equipped to meet the separation requirements of each of the three compound groups. LC separation of OAs was performed using the Dionex IonPac AS11 analytical column, AG11 guard column and the anion self regenerating (ASRS) Ultra suppressor column to de-salt the mobile phase (NaOH gradient from 1 to 60 mM over 8 min) before the MS analysis. LC separation of CHs were performed using the Dionex CarboPac PA20

analytical column, AminoTrap guard column to remove amino acids from the carbohydrate analysis and the ASRS-Ultra suppressor column to de-salt the mobile phase (NaOH gradient from 4 to 80 mM over 20 min). LC separation of AAs was performed using a Sielc Primesep 200 analytical column and a mobile phase of 30% acetonitrile and 70% deionised H_2O combined with a gradient of trifluoroacetic acid (0.05−0.30% over 6 min).

The MS was operated in positive ion mode for AA and in negative ion mode for OA and CH analysis. Nitrogen was used as curtain and collision gas. The general MS conditions were as follows: nebulizer gas = 45 psi, curtain gas = 15 psi, heater gas = 45 psi, heater temperature = 550 °C, collision gas = 5 psi and ionspray voltage = 4500/−4500 (depending on mode). Declustering potential, entrance potential, collision energy and collision cell exit potential was individually set for each compound to maximize the signal output. For tandem MS analysis the protonated molecule $[M+H]^+$ (AA analysis) and the deprotonated molecule $[M-H]^-$ (OA and CH analysis) was used as the parent ion and the ion transitions was chosen to maximize the signal output. Combined the LC separation and MS analysis resulted in a complete separation of all compounds, except the AAs Leu and Ile that have identical element compositions and molecular weights.

2.3. Flux measurements

The fluxes of CO_2 and CH_4 were determined using a closed chamber technique (Christensen et al., 2000; Ström and Christensen, 2007). On set-up[1] fluxes were measured at 2−4 day intervals from the onset of vascular plant development the 25th of June, throughout the peak of the growing season, until the 2nd of August. Measurements were distributed so that an individual plot was measured at a variety of different times of day (between 10 am and 6 pm) over the season. The chamber was a transparent 2.2 l poly propylene jar fitted with a rubber list at the base, to ensure an airtight seal against the Al-base. Immediately before the start of a measurement the chamber was carefully placed on the base to avoid disturbance. The change in gas concentration was recorded continuously for 3 min. Air from the chamber was passed through tubing (total additional volume 0.41 l) to the analytical box and after the non-destructive gas analysis back to the chamber. Due to the small chamber volume the continuous flow through the chamber was enough to ensure proper mixing of the gases. The analytical box contained a CH_4 analyser (DLT200, Fast Methane Analyser, Los Gatos Research) and a CO_2 analyser (infrared gas analyser, EGM-4, PP-systems, Hitchin, Hertfordshire, UK). CH_4 and NEE was measured with the transparent chamber and R_{eco} was thereafter measured by covering the chamber with a lightproof hood. GPP was calculated as the difference between NEE and R_{eco}.

In the 15 mixed fen plots in set-up[2] measurements were performed on four occasions at the peak of the growing season (5−18 of July) as described above with a few exceptions. The chamber was a transparent quadratic Plexiglas cube (0.101 m^3) with aluminium corners. The intake and outlet of gas was located at one of the sides 0.15 m and 0.25 m above ground, respectively. To ensure proper mixing of the air and representative sampling from the entire chamber two small fans were located at opposite sides in the upper part of the chamber.

2.4. Data treatment

Flux values were calculated, using a linear fitting, according to standard procedures for closed chamber measurements (e.g., Crill et al., 1988) and compiled as mg CO_2 or CH_4 m^{-2} h^{-1}. Negative fluxes denote an uptake of the gas from the atmosphere and positive a release from the ecosystem.

A general linear model repeated-measures analysis was used to test for differences between the species groups over the season with respect to: gas fluxes, pore water concentrations of total OA, AA and CH carbon in the pore water. Repeated-measures require gap-filling if any data is missing. Gap-filling was done by computing a mean of the two measurements taken, on that particular plot, before and after ($n = 2$) the missing data point. In total we did 210 individual plot measurements and out of these gap-filling was required on 3, 6 and 7% of the data for CH_4, NEE and R_{eco} respectively. No gap-filling was required for LMWOCs. A t-test was used to test for differences between the species groups in measured variables at the end of the season. The data was log-transformed before analysis to meet the requirements of normal distribution and equal variance. A bivariate correlation (Pearson correlation, 2-tailed test for significance) analysis was performed to determine which of the measured variables that was the best predictors of the observed gas fluxes. On set-up[1] the correlations were performed on the seasonal average of each plot ($n = 15$) and on biomass harvested ($n = 15$) in the plots in the end of the season. On set-up[2] the correlations were performed on the mean peak of the growing season flux ($n = 15$) and the percentages of basal cover of vegetation in each plot. To meet the requirement of a linear relationship the data used was log-transformed or un-transformed depending on best fit.

As more than one variable influence greenhouse gas production and fluxes in additive and/or multiplicative manners we performed a multiple regression analysis aiming to elucidate variables of particular importance. The analyses performed were step-wise regressions where a low tolerance and a variance inflation factor (VIF) greater than 5 was used to indicate potential multicolinearity problems (Rogerson, 2001). The analyses were performed on set-up[1] data on variables that correlated significantly in the bivariate correlation of seasonal means (Table 2) and to test for explanatory variables to seasonal trends.

All statistical analyses were done using SPSS 17.0 for Windows. Results of the statistics were regarded as significant if p-values were lower than 0.05.

3. Results

3.1. Miscellaneous

The seasonal mean fluxes, measured environmental variables and biomass harvested at the end of the season can be seen in Table 1.

Table 1
The seasonal mean of the ecosystem parameters measured in an arctic fen in NE Greenland on plots with low- (0−23%) and high-*Eriophorum scheuchzeri* (43−77%) coverage. Measured parameters were; gas fluxes (possitive values represents loss of C from the ecosystem to the atmosphere) of CO_2 (mg CO_2 m^{-2} h^{-1}) of net ecosystem exchange (NEE), ecosystem dark respiration (R_{eco}) and gross primary production (GPP) and CH_4 (mg CH_4 m^{-2} h^{-1}), soil temperature (T_s) at 10 cm (°C), water-table (WtD) and active layer (AL) depth (cm below peat surface) and plot biomass (g dry weight). Different letters indicate significant differences between the low and high plots in the seasonal mean at the 0.05 level.

	Low-*Erioph.*	High-*Erioph.*
CH_4 flux	5.44 ± 0.54 a	11.40 ± 2.59 b
NEE	−409 ± 38	−546 ± 105
R_{eco}	452 ± 20 a	612 ± 74 b
GPP	−860 ± 55	−1156 ± 164
T_s	7.41 ± 0.18	7.64 ± 0.30
WtD	−5.78 ± 0.29	−6.50 ± 0.39
AL	35.6 ± 0.8	36.9 ± 1.3
Biomass		
Carex	0.356 ± 0.05	0.206 ± 0.10
Dupontia	0.402 ± 0.08	0.291 ± 0.08
Erioph.	0.105 ± 0.02 a	0.632 ± 0.15 b
Total	0.791 ± 0.07	1.129 ± 0.28

Table 2
The seasonal mean pore water concentrations (µg C l^{-1}) of low molecular weight carbon compounds, i.e., organic acids (OA), amino acids (AA) and carbohydrates (CH), measured in an arctic fen in NE Greenland on plots with low- (0–23%) and high-*Eriophorum scheuchzeri* (43–77%) coverage. Different letters indicate significant differences between the low and high plots in the seasonal mean at the 0.05 level.

		Low-*Erioph.*	High-*Erioph.*
OA	Tartaric	6.76 ± 0.003	6.78 ± 0.017
	Succinic	1.66 ± 0.166 a	2.62 ± 0.329 b
	Oxalic	38.8 ± 0.636	40.4 ± 0.705
	Malic	8.33 ± 0.088	9.48 ± 1.04
	Lactic	53.1 ± 2.85	64.4 ± 6.90
	Glycolic	3.38 ± 0.256	3.08 ± 0.551
	Formic	15.5 ± 2.36 a	37.1 ± 7.30 b
	Citric	3.78 ± 0.030	3.89 ± 0.119
	Acetic	754 ± 76.5 a	1351 ± 194 b
	Total	*885 ± 77.9 a*	*1519 ± 195 b*
CH	Fructose	59.3 ± 6.12	57.4 ± 10.9
	Galactose	3.74 ± 0.846	3.20 ± 0.841
	Glucose	58.8 ± 6.38	53.8 ± 8.17
	Mannitol	3.38 ± 0.290	3.91 ± 0.508
	Sucrose	39.9 ± 3.60	49.9 ± 4.03
	Total	*165 ± 16.0*	*168 ± 20.7*
AA	Ala	7.43 ± 0.984	7.17 ± 0.698
	Arg	0.176 ± 0.039	0.272 ± 0.066
	Asn	96.1 ± 2.97	95.4 ± 5.90
	Asp	6.20 ± 0.555	7.28 ± 0.649
	Gln	0.782 ± 0.095 a	1.41 ± 0.258 b
	Glu	4.02 ± 0.260	5.17 ± 1.09
	Gly	0.231 ± 0.231	0.709 ± 0.341
	His	0.566 ± 0.098	0.612 ± 0.146
	Leu, Ile	1.77 ± 0.247	2.14 ± 0.233
	Lys	1.01 ± 0.121	1.14 ± 0.113
	Met	0.009 ± 0.009	0.030 ± 0.030
	Pro	0.898 ± 0.219	1.20 ± 0.203
	Ser	0.927 ± 0.927	1.27 ± 1.27
	Thr	0.268 ± 0.268	0.706 ± 0.328
	Tyr	0.281 ± 0.186	0.434 ± 0.176
	Val	0.145 ± 0.036	0.255 ± 0.070
	Total	*121 ± 4.90*	*125 ± 4.12*

The biomass harvest established that the distribution of plots in set-up[1] had resulted in two groups with significantly different *Eriophorum* biomass (*t*-test, $p = 0.0001$), containing 0–26% ($n = 10$) and 43–77% ($n = 5$) *Eriophorum* respectively, from now on referred to as low- and high-*Eriophorum*. The uneven replicate distribution was due to an initial attempt to get separate *Carex* and *Dupontia* groups. However, after vegetation development no significant difference between these plots in biomass of *Dupontia* and *Carex* was found and they were instead treated as a group with low-*Eriophorum* coverage.

The details of the measured environmental variables in set-up[1] and their fluctuations over the season can be seen in Fig. 1. As expected we found very little variation in environmental conditions between the low- and high-*Eriophorum* plots as these on purpose was positioned in a uniform area. Neither, did any of the environmental variables explain the %-cover of any of the species in this area. Additionally, all measured environmental variables were to some extent dependent of each other and consequently significantly correlated; T_s–WtD ($R = -0.39$, $p = 0.010$), T_s–AL ($R = -0.33$, $p = 0.031$), T_s–PAR ($R = 0.50$, $p = 0.001$), WtD–AL ($R = 0.69$, $p \leq 0.001$), WtD–PAR ($R = -0.47$, $p = 0.002$) and AL–PAR ($R = -0.41$, $p = 0.007$). Air temperature (not presented in Fig. 1) varied between 2.9 and 14.5 °C, with an average of 8.5 °C, and was highly correlated to T_s ($R = 0.82$, $p = 0.0001$).

The mixture of the three dominating sedges in the 15 mixed fen plots in set-up[2], ranged between 0 and 34% *Carex*, 19–86% *Dupontia* and 3–51% *Eriophorum*, indicating a slight dominance of *Dupontia* in the continuous fen ecosystem. At this larger community level species distribution seemed to be affected by WtD with a high correlation between *Eriophorum* coverage and WtD ($R = 0.75$, $p = 0.001$). In addition, there was a correlation between AL depth and *Eriophorum* coverage ($R = 0.62$, $p = 0.013$).

3.2. Pore water chemistry

The details and seasonal fluctuations in pore water concentrations of OAs, AAs and CHs measured in the plots of set-up[1] can be

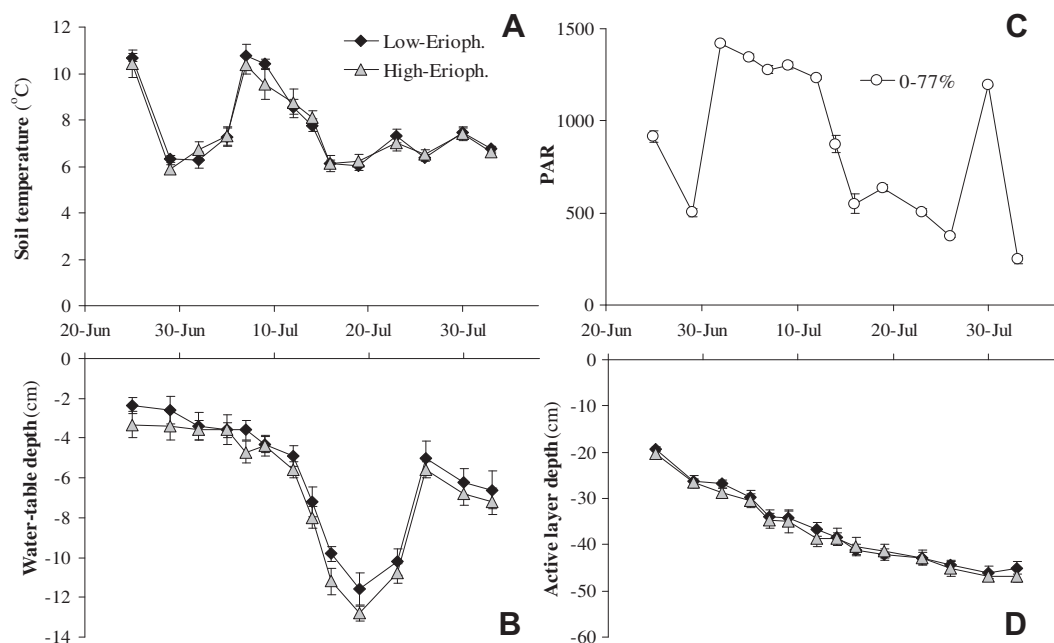
Fig. 1. The growing season environmental conditions in an Arctic fen in NE Greenland measured on plots with low- and high-*Eriophorum scheuchzeri* coverage. Panels show; A) soil temperature at 10 cm below the peat surface, B) water-table depth (cm below peat surface), C) photosynthetically active radiation (PAR, µmol m^{-2} s^{-1}) and D) active layer thickness (cm below peat surface).

seen in Fig. 2 (mg C l^{-1} pore water). The seasonal average concentrations of individual compounds can be seen in Table 2 (μg C l^{-1} pore water).

Of the analysed low molecular weight carbon compounds OAs dominated, constituting between 75 and 83% of the total pore water pool of OAs, CHs and AAs.

The concentration of OAs was affected by *Eriophorum* coverage with between 1.1 and 3.3 times higher concentrations in high- than in low-*Eriophorum* plots (Fig. 2A, repeated-measures analysis, $p = 0.003$). The difference was mainly due to a difference in acetic acid concentration (repeated-measures analysis, $p = 0.005$), since acetic acid completely dominated the OAs pool, constituting between 85 and 89% of the OA fraction. Additionally, there was a higher concentration of formic ($p = 0.003$) and succinic ($p = 0.012$) acid, which both accounted for a minor part of the OA fraction (1.6–2.4% formic and <1% succinic), in high- than low-*Eriophorum* plots. Other OAs present in the pore water (no difference between the groups) was lactic (4.2–6.4%), oxalic (2.6–4.5%) and malic, tartaric, citric and glycolic acid, which all occurred in concentrations below 1% of the total (Table 2). It should be noted

that we consistently use the term acid although the prevailing form may well be the anionic form. As an example acetic acid (CH_3-COOH) has a pKa of 4.75 (Weast, 1989) and would mainly be in anionic form (CH_3-COO^-, acetate) in the pH 6.9 pore water.

In contrast to OA no effect of *Eriophorum* coverage on CH or AA concentrations was found. Neither was any clear seasonal patterns found (Fig. 2B and C). The CH pool was dominated by fructose (37–43%), glucose (30–32%) and sucrose (23–27%) with some occurrence of galactose and mannitol (1–2%) (Table 2). The AA pool included all the common proteinogenic amino acids (except cysteine and phenylalanine), i.e., Alanine (Ala), Arginine (Arg), Aspartic acid (Asp), Asparagine (Asn), Glutamic acid (Glu), Glutamine (Gln), Glycine (Gly), Histidine (His), Isoleucine (Ile)/Leucine (Leu), Lysine (Lys), Methionine (Met), Proline (Pro), Serine (Ser), Threonine (Thr), Tryptophan (Trp), Tyrosine (Tyr), Valine (Val). The AA pool was strongly dominated by Asn (72–82%) followed by Ala (6%), Asp (5–6%) and Glu (3–4%). The reminder of the found AAs was present in the samples at concentrations < 3% (Table 2).

3.3. CH_4 and CO_2 fluxes

The details and seasonal fluctuations in CH_4 and CO_2 fluxes in set-up[1] can be seen in Fig. 3. The relationship between fluxes and *Eriophorum* coverage in the mixed fen plots in set-up[2] in Fig. 4.

Throughout the season the CH_4 flux in set-up[1] was affected by *Eriophorum* coverage with between 1.2 and 2.9 times higher fluxes from high- than from low-*Eriophorum* plots (Fig. 3A, repeated-measures analysis, $p = 0.007$). The effect of species composition on CH_4 fluxes was also reflected in a high correlation between peak season CH_4 flux from the mixed fen plots in set-up[2] and basal coverage of *Eriophorum* (Fig. 4A, $R = 0.87$, $p = 0.0001$) in the respective plots.

For the main part of the season R_{eco} was affected by *Eriophorum* coverage with between 1.0 and 1.8 higher R_{eco} from high- than from low-*Eriophorum* plots in set-up[1] (Fig. 3C, repeated-measures analysis, $p = 0.017$). The effect of species composition was also for R_{eco} reflected in a correlation between peak season R_{eco} in the mixed fen plots in set-up[2] and *Eriophorum* coverage (Fig. 4B, $R = 0.63$, $p = 0.012$).

Neither GPP or NEE was significantly affected by *Eriophorum* coverage in set-up[1], although nearly significant for GPP (Fig. 3B and D, repeated-measures analysis, GPP $p = 0.070$ and NEE $p = 0.208$). This was reflected in a lack of correlations between NEE or GPP and *Eriophorum* coverage in the mixed fen plots in set-up[2] (Fig. 4C, NEE not presented).

3.4. Controls of gas fluxes and pore water chemistry

The results of the correlation analysis performed to determine which of the variables measured in set-up[1] that was the best predictors of the observed gas fluxes and pore water chemistry can be seen in Table 3.

The mean seasonal CH_4 emission was correlated to substrate availability, i.e., the concentration of OAs in pore water. Further, significant correlations were found between CH_4 emission and GPP, NEE, R_{eco} and plant biomass (Table 3). No correlations between the seasonal mean CH_4 emissions and WtD, T_s or AL were found. Further, no correlations were found between the mean seasonal CH_4 emissions and the concentrations of CHs or AAs in pore water (Table 3). The primary explanatory variables for the mean seasonal CH_4 emission singled out by the step-wise multiple regressions analysis were: (1) GPP ($R = 0.81$, $p = 0.0002$) and (2) GPP and OA concentration in pore water ($R = 0.94$, $p \leq 0.0001$). All other variables correlated to CH_4 emission in Table 3 had to be removed due to a VIF factor > 5 and an indication of a multicolinearity problem.
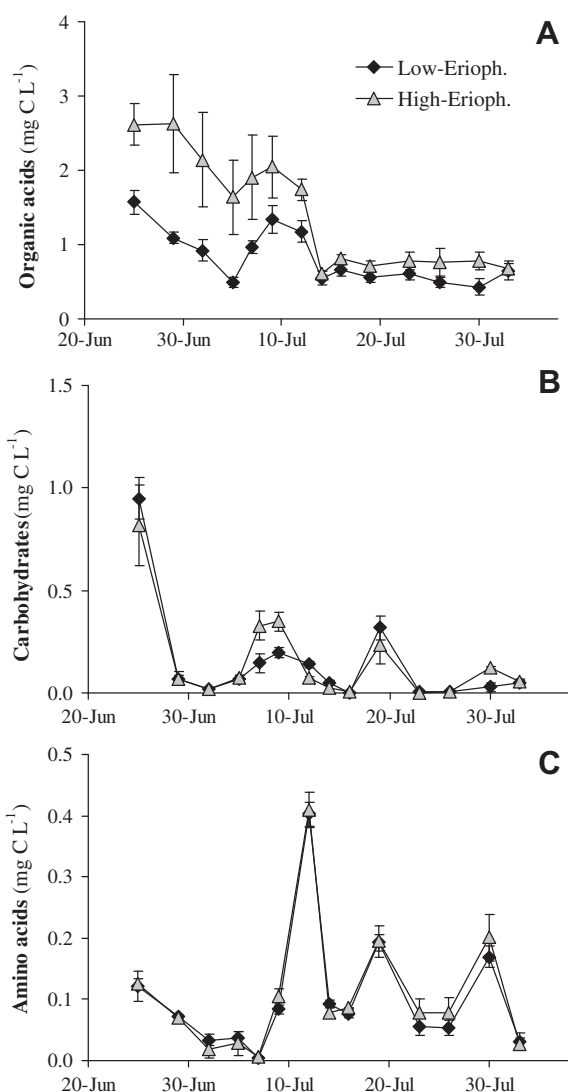

Fig. 2. The growing season concentration of low molecular weight carbon compounds in the pore water of an Arctic fen in NE Greenland measured in plots with low- and high-*Eriophorum scheuchzeri* coverage. Panels show; A) organic acids, B) carbohydrates and, C) amino acids.
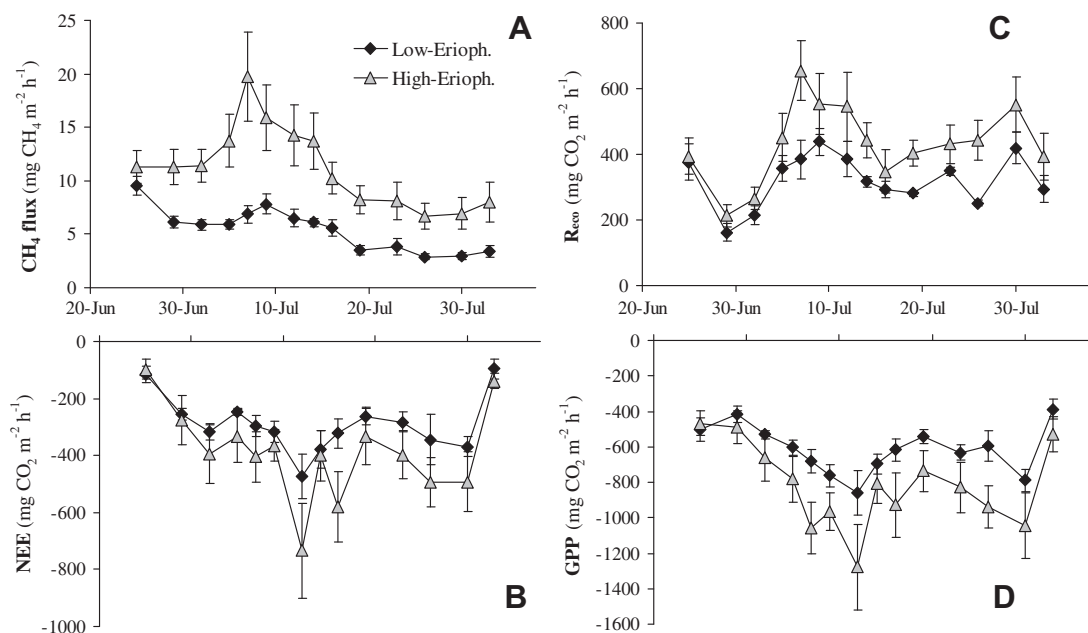
Fig. 3. The growing season fluxes of CH_4 (mg CH_4 m^{-2} h^{-1} ± SE, $n = 15$) and CO_2 (mg CO_2 m^{-2} h^{-1} ± SE, $n = 15$) from an Arctic fen in NE Greenland measured on plots with low- and high-*Eriophorum scheuchzeri* coverage. Panels show; A) CH_4 flux, B) net ecosystem exchange (NEE), C) ecosystem dark respiration (R_{eco}) and D) gross primary production (GPP). Positive values represent loss of C from the ecosystem to the atmosphere.

The mean seasonal CO_2 fluxes, i.e., NEE, R_{eco} and GPP, were all correlated to each other as well as to *Eriophorum* biomass and total plant biomass (Table 3).

The mean seasonal concentration of OAs was correlated only to *Eriophorum* biomass. No significant correlations between CH and AA concentration and any of the measured variables were found (Table 3).

There was a high temporal correlation between the seasonal trends in low- and high-*Eriophorum* plots for all measured variables, i.e., CH_4 flux ($R = 0.72$, $p = 0.004$), NEE ($R = 0.92$, $p < 0.0001$), GPP ($R = 0.91$, $p < 0.0001$), R_{eco} ($R = 0.85$, $p < 0.0001$), T_s ($R = 0.98$, $p < 0.0001$), WtD ($R = 0.99$, $p < 0.0001$), AL ($R = 0.99$, $p < 0.0001$). In order to use step-wise regressions to explain the seasonal trends independent data is required. Most of the measured environmental variables were correlated to each other and consequently not independent, i.e., T_s–WtD ($R = -0.39$, $p = 0.010$), T_s–AL ($R = -0.33$, $p = 0.031$), T_s–PAR ($R = 0.50$, $p = 0.001$), WtD–AL ($R = 0.69$, $p \leq 0.001$), WtD–PAR ($R = -0.47$, $p = 0.002$) and AL–PAR ($R = -0.41$, $p = 0.007$). Due to the problems with colinearity only the factor best explaining the seasonal variation in a variable is presented below. The seasonal trend in CH_4 emission was primarily explained by the OA concentration in pore water ($R = 0.70$, $p = 0.001$), the trend in GPP and NEE by AA concentration (GPP, $R = -0.46$, $p = 0.014$ and NEE, $R = -0.50$, $p = 0.007$) and the trend in R_{eco} by T_s ($R = 0.56$, $p = 0.002$). The seasonal trends in pore-water LMWOC was explained by, i.e., for OAs–WtD ($R = 0.51$, $p = 0.001$), for AAs–GPP ($R = 0.46$, $p = 0.014$) and for CHs–T_s ($R = 0.64$, $p = 0.001$).

4. Discussion

4.1. LMWOCs in pore water

The primary aim of this study was to investigate the concentrations of LMWOC, i.e., OAs, AAs and simple CHs, in the pore water. These compounds generally account for less than 10% of the dissolved organic matter (DOC) in soil but are highly bioavailable and highly influential on the carbon biogeochemistry and on nutrient

cycling in soils (Fischer et al., 2007). In Ström et al. (2003) we determined the concentration of DOC in the fen pore water to 24 mg C l^{-1}. If we assume that DOC has remained rather constant in subsequent years the LMWOCs in the current study would account for 4.5, 0.5 and 1.0% for OAs, AAs and CHs respectively.

Fermentative microbes in the soil produce a range of organic acids, including acetic, lactic, formic, and propionic acid, from plant residues (Gounou et al., 2010; Charlatchka and Cambier, 2000). We found that the concentration of both formic and acetic acid was significantly higher in high-*Eriophorum* than in low-*Eriophorum* plots (Table 2). Further, the mean seasonal concentration of OAs was correlated only to *Eriophorum* biomass indicating the importance of *Eriophorum* per se and not biomass in general for the production OA in the root zone (Fig. 2, Table 3), see more detailed discussion below. In wetlands acetic acid is a substrate of major importance for the methanogens (Ström and Christensen, 2007; Ström et al., 2003, 2005; Avery et al., 1999; Bellisario et al., 1999; Ferry, 1997; Boone, 1991; Oremland, 1988). In the current study acetic acid–C alone would account for 3.9% of DOC. The concentration of acetic acid–C in the pore water was also very high in comparison to what is generally found in soil solutions of various ecosystems such as temperate and boreal forests, while the concentrations of other LMWOCs was in the same order of magnitude (Giesler et al., 2007; Shen et al., 1996). The LMWOCs concentrations was, however, in the same order of magnitude as those found in the pore water of a subarctic mire in Abisko, i.e., 570–1030, 430–710 and 30–60 µg C l^{-1} pore water for OAs, AAs and CHs respectively (Ström and Christensen, 2007).

The amino acid-N pool contained 16 essential amino acids (Table 2), which have all been previously found in Arctic and tundra soil (Henry and Jefferies, 2002; Kielland, 1995; Sowden et al., 1977). The main source of dissolved free amino acids in ecosystems is probably proteolysis of soil proteins and peptides (Lipson et al., 2001; Raab et al., 1999). Lipson et al. (1999) found a large pulse of amino acids early in the growing season which was probably linked to the turnover of microbial biomass following snowmelt. Furthermore soil proteolytic activity was found to be sensitive to
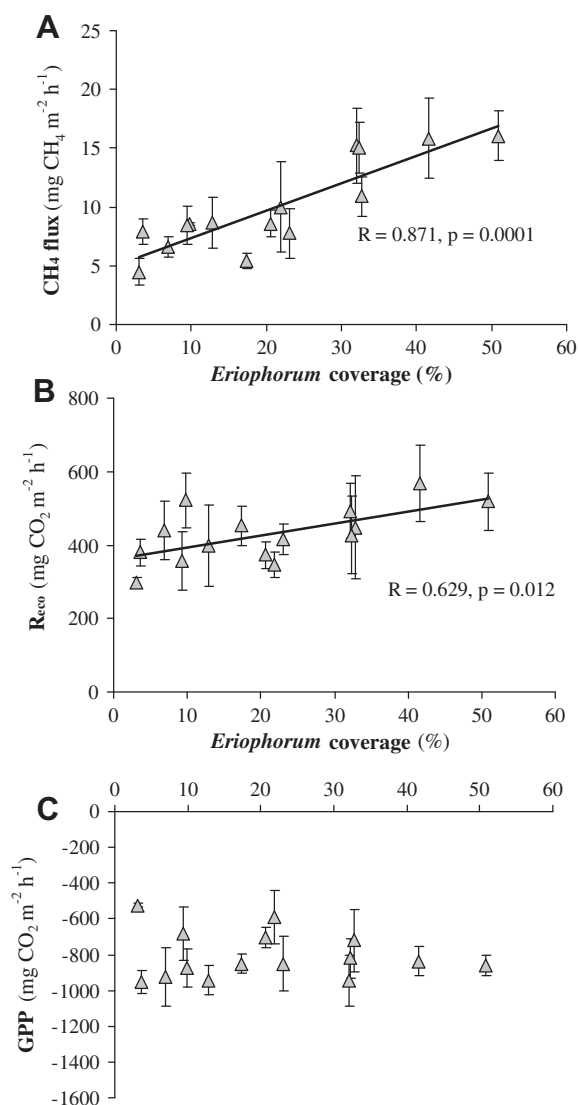
and *E. vaginatum*), can have a strong affect on CH_4 emission (Ström and Christensen, 2007; Ström et al., 2003, 2005). Here we validated these findings in an experiment performed in-situ with minimal between species variation in environmental conditions. The results showed significantly higher emissions from plots dominated by *Eriophorum* than from plots dominated by other species (set-up[1], Table 1, Fig. 3) and a highly significant correlation between *Eriophorum* coverage and CH_4 flux (set-up[2], Fig. 4). No correlations between the seasonal mean CH_4 emissions and WtD, T_s or AL were found in set-up[1] indicating that the differences between high- and low-*Eriophorum* plots were not due to differences in environmental variables (Table 3). A main explanation for the effect of *Eriophorum* on CH_4 fluxes was instead a higher supply of labile substrates (i.e., acetic acid) in the root vicinity of this species (Tables 2 and 3, Fig. 2). Stable isotope techniques have shown that a significant fraction of emitted CH_4 is derived from recently fixed carbon (Chanton et al., 1995) and suggested the importance of the acetate fermentation pathway, which is thought to dominate over CO_2 reduction when fresh organic material is utilized (Chasar et al., 2000; Bellisario et al., 1999). We have previously shown that the concentration of acetic acid in the pore water of the continuous fen in Zackenberg is a good predictor of substrate quality for CH_4 formation and that the potential CH_4 production of the peat profile is highly positively correlated to the acetic acid concentration at the respective depths ($R = 0.97$, $p < 0.001$, Ström et al., 2003). The Ström et al. (2003) study further showed that ^{14}C—acetic acid added to a continuous fen monolith collected at Zackenberg was emitted as $^{14}CH_4$ within 4 h of addition. Consequently, it is reasonable to assume that the ultimate fate of the pore-water OAs (whereof 85−89% is acetic acid) will end up as CH_4 emitted from the ecosystem. However, the question remains whether the observed pore-water concentration of acetic acid (Table 2 and Fig. 4) is enough to support acetoclastic methanogenesis and the observed methane flux (Table 1 and Fig. 3). When acetic acid is degraded by the acetoclastic reaction, the methyl group is reduced to CH_4 while the carboxylic group is oxidized to CO_2 (Boone, 1991), consequently through acetoclastic methanogenesis 1 g of acetic acid−C would only result in ½ g of CH_4−C. To perform a back of the envelope estimation of the acetic acid concentration per m^2 in the fen we used the AL and WtD from Table 1, the pore-water concentration of acetic acid from Table 2 and assumed a water content of the peat of 92% (unpublished data from Ström et al., 2003). This allowed us to roughly estimate the concentration of acetic acid to 21 and 37 mg C m^{-2} for low- and high-*Eriophorum* plots respectively. This indicates that if CH_4 was formed only from acetic acid−C the concentration found in pore water (seasonal mean, Table 2) would correspond to 2−2.5 h of CH_4 flux. Thus, a continuous input of acetic acid would be a requirement to support acetoclastic methanogenesis in the fen. In Ström et al. (2003) we used mini-rhizotrons to determine the root exudation of acetic acid from *D. psilosantha* (4.8 µg C g^{-1} root h^{-1}) and *E. scheuchzeri* (17.3 µg C g^{-1} root h^{-1}). This enables a rough estimation of the continuous input of acetic acid from vascular plants, taken that we know the amount of fine roots at anoxic peat depths. Joabsson and Christensen (2001) determined the amount of roots in the 5−25 cm part of the Zackenberg continuous fen peat to 17 mg roots cm^{-3} (note, a printing error in the unit in Joabsson and Christensen where g roots cm^{-3} should be mg roots cm^{-3}, Ekberg (formerly Joabsson) personal communication). Assuming the same root exudation as in Ström et al. (2003) and taking the species composition in each plot into consideration (and assuming equal exudation from *Carex* and *Dupontia*), the input of acetic acid from root exudation in our plots can be roughly estimated to 16 and 30 mg acetic acid−C m^{-2} h^{-1}, in low- and high-*Eriophorum* plots respectively. A rate of input which would support 1.3 h of CH_4 flux formed through acetoclastic methanogenesis in the high- and 1.5 h

Fig. 4. The growing season fluxes of CH_4 (mg CH_4 m^{-2} h^{-1} ± SE, $n = 15$) and CO_2 (mg CO_2 m^{-2} h^{-1} ± SE, $n = 15$) from an Arctic fen in NE Greenland measured on plots with varying coverage of *Eriophorum scheuchzeri*. Panels show; A) CH_4 flux, B) ecosystem dark respiration (R_{eco}) and C) gross primary production (GPP). Positive values represent loss of C from the ecosystem to the atmosphere.

temperature and increased approximately 4 times over a 20 °C rise in temperature (Lipson et al., 2001). We did not find any clear indications of higher AA concentrations in the beginning of the season (Fig. 2C) neither did we find any clear relationship between T_s and AA concentration. We, however, found a correlation between the seasonal trend in pore water AA concentration and GPP. There is growing evidence for the capacity of plants to take up low molecular organic N (Clemmensen et al., 2008; Svennerstam et al., 2007; Näsholm et al., 1998; Kielland, 1994) such as amino acids, which is often equally abundant as NH_4^+ and NO_3^- in organic soils (Nordin et al., 2004). The correlation between AAs and GPP in the current study may suggests a higher capacity for photosynthesis at times with high AA concentrations or vice versa higher root exudation of amino acids during periods of particularly high photosynthesis.

4.2. Effects of species composition and controls of gas fluxes

We have previously demonstrated that species composition, and in particular *Eriophorum* species (*E. scheuchzeri*, *E. angustifolium*

Table 3

The correlation matrix between the seasonal mean gas fluxes of CO_2 (mg CO_2 m^{-2} h^{-1}) and CH_4 (mg CH_4 m^{-2} h^{-1}), the pore water concentrations of organic compounds (mg C l^{-1}) and the other measured ecosystem properties. Abbreviations denote; for CO_2 fluxes, net ecosystem exchange (NEE), ecosystem dark respiration (R_{eco}) and gross primary production (GPP); for organic compounds, organic acids (OA), amino acids (AA) and carbohydrates (CH); for ecosystem properties, soil temperature (T_s) at 10 cm (°C), water-table (WtD) and active layer (AL) depth (cm below peat surface) and plot biomass (g dry weight). Bold numbers indicate significant correlations, ** correlation significant at the 0.01 level and * correlation significant at the 0.05 level.

	CH_4 flux	NEE	R_{eco}	GPP	OA	AA	CH
CH_4 flux	1						
NEE	**−0.698****	1					
R_{eco}	**0.823****	**−0.752****	1				
GPP	**−0.807****	**0.955****	**−0.911****	1			
OA	**0.684****	−0.154	0.471	−0.302	1		
AA	0.313	−0.097	0.070	−0.075	0.272	1	
CH	0.173	−0.441	0.114	−0.311	−0.167	0.309	1
T_s	0.208	−0.259	0.310	−0.293	−0.003	0.147	0.092
WtD	−0.085	−0.127	−0.278	0.037	−0.297	−0.030	−0.294
AL	0.300	−0.236	0.298	−0.267	0.230	0.143	−0.119
Biomass							
Carex	0.0001	−0.251	−0.272	−0.046	−0.257	−0.307	−0.086
Dupontia	−0.010	−0.421	0.191	−0.356	−0.419	−0.220	0.285
Erioph.	**0.926****	**−0.629***	**0.854****	**−0.776****	**0.700****	0.190	−0.020
Total	**0.783***	**−0.959****	**0.764***	**−0.953****	0.216	0.115	0.401

in the low-*Eriophorum* plots. Subsequently, our results give further support to the proposed importance of certain vascular plant species as suppliers of easily available substrates for the methanogenic bacteria (Ström and Christensen, 2007; Ström et al., 2003; Greenup et al., 2000; Joabsson et al., 1999a; Chanton et al., 1995; Jackson and Caldwell, 1992; Whiting and Chanton, 1992; Van Veen et al., 1989). But clearly points to the importance of a continuous input for acetoclastic methanogenesis to be sustainable.

Positive correlations between plant productivity, i.e., GPP, NEE or net ecosystem productivity (NEP), and CH_4 emissions have been found in several other studies (Ström and Christensen, 2007; Joabsson and Christensen, 2001; Christensen et al., 2000; Joabsson et al., 1999b; Thomas et al., 1996; Waddington et al., 1996; Bubier, 1995; Chanton et al., 1995; Whiting and Chanton, 1992, 1993). The relationship has primarily been attributed to a close linkage between provision of methanogenic substrate and vascular plant production, a connection between plant biomass and CH_4 transport capacity or a combined affect of these (Joabsson et al., 1999a). Our results show a correlation between the mean seasonal GPP and the CH_4 flux at plot level ($R = -0.81$, $p \leq 0.001$, Table 3) and the difference in GPP between low- and high-*Eriophorum* plots (Table 1, Fig. 3) is nearly significant ($p = 0.070$). We, however, see no clear effect of *Eriophorum* coverage on GPP at community level (Fig. 4). It may be argued that the primary driver of *Eriophorum*'s effect on CH_4 emissions is not a higher GPP in this species but rater a different allocation pattern, with more labile carbon allocated below ground. A reasoning that is supported by a very high correlation between CH_4 flux and *Eriophorum* biomass ($R = 0.93$, $p = 0.001$) in set-up[1] and *Eriophorum* coverage in set-up[2] ($R = 0.87$, $p = 0.0001$). A different allocation pattern in *Eriophorum* may in addition to some extent explain the relationship between R_{eco} and *Eriophorum* biomass ($R = 0.85$, $p \leq 0.001$, Table 3 and Fig. 3) and possibly also between R_{eco} and the CH_4 flux ($R = 0.82$, $p \leq 0.001$).

Methane transport through vascular plants is frequently mentioned as one of the major pathways for soil-atmosphere CH_4 fluxes in wetlands (Greenup et al., 2000; Bellisario et al., 1999; Frenzel and Rudolph, 1998; King et al., 1998; Schimel, 1995). In general the increased emissions from vegetated areas have been primarily attributed to plant-mediated transport of CH_4 produced at anoxic peat depths through the aerenchymatous tissue of sedges directly to the atmosphere (King et al., 1998). *Eriophorum* species are often mentioned as being particularly effective transporters of CH_4 (Joabsson and Christensen, 2001; Greenup et al., 2000; Frenzel and Rudolph, 1998; Schimel, 1995). Although hard to verify from the

experimental design of the current study it cannot be excluded that the plant-mediated transport of CH_4 also is higher in *Eriophorum*, adding to the positive effect of this species on CH_4 emissions.

In addition to substrate quality and availability several environmental variables have been identified as controls of methane production and ultimately of net CH_4 emission. These include soil temperature and water-table depth (Ström and Christensen, 2007; Waddington et al., 1996; Torn and Chapin, 1993). To pinpoint the effect of vascular plants on the CH_4 and CO_2 fluxes the low- and high-*Eriophorum* plots in set-up[1] were distributed over a continuous fen area with very little variation between these environmental variables. Consequently, it is not surprising that these traditionally studied variables did not explain any of the variation between the low- and high-*Eriophorum* plots (Table 3). We, however, found indications that environmental variables play a role in explaining some of the observed seasonal trends, i.e., WtD affected the seasonal trend in OA concentration and T_s the trend in R_{eco} and CH concentration in pore water. However, in order to correctly use step-wise regressions and to avoid multicolinearity problems de-trending the data would have been necessary, since most environmental variables were dependent on each other. Several attempts was made to de-trend the material and remove diurnal and seasonal dynamics in CO_2 and CH_4 fluxes, using PAR, soil temperature and water-table and active layer thickness, according to various linear and non-linear methods (e.g., Lund et al., 2009; Lindroth et al., 2007; Saarnio et al., 2003). However, the computations resulted in very low R^2 values and the modelled data could not be used with confidence. Consequently, in all models problems with colinearity occurred when a second explanatory variable was included. The results from the mixed continuous fen plots in set-up[2], however, points to the importance of WtD for CH_4 emission as well as for species composition. At this larger community level, we found very high correlations between WtD and *Eriophorum* coverage ($R = 0.75$, $p = 0.001$) and WtD and CH_4 flux ($R = 0.81$, $p = 0.0001$). It may be concluded that WtD is the main driver of CH_4 fluxes at a community level, e.g., comparing fluxes from continuous fen, hummocky fen and grasslands. While the fluxes from water saturated plots is primarily driven by vascular plant allocation patterns and supply of labile substrate to the root zone (i.e., acetic acid, Table 3).

5. Conclusions

The pool of labile LMWOC compounds in this Arctic fen was dominated by OAs, constituting between 75 and 83% of the total

pore water pool of OAs, CHs and AAs. The dominant OA was acetic acid, an easily available substrate for methanogens, which constituted ≥85% of the OA pool. We estimated that the concentration of acetic acid−C found in pore water would support 2−2.5 h of CH_4 flux and an additional continuous input of acetic acid−C through root exudation that would support 1.3−1.5 h of CH_4 flux. Thus, the results clearly points to the importance of a continuous input for acetoclastic methanogenesis to be sustainable.

Eriophorum had a very strong effect on parts of the carbon cycle in the Arctic fen. The mean seasonal CH_4 flux was twice as high in *Eriophorum* dominated plots, most likely due to a 1.7 times higher concentration of OAs in these plots. Further, the ecosystem respiration was 1.3 times higher in *Eriophorum* dominated plots. These results offer further support to the importance of certain vascular plant species for the carbon cycle of wetland ecosystems.

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