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Differential response of carbon cycling to long-term nutrient input and altered hydrological conditions in a continental Canadian peatland

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Figure S1: View of the study sites 1-4 of the Wylde Lake peatland.

Table S2: Formulas to calculate indices for organic matter quality.

index	formula	reference
UV-vis data		
$SUVA_{254}$ [l m^{-1} mg^{-1}]	$\frac{\text{absorption at 254 nm} * \text{UV} - \text{vis dilution factor}}{\text{cuvette length [m]} * \text{DOC concentration [mg l} - 1] * \text{DOC dilution factor}}$	(Weishaar et al. 2003)
E2:E3	$\frac{\text{absorption at 250 nm}}{\text{absorption at 365 nm}}$	(Peuravuori and Pihlaja 1997)
fluorescence data		
HIX	$\frac{\sum \text{em 435 nm} \rightarrow \text{ em 480 nm at ex 254 nm}}{(\sum \text{em 300 nm} \rightarrow \text{ em 345 nm} + \sum \text{em 435 nm} \rightarrow \text{ em 480 nm) at ex 254 nm}}$	(Ohno 2002)

Table S3: Correlation coefficients (R^2) and p-values for NEP, R_{eco}, GPP, CH_4 flux, T_{water}, wtd and DIC and CH_4 concentrations in 5, 15, 25, 35, 45 and 55 cm soil depth. P-values < 0.05 indicate a statistically significant correlation. "+" and "-" indicate the direction of the correlation.

NEP vs.:	**R_{eco}**	**GPP**	**CH_4**	**CH_4 conc.** 5 cm	15 cm	25 cm	35 cm	45 cm	55 cm	**DIC conc.** 5 cm	15 cm	25 cm	35 cm	45 cm	55 cm	**wtd**	**Twater**
Site 1	n.s	n.s	n.s.	n.s	n.s	n.s	n.s	n.s	n.s	n.s	n.s	n.s	n.s	n.s	n.s	n.s	n.s
Site 2	n.s	n.s	n.s.	n.s	n.s	n.s	n.s	n.s	n.s	n.s	n.s	n.s	n.s	n.s	n.s	n.s	0.20 (0.043) +
Site 3	n.s	n.s	0.20 (0.025) -	n.s	n.s	0.23 (0.024) -	0.17 (0.049) -	0.27 (0.016) -	*0.15 (0.065)* -	n.s	n.s	n.s	n.s	n.s	n.s	0.53 (0.002) -	0.62 (<0.001) +
Site 4	n.s	n.s	n.s.	n.s	n.s	n.s	n.s	n.s	n.s	n.s	n.s	n.s	n.s	n.s	n.s	*0.13 (0.091)* -	0.23 (0.036) +

R_{eco} vs.:	**GPP**	**R_{eco}**	**CH_4 conc.** 5 cm	15 cm	25 cm	35 cm	45 cm	55 cm	**DIC conc.** 5 cm	15 cm	25 cm	35 cm	45 cm	55 cm	**wtd**	**Twater**
Site 1	n.s	0.69 (<0.001) +	0.57 (0.002) -	0.66 (<0.001) -	n.s	0.47 (0.006) -	0.70 (<0.001) -	n.s	0.41 (0.011) -	n.s	n.s	n.s	n.s	n.s	0.60 (0.001) -	0.47 (0.006) +
Site 2	n.s	0.41 (<0.001) +	n.s	n.s	n.s	0.16 (0.057) -	0.26 (0.017) -	0.35 (0.006) -	n.s	n.s	n.s	n.s	n.s	n.s	0.70 (<0.001) -	0.43 (0.002) +
Site 3	n.s	0.60 (<0.001) +	n.s	n.s	0.32 (0.009) -	0.44 (0.002) -	0.56 (<0.001) -	0.42 (0.002) -	n.s	n.s	n.s	n.s	n.s	n.s	0.74 (<0.001) -	0.37 (0.012) +
Site 4	n.s	0.43 (0.001) +	n.s	0.28 (0.021) +	0.47 (0.002) +	n.s	n.s	n.s	n.s	0.31 (0.016) +	0.58 (<0.001) +	0.47 (0.002) +	0.26 (0.027) +	n.s	0.21 (0.043) -	0.60 (0.001) +

GPP vs.:	**CH_4**	**CH_4 conc.** 5 cm	15 cm	25 cm	35 cm	45 cm	55 cm	**DIC conc.** 5 cm	15 cm	25 cm	35 cm	45 cm	55 cm	**wtd**	**Twater**
Site 1	0.7 (0.006) -	0.66 (<0.001) -	0.84 (<0.001) -	*0.22 (0.061)* -	0.39 (0.013) -	0.40 (0.012) -	n.s	n.s	n.s	n.s	n.s	n.s	n.s	0.50 (0.004) -	0.43 (0.009) +
Site 2	0.36 (0.001)	n.s	*0.14 (0.071)*	n.s	*0.16 (0.057)*	0.22 (0.028)	0.26 (0.017)	n.s	n.s	n.s	n.s	n.s	n.s	0.58 (<0.001)	0.52 (<0.001)

	-		-		-	-	-							-	+
Site 3	0.54 (<0.001)	n.s	n.s	0.41 (0.003)	0.44 (0.002)	0.59 (<0.001)	0.40 (0.003)	n.s	n.s	n.s	n.s	n.s	n.s	0.71 (<0.001)	0.55 (<0.001)
	-			-	-	-	-							-	+
Site 4	n.s.	n.s	0.44 (0.003)	*0.16 (0.073)*	n.s	0.29 (0.018)	0.35 (0.010)	n.s	0.26 (0.026)	0.26 (0.026)	*0.14 (0.087)*	n.s	n.s	n.s	0.51 (0.001)
			+	+		-	-		-	-	-				+

-

CH_4 vs.:	**CH_4 conc.**						**DIC conc.**	-	-	-	-	-	**wtd**	**Twater**
	5 cm	**15 cm**	**25 cm**	**35 cm**	**45 cm**	**55 cm**	**5 cm**	**15 cm**	**25 cm**	**35 cm**	**45 cm**	**55 cm**		
Site 1	0.57 (0.002)	0.54 (0.002)	n.s.	0.27 (0.039)	0.59 (0.001)	n.s.	0.421 (0.010)	n.s.	n.s.	n.s.	n.s.	n.s.	0.55 (0.002)	0.62 (<0.001)
	-	-		-	-		-						-	+
Site 2	n.s.	*0.16 (0.059)*	n.s.	0.40 (0.003)	0.50 (<0.001)	0.48 (<0.001)	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	0.38 (0.005)	0.45 (0.002)
		-		-	-	-							-	+
Site 3	n.s.	n.s.	*0.17 (0.050)*	0.33 (0.008)	*0.51 (0.050)*	0.41 (0.002)	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	0.565 (0.001)	0.57 (0.001)
			-	-	-	-							-	+
Site 4	n.s.	*0.14 (0.088)*	0.29 (0.019)	n.s.	n.s.	n.s.	n.s.	0.28 (0.020)	0.55 (<0.001)	0.40 (0.005)	n.s.	n.s.	n.s.	0.23 (0.036)
		+	+					+	+	+				+

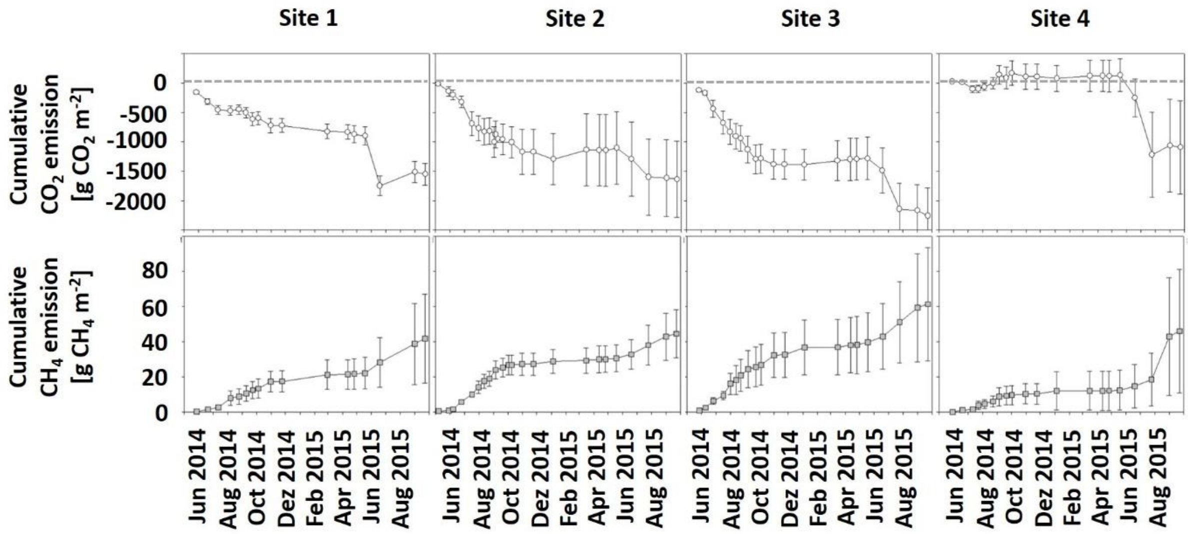

Figure S4: Cumulative fluxes of CO_2 [g CO_2 m^{-2}] and CH_4 [g CH_4 m^{-2}] ± SE during the study period in hollows of the sites 1-4. A negative value for CO_2 indicates a net CO_2 uptake, while positive numbers for CH_4 indicate net emission.

Isotopic signatures of pore-water

To obtain high resolution depth profiles of signatures of CH_4 and DIC in the peat, pore-water peepers of 60 cm length and a 1 cm resolution were inserted on three occasions in June, July and September 2015. Pore-water peepers were filled with distilled water, then covered with a permeable membrane (0.2 µm pore size, OE, 66, Schleicher & Schuell) which was fixed with a perforated Plexiglass cover. For isotope analysis, pore-water samples were extracted from the chambers with 1 ml syringes and a needle and filled into 2 ml GC vials respectively 10 ml crimp vials prefilled with 20 and 100 µL of 4 M HCl. Vials were sealed and shipped to the UMünster Lab in Germany, where rations of $\delta^{13}C$ of CO_2 and CH_4 were determined by Cavity Ringdown Spectroscopy (CRDS; Picarro G2201-*i*, Picarro Inc., Santa Clara, US), as described in the manuscript.
Isotopic signatures of CH_4 and CO_2 in pore-water ranged from -75.81 ± 0.19 to -39.87 ± 0.48 ‰ for CH_4 and from -26.25 ± 1.25 to +1.63 ± 1.06 ‰ for CO_2. Maximum CH_4 and CO_2 values were measured at Site 4 in 7 cm depth in June and at site 3 in 59 cm depth in July respectively. Minimum $\delta^{13}C$ values were measured at site 2 in 55 cm depth in September or in 9 cm depth in July.
Both $\delta^{13}C$-CH_4 and CO_2 signatures showed a temporal trend which was decreasing for CH_4 and increasing for CO_2. This trend was most distinctive at site 4 for CH_4 and overall more distinctive for CH_4 than for CO_2 (see Fig. 4).
$\delta^{13}C$-CH_4 became more depleted with depth while $\delta^{13}C$-CO_2 values got less depleted. Whereas for $\delta^{13}C$-CO_2, this trend was more or less linear with depth, $\delta^{13}C$-CH_4 profiles exhibited a more complex pattern. Profiles at sites 1 and 2 revealed a D-shaped curve. Signatures at sites 3 and 4 revealed an S-shaped curve (see Fig. S6). Average $\delta^{13}C$-CH_4 signatures in 20 to 60 cm depth at site 3 differed significantly from those at sites 2 and 4 in July ($p < 0.05$) with lowest values at site 3 and highest at site 4. In September, signatures became more negative with vicinity to the reservoir shore, but differences were not significant. For mean $\delta^{13}C$-CO_2 signatures, significant differences between the sites 1 and 2 and the sites 3 and 4 were found in July ($p < 0.01$) with the sites 1 and 2 and the sites 3 and 4 not differing amongst themselves. In September, $\delta^{13}C$-CO_2 signatures at site 1 differed significantly from those at the other sites ($p < 0.05$). $\delta^{13}C$-CO_2 values were generally decreasing with distance to the reservoir shore at both sampling dates with average values at site 1 reaching -8.67 ± 2.57 and -6.55 ± 2.16 ‰ compared to values at site 4 that came to -2.92 ± 2.31 respectively -4.78± 4.88 ‰.

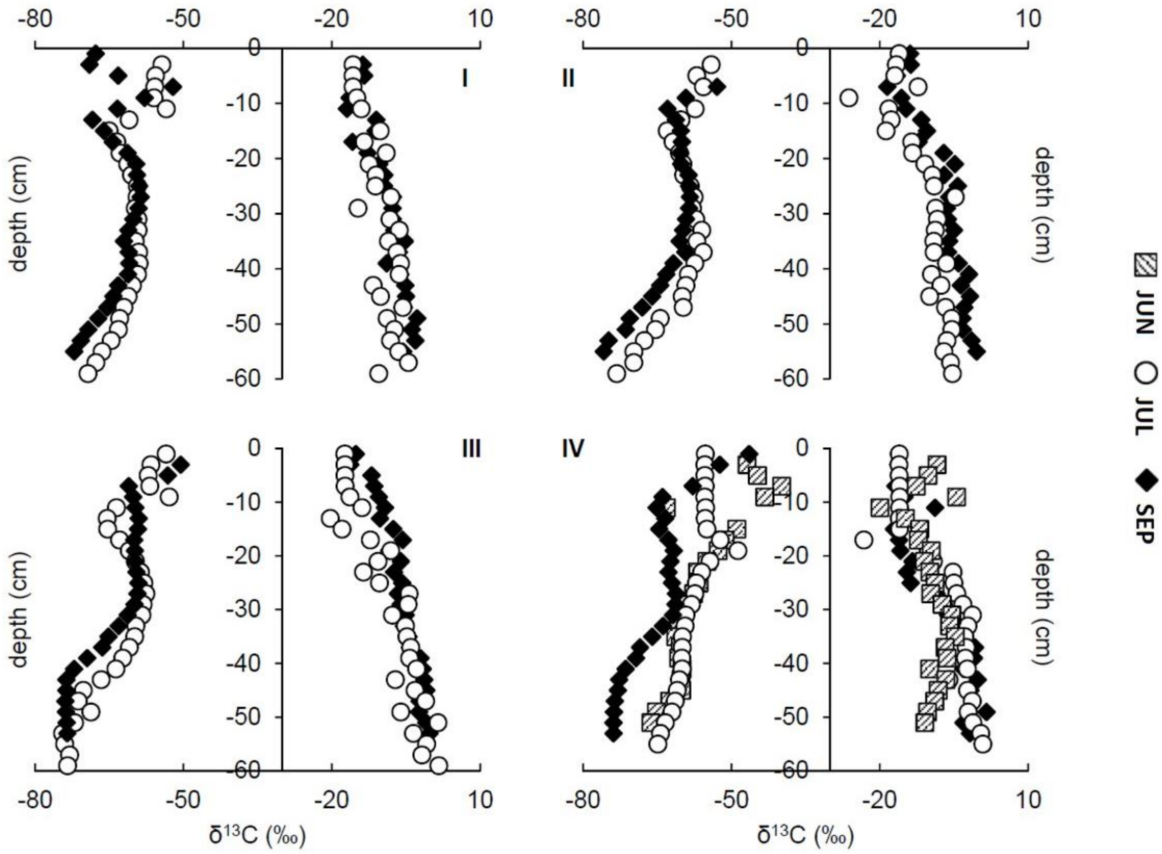

Figure S5: Depth profiles of δ^{13}C-CH_4 (left) and δ^{13}C-CO_2 (right) signatures in the peat at sites 1 to 4 obtained with pore-water peepers. Squares = June (06/17), circles = July (07/23), diamonds = September (09/17).

Table S6: Comparison values for organic matter quality indices of pore water.

soil type	location	value	study
$SUVA_{254}$ [l mg^{-1} m^{-1}]			
bog to fen	Luther Marsh, Ontario, Canada	2.54 (+/- 0) – 3.85 (+/- 0.20)	this study
intermediate, raised and lowered water table site of a poor fen peatland complex	Seney, Michigan, USA	3.36 - 3.88	(Hribljan et al. 2014)
bog, forested wetland and fen	Juneau, Alaska, USA	3.51 - 4.41	(Fellman et al. 2008)
ombrotrophic peatland	north Wales, UK	4.00 (+/- 0.47), (3.44 to 4.77)	(Peacock et al. 2014)
poorly drained thermokarst wetland sites, moderately well drained and well drained sites	central Alaska, USA	4.0 (+/- 0.06)	(Wickland et al. 2007)
north fen	Stordalen peatland complex, Sweden	2.23 (1.33 - 2.95)	(Olefeldt and Roulet 2012)
south fen	Stordalen peatland complex, Sweden	2.16 (1.35 - 3.02)	(Olefeldt and Roulet 2012)
bog	Stordalen peatland complex, Sweden	2.68 (1.44 - 3.82)	(Olefeldt and Roulet 2012)
E2:E3			
bog to fen	Luther Marsh, Ontario, Canada	4.40 (+/- 0.057) - 6.38 (+/- 0)	this study
intermediate, raised and lowered water table site of a poor fen peatland complex	Seney, Michigan, USA	4.49 - 5.51	(Hribljan et al. 2014)
soil type	location	value	study
ombrotrophic peatland	north Wales, UK	3.70 (+/- 0.14) (3.44 - 3.84)	(Peacock et al. 2014)
north fen	Stordalen peatland complex, Sweden	4.70 (4.19 - 5.29)	(Olefeldt and Roulet 2012)
south fen	Stordalen peatland complex, Sweden	4.56 (3.78 - 5.07)	(Olefeldt and Roulet 2012)
bog	Stordalen peatland complex, Sweden	4.88 (3.64 - 6.52)	(Olefeldt and Roulet 2012)
HIX			
bog to fen	Luther Marsh, Ontario, Canada	0.90 (+/- 0.02) – 0.94 (+/- 0.00)	this study

poorly drained thermokarst wetland sites, moderately well drained and well drained sites	central Alaska, USA	0.94 - 0.96	(Wickland et al. 2007)

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