The importance of freshwater systems to the net exchange of atmospheric carbon dioxide and methane with rapidly changing high Arctic landscapes

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Supporting Information

Numerical analysis

We used hierarchical clustering analysis (IBM SPSS Statistics 23) to organize ponds and lakes into similar categories based on concurrent greenhouse gases and chemistry analyses (10 sites; n=62). We used between-group linkage and squared Euclidean distances to group similar sites together and delineate distinct high Arctic freshwater types. We then used linear-mixed models (SPSS) to quantify differences in greenhouse gases concentrations and fluxes between different high Arctic freshwater types. Linear-mixed models are ideal for analysing non-independent, repeated measures data as they integrate inherent errors in repeated sampling designs to more clearly distinguish statistical differences between groups. Linear mixed model details included: use of an auto-regressive moving average (1,1) repeated covariance model; use of a Maximum Likelihood estimation method; and variables organized by freshwater type (fixed) and year (random).

Bottle – Automated system dissolved CO_2 concentration comparison

Though bottle (time-series) and automated system (diurnal) dissolved CO_2 concentrations were not directly compared in this study, the concentrations measured in Pond 01 and Skeleton Lake using each approach were near identical in most cases (Figure S1). In 2008 (Skeleton Lake) and 2009 (Pond 01), however, calibration of the automated systems appeared to have shifted during transit, causing a slight step difference in measured CO_2 concentrations between the two approaches.

Ebullition fluxes

Ebullition can also liberate CO_2 and CH_4 from freshwater systems. We used submerged inverted 30-cm plastic funnels with a bubble collection chamber to quantify ebullition fluxes of CO_2 and CH_4 from the surface of Skeleton Lake and Pond 01. Traps were deployed continuously at both sites during the 2007 and 2008 summers and checked weekly for bubble volume accumulation. Ebullition volume was measured by drawing into a syringe, through a rubber septum in the collection chamber, the accumulated gas. However, we did not measure gas concentrations of this trapped gas because CO_2 and CH_4 can diffuse back into surface waters while sitting in the trap. Instead, fresh bubbles were collected for CO_2 and CH_4 analyses by probing the sediments and collecting them into a hand held bubble trap. Samples were then immediately transferred to evacuated, stoppered 30 ml Wheaton bottles and analyzed for CO_2 and CH_4 concentrations on the GC in a manner similar to that described in the main manuscript for water samples. Bubble CO_2 and CH_4 concentrations were multiplied by bubble volume collected over the weeklong period to determine ebullition fluxes.

Tables

Table S1: Mean weather conditions measured by a polar semidesert eddy covariance/meteorological station about 1 km from base camp during the growing season between 2008 and 2012 in the Lake Hazen watershed.

Month	Air temp. (°C)	Rainfall (mm)	Wind speed (kph)	PAR (μmol m^{-2} s^{-1})	Air pressure (kPa)	Soil moisture (m^3 m^{-3})	Soil temp. (°C)
June	5.0	3.8	2.9	699	99.4	0.16	6.9
July	8.4	19.3	2.9	596	98.8	0.15	12.0
August	5.7	10.5	2.7	384	98.7	0.14	7.4

Table S2 Sampling years and dates for greenhouse gases concentrations collected using bottles (B) or automated systems (AS), and general chemical analyses (C) of several freshwater systems throughout the Lake Hazen watershed.

Water body		2005	2007	2008	2009	2010	2011	2012
Pond 01	B	6-21/7	24/6-21/7	6/7-4/8	29/6-22/7	16/6-20/7	6/7-30/7	-
	AS	-	24/6-21/7	10/7-2/8	29/6-21/7	19/6-5/7	-	-
	C	6-23/7	28/6-18/7	9/7-2/8	2-22/7	28/6-20/7		-
Pond 02	B	6-21/7	8/7	9/7-2/8	-	10-20/7	6/7-30/7	-
	C	6-22/7	6/7	9/7-2/8	-	10-20/7	-	-
Pond 03	B	10/7	13-14/7	29/7	-	12-17/7	6/7-30/7	-
	C	-	14/7	-	-	12-17/7	-	-
Pond 07	B	15/7	9/7	29/7	-	13-18/7	6/7-30/7	-
	C	-	10/7	-	-	13-18/7	-	-
Pond 10	B	15/7	-	-	-	13-18/7	6/7-30/7	-
	C	-	-	-	-	13-18/7	-	-
Pond 11	B	15/7	-	-	-	12-17/7	4/7-30/7	4/7-31/7
	C	-	-	-	-	12-17/7	-	31/7
Pond 12	B	15/7	14-16/7	29/7	-	12-17/7	-	-
	C	-	14/7	-	-	12-17/7	-	-
Pond 16	B	-	-	-	-	13-18/7	6/7-30/7	
	C	-	-	-	-	13-18/7	-	
Skeleton Lake	B	-	25/6-19/7	6/7-3/8	29/6-22/7	18/6-19/7	4/7-30/7	4/7-31/7
	AS	-	-	8/7-3/8	1-21/7	25/6-20/7	-	-
	C	-	14/7	10/7-2/8	2-22/7	28/6-17/7	-	-
Lake Hazen shoreline	B	4-20/7	24/6-21/7	6/7-4/8	29/6-22/7	22/6-20/7	6/7-30/7	-
	C	6-13/7	-	10/7-3/8	2-22/7	28/6-20/7	-	-

Table S3 Empirical relationships for k (cm hr^{-1}; Hamilton *et al.*, 1994) used in the mass flux equation for greenhouse gases samples (Equation 1 in the manuscript).

if $U<3$ m s^{-1}:	$k_{600} = 0.76U$
	$k_{CO2} = k_{600} * (600^{0.67}/SC_{CO2}{}^{0.67})$
	$k_{CH4} = k_{600} * (600^{0.67}/SC_{CO2}{}^{0.67})$
if $U \geq 3$ m s^{-1}:	$k_{600} = 5.6U – 14.14$
	$k_{CO2} = k_{600} * (600^{0.50}/SC_{CO2}{}^{0.50})$
	$k_{CH4} = k_{600} * (600^{0.50}/SC_{CO2}{}^{0.50})$

Notes: U is in-situ wind speed (m s^{-1}) measured at 1 m on automated systems or at a nearby meteorological station; k_{600} (cm hr^{-1}) is the exchange coefficient

Table S4 Pearson correlation coefficients of greenhouse gases and general chemistry of freshwater types in the Lake Hazen watershed during the growing seasons of 2005, 2007-2012. Statistical significance at α=0.05 indicated in **bold (**IBM SPSS Statistics 23).

	CO_2				CH_4			
	Evap.	**Melt.**	**Shore.**	**LH Shore**	**Evap.**	**Melt.**	**Shore.**	**LH Shore**
Air_P	.542	.050	.350	**-.565***	**-.803***	.097	.144	-.429
$Water_T$	.131	-.409	.397	-.308	.258	**-.483***	.266	.187
CO_2	1	1	1	1	-.526	**.630****	**.530***	.418
CH_4	-.526	**.630****	**.530***	.418	1	1	1	1
W_S	-.048	-.066	-.063	**.624***	-.329	-.289	.287	-.276
DIC	.720	.005	**.818****	**.694****	-.724	**-.567***	.387	.291
NH_4^+	.453	.139	**.783****	-.255	-.536	-.183	.409	-.142
$NO_3^-+NO_2^-$	-.314	-.003	.345	**.689****	**.884****	-.120	**.661****	.158
TDN	.285	**-.576***	**.692****	.351	-.341	**-.527***	**.579****	.335
DON	.278	-.467	**.600****	.297	-.333	-.235	**.554****	.236
PN	-.071	-.093	.387	.475	-.001	-.346	-.192	.403
TP	.597	-.132	.033	.346	-.211	.175	-.117	-.118
TDP	**.794***	.014	**.539****	**.616***	-.285	.251	.397	-.025
PC	.669	-.141	.359	**.526***	-.743	-.401	-.146	**.613***
DOC	**.913****	**-.670****	**.462***	-.510	-.622	**-.552***	.396	-.034
Cl^-	.227	.044	**.458***	**.641***	-.680	-.303	.329	.149
SO_4^{2-}	.154	**-.582***	-.291	**.668****	.004	**-.706****	-.027	.282
Na^+	-.315	**-.481***	**.654****	**.715****	-.376	**-.573***	**.474***	.331
K^+	.156	.147	**.793****	**.712****	-.644	-.215	**.467***	.416
Ca^{2+}	.561	-.340	**.587****	**.703****	-.014	**-.824****	.282	.200
Mg^{2+}	.349	-.364	.327	**.718****	-.478	**-.751****	**.448***	.380
Fe	**.974****	**-.575***	**.741****	**--**	-.483	-.029	.278	--
Alkalinity	.746	-.015	**.818****	**.697****	**-.755***	**-.592****	**.487***	.266
HCO_3^-	**.783***	-.015	**.818****	**.698****	-.744	**-.591****	**.487***	.266
CO_3^{2-}	-.472	--	**--**	**--**	-.287	**--**	**--**	--
TDS	.436	-.150	**.439***	-.230	-.251	-.383	.360	.011
Chl-a	-.636	-.317	.277	-.068	.131	-.251	-.076	-.039
pH	**-.854***	-.392	-.169	-.261	.088	**-.512***	-.073	-.175

Evap.: Evaporative ponds; Melt.: Meltwater systems; Shore.: Shoreline ponds; LH Shore: Lake Hazen Shoreline; Air_P: baraometric pressure; $Water_T$: water temperature; dCO_2: dissolved carbon dioxide concentration; dCH_4: dissolved methane concentration; W_S: wind speed; DIC: dissolved inorganic carbon; NH_4^+: ammonium; $NO_3^-+NO_2^-$: nitrate + nitrite; TDN: total dissolved nitrogen; DON: dissolved organic nitrogen; PN: particulate nitrogen, TP: total phosphorus; TDP: total dissolved phosphorus; PC: particulate carbon; DOC: dissolved organic carbon; Cl^-: chloride; SO_4^{2-}: sulphate; Na^+: sodium; K^+: potassium; Ca^{2+}: calcium; Mg^{2+}: magnesium; Fe: total iron; HCO_3^{2-}: bicarbonate; CO_3^{2-}: carbonate; TDS: total dissolved solids; Chl-a: chlorophyll-a; pH: $\log[H^+]$

Table S5 Freshwater ebullition fluxes of carbon dioxide (CO_2) and methane (CH_4) during the growing seasons of 2007 and 2008 in Skeleton Lake and Pond 01 in the Lake Hazen watershed.

Pond/Lake	**Bubble volume (mL)**	**CO_2 Bubble concentration ($mgCO_2\ L^{-1}$)**	**CO_2 Bubble flux ($mgCO_2\ m^{-2}\ d^{-1}$)**	**CH_4 Bubble concentration ($mgCH_4\ L^{-1}$)**	**CH_4 Bubble flux ($mgCH_4\ m^{-2}\ d^{-1}$)**
Pond 01					
30-Jun.-2007	1.76	0.60	0.06±0.01	0.07	0.01±0.00
10-Jul.-2007	2.01	0.33	0.00±0.00	0.09	0.00±0.00
17-Jul.-2007	1.07	18.53	0.13±0.01	60.7	0.43±0.04
23-Jul.-2008	0.20	0.42	0.00±0.00	0.18	0.00±0.00
31-Jul.-2008	1.17	0.53	0.04±0.03	0.52	0.03±0.03
Skeleton L.					
04-Jul.-2007	5.51	0.46	0.01	-	-
10-Jul.-2007	6.53	0.28	0.01±0.00	0.00	0.00±0.00
17-Jul.-2007	5.86	0.29	0.01±0.00	0.05	0.00±0.00
23-Jul.-2008	2.50	0.64	0.09±0.00	0.04	0.01±0.00
31-Jul.-2008	2.00	0.61	0.07±0.06	0.04	0.00±0.00

Figures

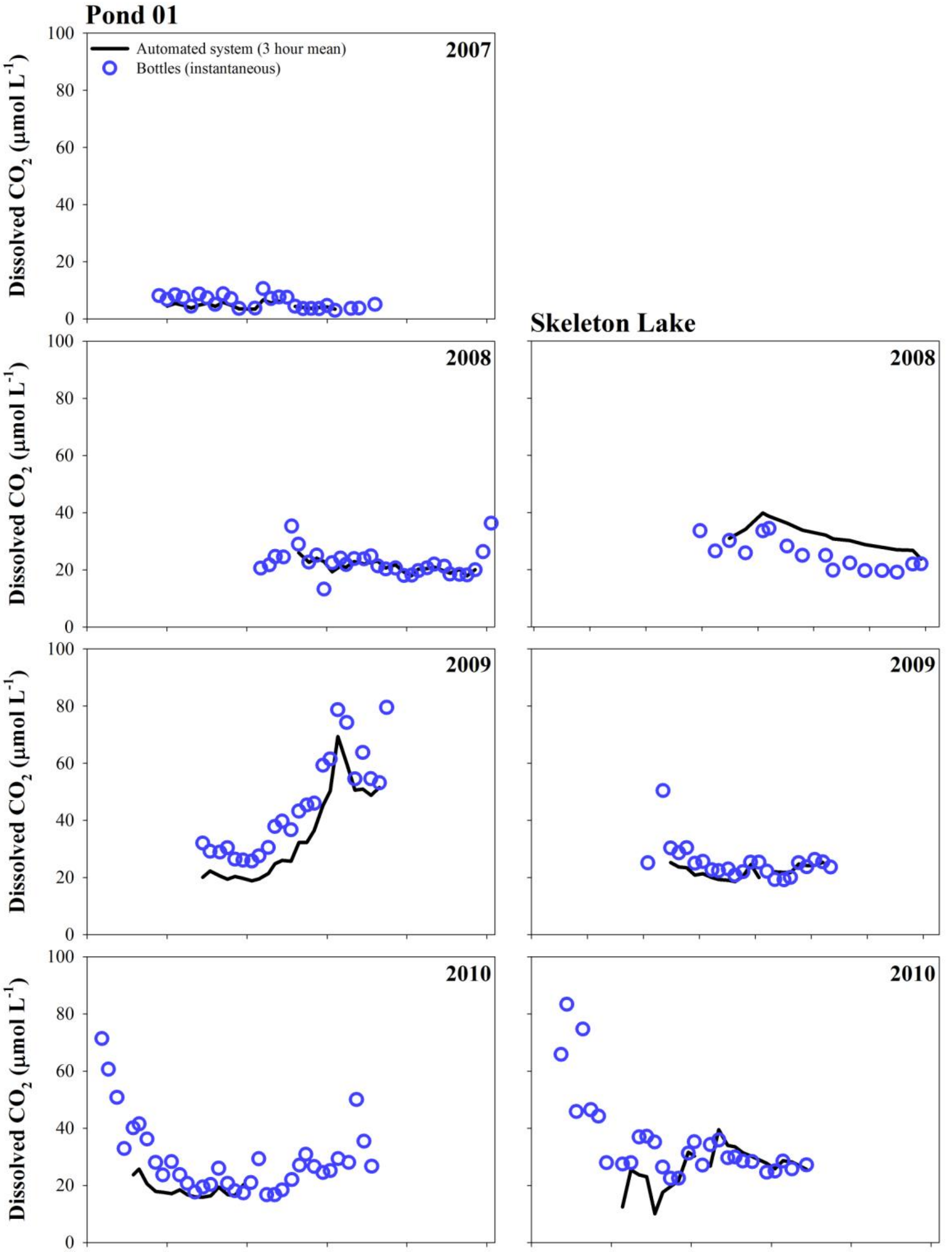

Figure S1 Comparison of dissolved CO_2 concentrations between manually-collected bottle samples and automated systems in Pond 01 and Skeleton Lake during the growing seasons of 2007-2010.

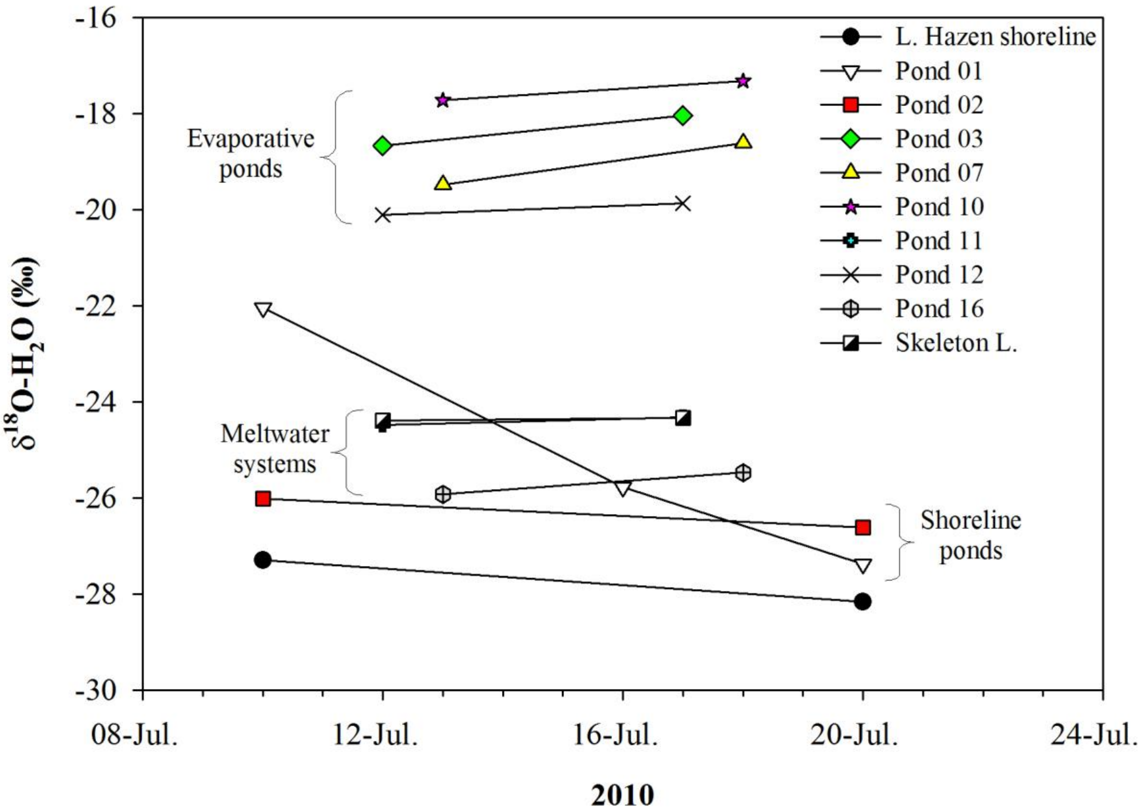

Figure S2 Measurements of stable oxygen isotopic composition of water ($\delta^{18}O\text{-}H_2O$) from ten freshwater systems in the Lake Hazen watershed in July 2010. Grouping of freshwater system types followed those delineated in the hierarchical cluster analyses (see Results and Discussion).

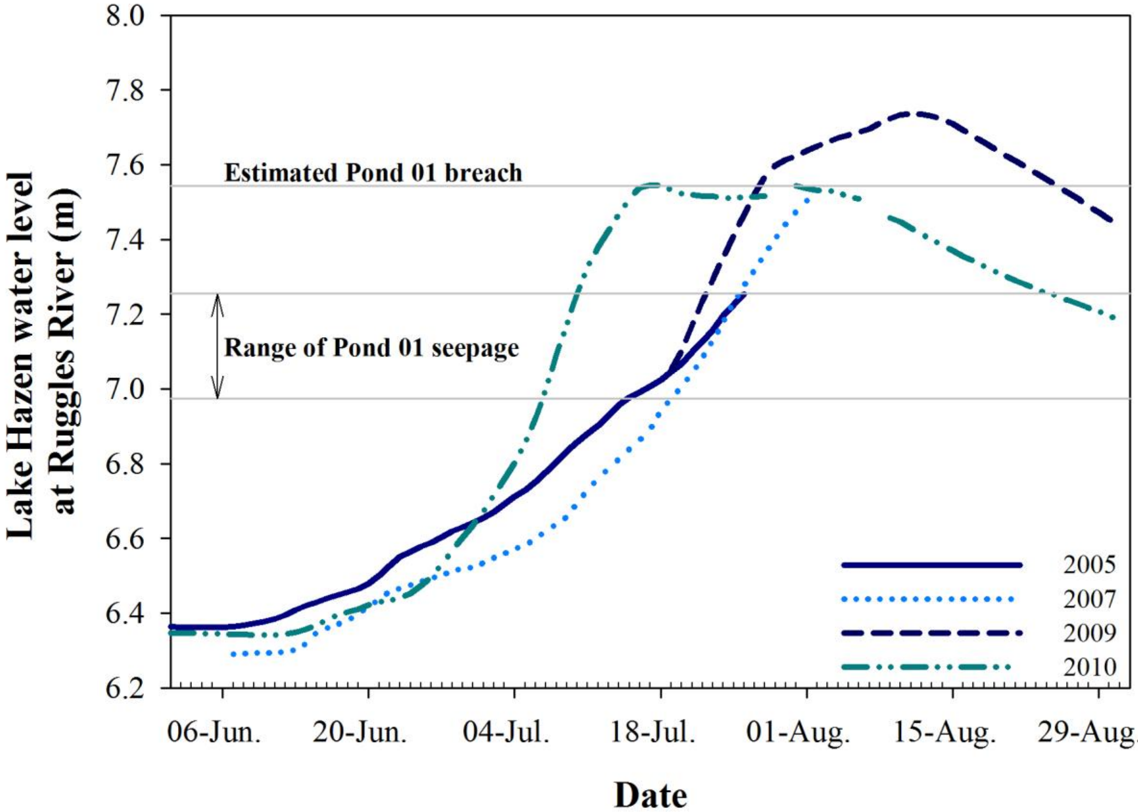

Figure S3 Lake Hazen water level data during the summer growing seasons of 2005, 2007, and 2009-10 at Ruggles River (Water Survey of Canada, 2015). The range of water level when Pond 01 received Lake Hazen seepage water through its gravel berm is indicated and based on rapid changes in greenhouse gases concentrations. Rapid dilution of methane (CH_4) concentrations and field observations were used to determine the water level of pond breach and flushing.

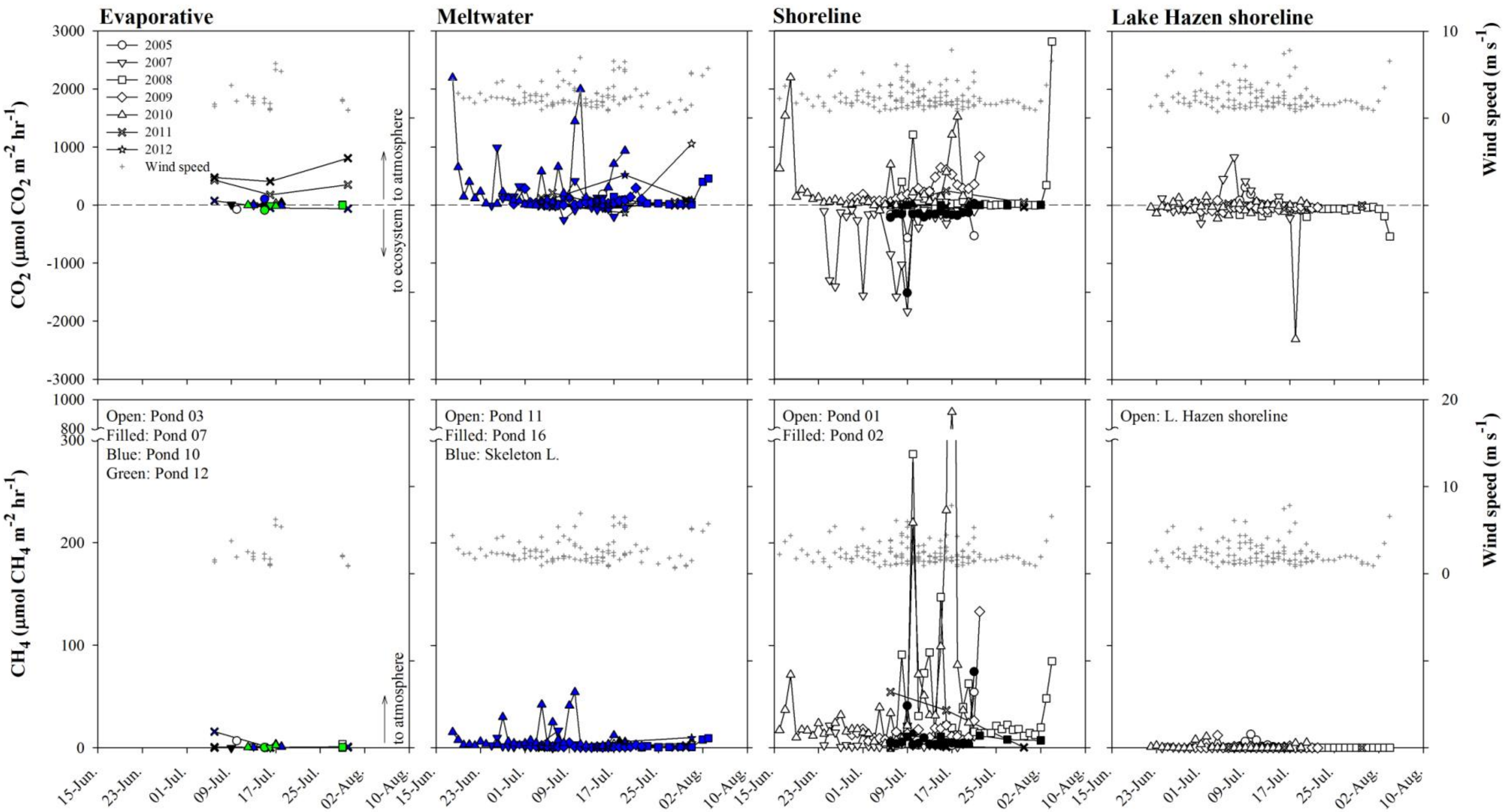

Figure S4 Carbon dioxide (CO_2) and methane (CH_4) fluxes during the 2005, 2007-2012 growing seasons (June-August) from four different freshwater types in the Lake Hazen watershed. Fluxes calculated using empirical equations and site conditions including water temperature, wind speed, barometric pressure and gas concentrations in water (see Methods). Daily wind speed from nearest measurements indicated by grey points.

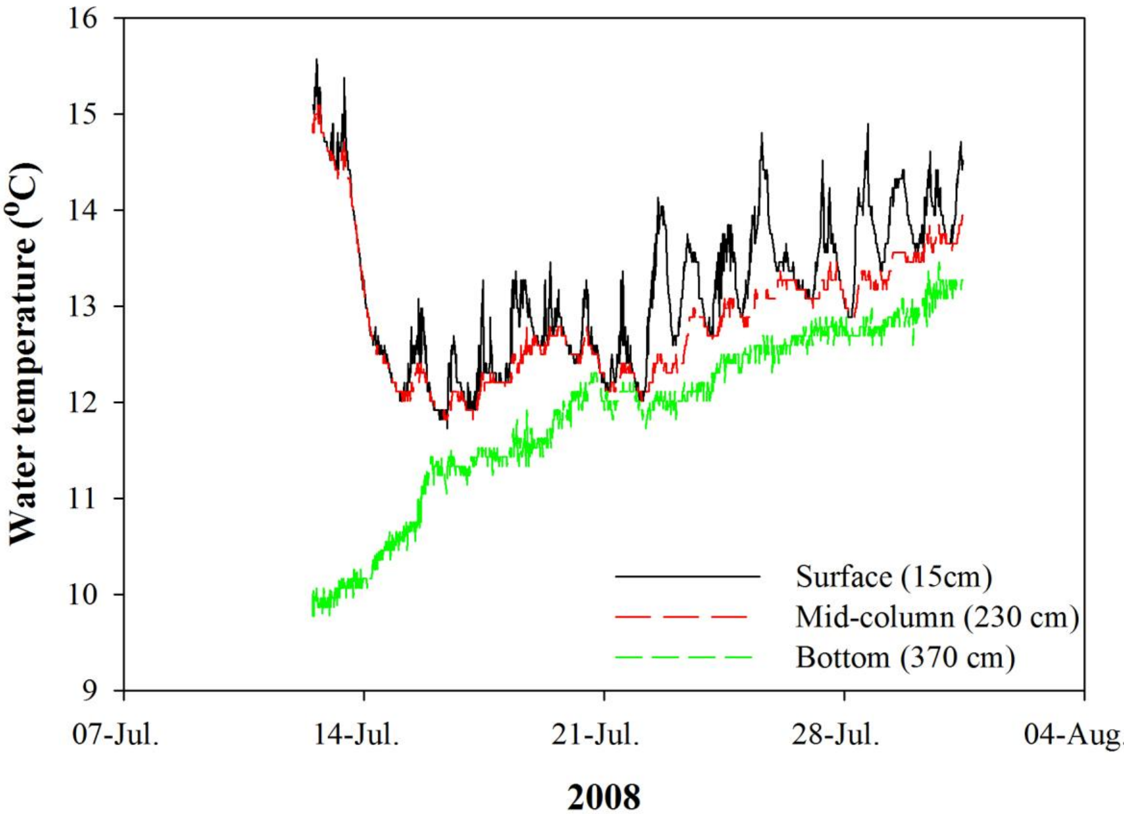

Figure S5 Water temperature stratification in Skeleton Lake (Meltwater pond) during the summer growing season of 2008.

References

Hamilton JD, Kelly CA, Rudd JWM, Hesslein RH, Roulet NT (1994) Flux to the atmosphere of CH_4 and CO_2 from wetland ponds on the Hudson-Bay lowlands (hbls). *Journal of Geophysical Research-Atmospheres*, **99**, 1495-1510.

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