Carbon dioxide and methane fluxes of freshwater systems in the rapidly changing high Arctic

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 - Abstract. A warming climate is rapidly changing the distribution and exchanges of carbon within high Arctic ecosystems. Few data exist, however, which quantify exchange of both carbon dioxide (CO₂) and methane (CH₄) between the atmosphere and freshwater systems, or estimate freshwater contributions to total catchment exchange of these gases, in the high Arctic. During the summers of 2005 and 2007-2012, we quantified CO₂ and CH₄ concentrations in, and atmospheric exchange with, common freshwater systems in the high Arctic watershed of Lake Hazen, Nunavut, Canada. We identified four types of biogeochemically-distinct freshwater systems in the watershed, however mean CO₂ concentrations (21–28 μmol L⁻¹) and atmospheric exchange (-0.013 to +0.046 g C-CO₂ m⁻² d⁻¹) were similar between these systems. Seasonal flooding of ponds bordering Lake Hazen generated considerable CH₄ emissions to the atmosphere (+0.008 g C-CH₄ m⁻² d⁻¹), while all other freshwater systems were minimal emitters of this gas (<+0.001 g C-CH₄ m⁻² d⁻¹). When using ecosystem-cover classification mapping and data from previous studies, we found that freshwaters were unimportant contributors to total watershed carbon exchange, in part because they covered less than 10% of total area in the watershed. High Arctic watersheds are experiencing warmer and wetter climates than in the past, which may have implications for moisture availability, landscape cover, and the exchange of CO₂ and CH₄ of underproductive, but expansive, polar semidesert ecosystems.

Keywords: carbon dioxide, methane, high Arctic, ponds, lakes, climate change, watershed

1 Introduction

Freshwater ecosystems cover less than 10% of global ice-free land area (Lehner and Doll, 2004) and have been typically overlooked as substantial contributors to, or sinks of, atmospheric carbon greenhouse gases (GHGs; Bastviken et al., 2011). However, recent studies suggest inland lakes collectively receive and process carbon at magnitudes similar to oceanic uptake and sediment burial, making them important systems within the global carbon

cycle (Cole et al., 2007; Battin et al., 2009; Tranvik et al., 2009; Maberly et al., 2013; Raymond et al., 2013).

Northern latitudes, between approximately 45 and 75 °N, contain the highest abundance of lakes, ponds and wetlands on the planet (Lehner and Doll, 2004) due to historical glaciations and moderate annual precipitation.

These regions also contain the world's largest below-ground stores of organic carbon (Tarnocai et al., 2009). These carbon and lake-rich northern ecosystems, therefore, have been critically-important sinks historically, and potentially strong emitters of this legacy carbon moving forward (ACIA, 2004).

Most northern lakes are net sources of the GHG carbon dioxide (CO₂) to the atmosphere (Jonsson et al., 2003; Tranvik et al., 2009, Laurion et al., 2010). Cold climates, short growing seasons, and light limitation in stained, carbon-rich waters can inhibit activities of aquatic primary producers (Karlsson et al., 2009), and therefore the uptake of atmospheric CO₂ by the lake ecosystem. Conversely, heterotrophic respiration by microbes, amplified under favourable biogeochemical conditions, continues perennially in most lake waters and sediments, therefore continuously releasing CO₂ to the water column. Turbulence, water temperature, degree of ice-cover and other factors may then influence the intensity of CO₂ emissions to the atmosphere. Lakes in carbon-rich lower Arctic regions (~60-70 °N, AMAP, 1998) can account for more than three-quarters of a landscape's net CO₂ emissions to the atmosphere (Abnizova et al., 2012). At the same time, saturated peatlands and shallow ponds and lakes throughout much of the lower Arctic can also be robust emitters of the potent GHG methane (CH₄) to the atmosphere. Permafrost in northern soils is an effective barrier to drainage of soils, and combined with generally low-elevation topography, means shallow standing water is prevalent throughout northern latitudes. Anoxic conditions in saturated, shallow, organic-rich soils have strong potential for methanogenic production and release of CH₄ into water (Tagesson et al., 2012). Due to its poor solubility, CH₄ can then be effectively released to the atmosphere from these ecosystems by ebullition and even minor wind turbulence, perhaps contributing up to 12% of all global emissions (Lai, 2009; Walter et al., 2006). These dynamic and carbon-rich environments, though, are not ubiquitous across the North, particularly towards the highest latitude regions.

In the high Arctic (>~70°N; AMAP, 1998), lake abundance and area are dramatically reduced on the landscape. The prevalence of cold and dry high pressure air masses results in a semi-arid climate with relatively well-drained and unproductive inorganic soils (Campbell and Claridge, 1992). This environment, therefore, discourages surface water retention with often less than 5% of the landscape being covered by aquatic systems. These conditions, in most cases, restrict primary production and accumulation of organic matter across these

landscapes compared to the lower Arctic, with mostly unknown implications for carbon GHG exchange in high Arctic lakes and ponds. Considering these challenging conditions, it may be easy to overlook the high Arctic, and its freshwater systems, as important contributors to global carbon cycling (Soegaard et al., 2000; Lloyd, 2001; Lund et al., 2012, Lafleur et al., 2012). However, recent studies have shown that where conditions are favourable (e.g., moist, organic-rich lowlands), high Arctic ecosystems exchange GHGs at rates similar to ecosystems at more southerly latitudes (Emmerton et al., 2016). Lack of a broad understanding of carbon cycling in high Arctic freshwater systems is further complicated by rapidly changing climate and landscapes across these latitudes due to human-induced warming.

High Arctic ecosystem productivity is currently changing as a warming climate substantially alters polar watersheds (IPCC, 2007a). Some climate models predict that in the Canadian Arctic, autumn and winter temperatures may rise 3-5°C by 2100, and up to 9°C in the high Arctic (ACIA, 2004; IPCC, 2007b). Mean annual precipitation is projected to increase ~12% for the Arctic as a whole over the same period, and up to 35% in localized regions where the most warming will occur (ACIA, 2004; IPCC, 2007b). Such warming and wetting is already modifying Arctic landscape energy balances (Euskirchen et al., 2007) resulting in glacial melt (Pfeffer et al., 2008), permafrost thaw (Froese et al., 2008), reorganized hydrological regimes (i.e., drying or wetting; Smith et al., 2008) and extended growing seasons (Myneni et al., 1997). These changes are also perturbing watershed carbon cycling through, for example, the liberation of carbon from thawing permafrost, and increases in biological productivity on landscapes and in lakes, ponds and wetlands (Mack et al., 2004; Smol et al., 2005; Walker et al., 2006; Smol and Douglas, 2007). However, the net result of these processes on high-latitude freshwater carbon GHG exchange is not well delineated, nor is the relative contribution of freshwater systems to total landscape CO₂ and CH₄ exchange. This information, from a rapidly changing and extensive biome (>10⁶ km²) is critical for improved global carbon models and budgeting.

The primary objective of this study was to measure the net atmospheric exchange of CO₂ and CH₄ with common high Arctic freshwater ecosystems, and place these findings in context with similar terrestrial studies from the same high Arctic location. Using these sources together, we aim to delineate a clearer, watershed-scale understanding of high Arctic exchange of CO₂ and CH₄.

2 Methods

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2.1 Location and sampling overview

We conducted our research at the Lake Hazen base camp in central Quttinirpaaq National Park, Ellesmere Island, Nunavut (81.8° N, 71.4° W), Canada's most northerly protected area (Figure 1). Lake Hazen (area: 542 km²; max. depth: 267 m) is the world's largest high Arctic lake, and is surrounded by a substantial watershed (6,901 km²) composed of carbonate, evaporite and dolomite rock (Trettin, 1994) and crysolic soils. About 38% of the Lake Hazen watershed is glaciated with the balance of area covered by a polar semidesert (>80% of ice-free area; Edlund, 1994), small lakes, ponds and meadow wetlands. The lower Lake Hazen watershed is a high Arctic thermal oasis (France, 1993) as it experiences anomalously warm growing season (June-August) conditions because it is protected from cold coastal weather by the Grant Land Mountains and Hazen Plateau (Table S1). For example, mean July air temperature is typically 8-9 °C at the base camp, compared to July 1981-2010 climate normals of 6.1 °C and 3.4 °C at the coastal Eureka and Alert weather stations on Ellesmere Island, respectively (Environment Canada, 2016). Soils in the region are also atypically warm during the summer because of low moisture content and efficient radiative heating due to an abundance of clear-sky days. These conditions, coupled with continuous daylight during the growing season, have resulted in a greater diversity and abundance of vegetation and wildlife in the Lake Hazen watershed compared to surrounding areas (France, 1993), despite receiving only ~34 mm of precipitation during the growing season (Table S1). Ultra-oligotrophic Lake Hazen itself dominates the freshwater area of the watershed (Keatley et al., 2007) and receives most of its water annually from rivers discharging melt water from glaciers. Water exits Lake Hazen via the Ruggles River. Ice-cover can remain on Lake Hazen throughout the growing season, though in recent years the lake has gone ice-free more frequently, usually by late July. Ponds and a few small lakes are scattered throughout the lower watershed and are mostly shallow, small in area (~70% are <1 ha) and typically go ice-free by mid- to late-June each year.

To quantify net GHG exchange of typical high Arctic freshwater bodies, we identified several <u>permanent</u> ponds or small lakes to sample within walking distance of base camp <u>to the northwest</u> of Lake Hazen (Figure 1). These systems were chosen systematically to incorporate a gradient of watershed position, surface area, mean depth, emergent vegetation productivity, and hydrological connectivity (<u>Table 1</u>). We also sampled <u>shoreline water</u> of Lake Hazen which <u>potentially</u> interacted with ponds located <u>adjacent to</u> its shoreline. <u>Due to logistical issues</u> related to accessing this remote area over consistent time periods each year, and due to the distances of some ponds

from base camp, we completed an overall unbalanced sampling program in space and time. As a result, we focused on delineating biogeochemical differences between different types of high Arctic lakes, rather than on inter-annual biogeochemical trends within lakes. Regardless, all sampling occurred during the summer growing seasons of 2005 to 2012 (except for 2006), between mid-June and early August (Table 2, S2).

2.2 Dissolved CO₂ and CH₄ concentrations of high Arctic freshwaters

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Two approaches were used to quantify concentrations of dissolved CO₂ and CH₄ in surface waters. The first approach was employed at all sites and used the common method of collecting water directly into evacuated 160-mL Wheaton glass serum bottles capped with butyl rubber stoppers (Hamilton et al., 1994; Kelly et al., 1997). Each bottle contained 8.9 g of potassium chloride (KCl) preservative to kill all microbial communities (Kelly et al., 2001), and 10 mL of ultra high purity dinitrogen (N₂) as a gas headspace. To collect a sample, a bottle was submersed ~5 cm below the water surface and punctured with an 18-gauge needle. Barometric pressure and water temperature were recorded. Dissolved gas samples were stored in the dark at ~5°C until return to the University of Alberta, where they were analyzed in the accredited Biogeochemical Analytical Service Laboratory (BASL). There, samples were placed in a wrist-action shaker for 20 minutes to equilibrate dissolved CO2 and CH4 with the N2 headspace. Headspace CO₂ and CH₄ concentrations were quantified on a Varian 3800 gas chromatograph (GC) using a flame ionization detector at 250°C with ultra high purity hydrogen (H₂) as a carrier gas passing through a hayesep D column at 80°C. A ruthenium methanizer converted CO₂ to CH₄. Four gas standards (Praxair, Linde-Union Carbide), ranging from 75 to 6000 parts-per-million for both CO₂ and CH₄, were used to calibrate the GC. A Varian Star Workstation program integrated peak areas and only calibration curves with an r² >0.99 were accepted for analyses. A standard was re-analyzed every 10 samples to reconfirm the calibration, and duplicate injections were performed on all samples. Headspace CO2 and CH4 concentrations were converted to dissolved molar concentrations using Henry's Law, and corrected for temperature and barometric pressure differences between sample collection and analysis. To quantify dissolved inorganic carbon (DIC) concentrations, samples were acidified with 0.5 mL H₃PO₄ to convert all DIC to CO₂, and then immediately reanalyzed on the GC. DIC concentrations were calculated as above.

The second approach involved two automated systems to determine detailed diel changes in surface water dissolved CO₂ concentrations at two different sites (Skeleton Lake and Pond 01; Figure 1; Table S2). Dissolved CO₂ concentrations were measured every three hours during several summers. These systems functioned by equilibrating,

over a 20-minute period, dissolved CO₂ from pumped surface waters, with a gas cell in a Celgard MiniModule Liqui-Cel. The equilibrated gas was then analysed for CO₂ concentration by a LI-COR (Lincoln, NE) 820 infrared gas analyzer. The systems also measured dissolved oxygen (O₂) concentrations using a QubitTM flow-through sensor. Concentrations were then converted to aqueous molar concentrations using Henry's Law and water temperature quantified with a Campbell Scientific (Logan, UT) 107-L thermistor. The systems were housed in watertight cases along the shore from which a sample line extended out into the surface waters, and upon which was mounted a CS 014A anemometer (1 m height) and a Kipp & Zonen (Delft, The Netherlands) photosynthetically-active radiation (PAR) LITE quantum sensor. All data were recorded on Campbell Scientific CR10X dataloggers.

2.3 Dissolved CO₂ and CH₄ fluxes of high Arctic freshwaters

Though several models exist for quantifying turbulent gas fluxes of lakes (e.g., MacIntyre et al., 2010), we decided to use the stagnant film model described by Liss and Slater (1974) to quantify net CO₂ and CH₄ mass fluxes between surface waters and the atmosphere at our remote location. This decision was made because of 24-hour daylight at our high-latitude location dampened diurnal surface temperature changes to less than 1°C, the general shallowness of the systems, and the steady, sometimes gusty, wind conditions on site. The stagnant film model assumes gas concentrations in both surface waters and the atmosphere are well-mixed, and that gas transfer between the phases occurs via diffusion across a diminutive stagnant boundary layer. Diffusive gas transfer across the boundary layer is assumed to follow Fick's First Law:

Gas flux (
$$\mu$$
mol m⁻² hr⁻¹) = k($C_{SUR} - C_{EOL}$) (1)

where C_{SUR} (µmol L^{-1}) is the concentration of the gas in surface waters, C_{EQL} (µmol L^{-1}) is the atmospheric equilibrium concentration, and k is the gas exchange coefficient, or the depth of water per unit time in which the concentration of the gas equalizes with the atmosphere (i.e., piston velocity). Values of k (cm hr⁻¹) were calculated using automated systems wind measurements and occasionally from nearby (within 2 km) eddy covariance towers (Campbell Scientific CSAT3 Sonic Anemometers; 30 min. means), and published empirical relationships (Table S3; Hamilton et al., 1994). To determine the direction of the flux, atmospheric equilibrium CO_2 and CH_4 concentrations were quantified using Henry's law, in-situ barometric pressure and air temperature, and mean annual CO_2 and CH_4 concentrations in the atmosphere during the year of sampling (Environment Canada, 2015). If dissolved CO_2 and CH_4 concentrations in surface waters were above or below their corresponding calculated atmospheric equilibrium

concentrations, the freshwater systems were considered a source (+) or sink (-) relative to the atmosphere, respectively.

We also measured ebullition fluxes of CH_4 to the atmosphere from two freshwater systems (Skeleton Lake, Pond 01) during two growing seasons using manual bubble collection and GC analysis (see Supporting Information).

2.4 Supporting measurements

We quantified additional physical and chemical parameters in surface waters at the same sites as we collected our GHG samples, although at reduced sampling frequencies (Table 2. S2). At each site, temperature, pH, specific conductivity and dissolved O₂ were measured in-situ using a YSI (Yellow Springs, OH) 556 MPS multiprobe. Water samples were also collected for general chemical analyses (total dissolved nitrogen [TDN], particulate N, NO₃-+NO₂-, NH₄+, total phosphorus [TP], total dissolved phosphorus [TDP], alkalinity, dissolved organic carbon [DOC], total dissolved solids, major cations/anions, dissolved iron, chlorophyll-a [chl-a]) into pre-cleaned HDPE bottles. These samples were immediately processed in the Lake Hazen/Quttinirpaaq Field Laboratory clean room after water collection, and stored in the dark at ~5°C or frozen until analysed at the BASL.

2.5 Numerical analysis

We used hierarchical clustering analysis (IBM SPSS Statistics 23) to organize ponds and lakes into type categories based on concurrent GHG and chemistry analyses (10 sites; n=62; Table 2). Because sampling was unbalanced in frequency and time between sites due to logistical challenges (Table 2; see section 2.1), potential overlap of chemistries between individual lakes was high, therefore setting a conservative standard for classifying distinct lake types. 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 GHG concentrations and fluxes between these different high Arctic freshwater types. Linear-mixed models are ideal for analysing non-independent and repeated measures data as they integrate inherent errors in repeated sampling designs to more clearly distinguish statistical differences between groups. These models also can efficiently handle unbalanced designs by standardizing results from each site within 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).

2.6 Net atmospheric exchange of CO₂ and CH₄ of a large high Arctic watershed

To better understand the role of freshwater ecosystems in regional fluxes of carbon GHGs, freshwater CO₂ and CH₄ fluxes measured in this study were coupled with terrestrial fluxes measured in the watershed during the 2008-12 growing seasons (Emmerton et al., 2014, 2016). The authors measured, using eddy covariance flux towers (CO₂, CH₄) and static chambers (CH₄), growing season carbon GHG exchange with terrestrial polar semidesert and meadow wetland landscapes from 2008-12. Areal coverage of the different ecosystem types in the watershed was isolated from a previous classification of Quttinirpaaq National Park (Edlund, 1994) using a Geographical Information System (ArcGIS v.10.3; ESRI, Redlands, US). Mean growing season fluxes from each measured ecosystem were then weighted to matching coverage area in the watershed to estimate the total carbon gas exchange with the atmosphere. Glacial ice was assumed to be a net-zero contributor of total watershed gas exchange in this scaling exercise.

3 Results

3.1 Biogeochemical classification of high Arctic freshwaters

Four distinct types of freshwater systems were evident from our sampling in the Lake Hazen watershed (Table 3; Error! Reference source not found. Figure ; hierarchical cluster analysis; see Methods). "Evaporative" ponds (Ponds 07, 10, 12) occurred in the upland of the Lake Hazen catchment and were hydrologically-isolated from their surrounding basins post-snowmelt. These ponds were relatively high in concentrations of total dissolved solids, most measured ions, DIC, DOC, organic particles, TDP and chl-a. Pond 03, though not technically clustered with others, was forced to the Evaporative pond category based on lack of consistent inflowing water and high concentrations of most dissolved ions. This delegation was further consistent with isotopic measurements of oxygen (8¹⁸O-H₂O) in water taken from each aquatic system in July 2010 (Figure S2). "Meltwater" systems, including Ponds 11, 16 and Skeleton Lake, also occurred in the upland of the Lake Hazen watershed, but received consistent water supply through the growing season primarily from snowmelt, permafrost/ground ice thaw water or upstream lake drainage. The general chemistry of these systems was therefore consistent and without extremes during the growing season (see section 3.2). Typical meltwater streams draining to these ponds were high in TDN and sulfate (SO₄²), but low in DOC (Table 3), though streams drained through marginal wetlands surrounding the lakes and ponds downstream of our sampling sites. "Shoreline" ponds (Ponds 01, 02) occurred along the margin of Lake

Hazen and were typically physically isolated from the large lake by porous gravel berms, and surrounded by wetland soils and flora during spring low water conditions. As glacial melt accelerated throughout the growing season, though, the water level of Lake Hazen rose and could seep through the berms to incrementally flood the ponds and surrounding wetlands (Figure S3). Shoreline ponds changed chemically during the onset of flooding as indicated, for example, by an increase in the concentration of NO₃⁻+NO₂⁻ (Table 3). A separate smaller cluster of Pond 01 samples occurred during particularly high-water periods when Lake Hazen breached the berms (Error! Reference source not found. Figure). The flooding water from the "Lake Hazen shoreline" was cold, dilute in dissolved ions, organic matter, TDN, and chl-a, but considerably higher in NO₃⁻+NO₂⁻ compared to other water bodies.

3.2 Dissolved concentrations and net atmospheric exchange of CO_2 and CH_4 of high Arctic freshwaters 3.2.1 CO_2

Growing season concentrations of dissolved CO_2 in sampled high Arctic freshwaters from 2005 to 2012 varied substantially within and between the system types, and therefore overall resulted in non-significant differences between them (Figure 2, 3, S4, S5).

On average, Evaporative ponds had the highest mean CO₂ concentrations (mean±SE; 27.9±4.9 µmol L⁻¹) compared to other pond types (Figure 3), primarily due to conditions in Pond 03 and Pond 07. These ponds were the shallowest of the four sampled and were rich in dissolved iron, DIC, and TDP. CO₂ concentrations were above atmospheric equilibrium concentration (Figure 2) and therefore these ponds were sources of the gas to the atmosphere (+177±66 µmol CO₂ m⁻² hr⁻¹; Figure 3). The other Evaporative ponds (Ponds 10, 12) were deeper and had CO₂ concentrations that were typically near those of the atmosphere. This contributed to their near-zero exchange of CO₂ with the atmosphere (-5±17 µmol CO₂ m⁻² hr⁻¹). Together, dissolved CO₂ concentrations correlated closely and positively with DOC and dissolved iron concentrations in Evaporative ponds (Table S4). When combining all Evaporative ponds together, they were net sources of CO₂ to the atmosphere (+73±93 µmol CO₂ m⁻² hr⁻¹; Figure 3).

Meltwater systems had lower, but insignificantly different, CO_2 concentrations (26.2±3.9 µmol L^{-1}) than Evaporative ponds (Figure 3). Meltwater systems showed only gradual, venting-related declines of CO_2 concentrations through the summer, with strong consistency in concentrations between sampling times and sites (Figure 2). However, they emitted higher, though not significantly different, fluxes of CO_2 to the atmosphere overall (+160±66 µmol m^{-2} hr⁻¹; Figure 3) compared to the other types of systems. CO_2 concentrations of these systems

correlated strongly and positively with CH_4 concentrations, but negatively with \underline{DOC} concentrations and measurements that were of high concentrations in Meltwater streams draining into the systems (e.g., $SO_4^{2^-}$, TDN; Table 3, S4). Mean diurnal trends in CO_2 concentrations across all sampling years, as measured by the automated system at Skeleton Lake, showed that CO_2 and O_2 concentrations had little association together (Pearson correlation: $\underline{r} = -0.18$, $\underline{df} = 7$; $\underline{p} = 0.67$), but $\underline{CO_2}$ associated strongly and negatively with water temperature ($\underline{r} = -0.97$, $\underline{df} = 7$, $\underline{p} < 0.001$; Figure 4).

Mean CO₂ concentrations of Shoreline ponds (22.5±3.7 μmol L⁻¹; Figure 3) were similar to the other pond types, which obscured their considerable seasonal changes within and between growing seasons. From 2005 to 2007, both Pond 01 and Pond 02 received little floodwater from Lake Hazen due to lower lake water levels (Figure 2). These conditions resulted in dense wetland vegetation growth surrounding the ponds and low mean daily dissolved CO₂ concentrations (6.5±0.4 μmol L⁻¹) and strong uptake of atmospheric CO₂ (-329±59 μmol m⁻² hr⁻¹). The drier wetland state of these ponds changed in following summers when Lake Hazen rose substantially upon greater inputs of glacial meltwaters (WSC, 2015), causing the rising waters to seep through porous berms into the ponds through July. In concert with flooding, concentrations of CO₂ from 2008-11 of each pond together increased substantially (30.1±1.5 μmol L⁻¹) resulting in strong net emissions of CO₂ to the atmosphere (+228±44 μmol m⁻² hr⁻¹). Changing dissolved CO₂ concentrations correlated positively with dissolved nutrients and ions (Table S4). Diurnal trends of CO₂ and O₂ concentration measured by the automated system at Pond 01 over several growing seasons showed opposite diel patterns of the gases, with greater O₂ during the warmest and lightest parts of the day (r=-0.98, df=7, p<0.001; Figure 4). However, the net result of strong seasonality in these ponds was slight net emission of CO₂ to the atmosphere (+42±60 μmol m⁻² hr; Figure 3) that was not statistically-different from other types of freshwaters.

Lake Hazen shoreline water, though not necessarily representative of the entire lake itself, was characteristic of its moat occurring early each growing season, and of water that intruded Shoreline ponds in July. This water was generally near atmospheric equilibrium concentrations of CO_2 (21.0±7.8 µmol L⁻¹; Figure 2) with stable and low CO_2 uptake throughout the season (-44±66 µmol m⁻² hr; Figure 3). CO_2 concentrations of this shoreline water related strongest and positively with DIC, NO_3 + NO_2 , major ions and wind speed (Table S4).

3.2.2 CH₄

Each of Evaporative, Meltwater and Lake Hazen shoreline freshwaters had statistically similar and low CH₄ concentrations (0.06-0.14 μmol L⁻¹) and fluxes (+0 to +3 μmol m⁻² hr⁻¹) across all growing seasons (Figure 2.3. S4, S5). Evaporative ponds had generally flat seasonal CH₄ concentration and flux trends (Figure 2), except for an outlier sample from Pond 10 in mid July 2011. CH₄ concentrations correlated strongest with NO₃+NO₂ and alkalinity (Table S4). Meltwater systems were also generally low in CH₄ concentrations and fluxes through the summers and associated positively and closely with CO₂ concentrations, and strongly but negatively with SO₄², alkalinity and other ions (Table S4). Notable flux emissions from these systems only occurred during episodic wind events, also similar to CO₂ (Figure S5). However, unlike CO₂, higher CH₄ concentrations were sustained into July in Skeleton Lake in 2010 (Figure 2). Lake Hazen shoreline water showed low and stable CH₄ concentrations and fluxes each growing season with infrequent and small releases of the gas to the atmosphere. CH₄ concentrations in this water correlated positively only with particulate carbon concentrations (Table S4).

Shoreline ponds, alternatively, had significantly higher CH₄ concentrations relative to the other systems (1.18±0.16 µmol L⁻¹; Figure 3) and showed a dynamic seasonal pattern dominated by the timing of flooding (Figure 2). In 2005 and 2007 before substantial seasonal flooding started to occur, CH₄ concentrations (0.29±0.03 µmol L⁻¹) and fluxes to the atmosphere (+8±2 µmol m⁻² hr⁻¹) were low. As the Shoreline ponds began to receive NO₃⁻+NO₂⁻-rich flood water from Lake Hazen by mid-summer in subsequent years (Table 3), 2008-11 CH₄ concentrations and fluxes increased substantially (1.70±0.13 µmol L⁻¹; +41±10 µmol m⁻² hr⁻¹) and correlated closely with dissolved organic and inorganic nitrogen (Table S4). This significant increase in CH₄ flux emissions from Shoreline ponds during flooding (>five times higher than during dry periods) was coupled with large increases in pond surface areas, effectively producing even higher total CH₄ emissions to the atmosphere. Towards the end of July during flooding conditions, full berm breach of the Shoreline ponds by rising Lake Hazen waters occurred resulting in rapid dilution of CH₄ concentrations, but logistical constraints prevented later summer sampling to investigate if concentrations rebounded thereafter. Overall, aided by poor solubility of CH₄ in water and episodic wind events (Figure S5), the flooding of Shoreline ponds drove significantly larger CH₄ emissions to the atmosphere compared to other pond types (+28±5 µmol m⁻² hr⁻¹; Figure 3).

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3.3 Net atmospheric exchange of CO₂ and CH₄ of a large high Arctic watershed

When scaled to total watershed area including Lake Hazen (7,443 km²), polar semidesert landscapes were inconsequential to total CO₂ exchange (-1,253 Mg C-CO₂; 9% of total exchange) despite comprising a substantial proportion of the catchment (3,819 km²; 51%; Table 4). All types of standing freshwaters sampled in the watershed from this study showed statistically-similar CO₂ fluxes compared to the polar semidesert. When assuming its shoreline waters were representative of the entire lake area as recent evidence suggests (unpublished data, 2015), the expansive Lake Hazen (542 km²; 7%) exchanged relatively little CO₂ with the atmosphere (-721 Mg C-CO₂; 5%), as did smaller freshwater systems (144 km²; 2%) in the watershed (600 Mg C-CO₂; 4%). In clear contrast, during the growing season, moist and vegetated meadow wetland ecosystems were found to consume CO₂ at rates similar to wetlands in the southern Arctic (-0.96 g C-CO₂ m² d⁻¹; Emmerton et al., 2016). Consequently, meadow wetlands exchanged an estimated 82% (-11,368 Mg C-CO₂) of total CO₂ with the atmosphere despite occupying only 2% (129 km²) of the area in the Lake Hazen watershed. Total CO₂ exchange of the watershed was -10,236 Mg C-CO₂ (-1.38 g C-CO₂ m²²) during the growing season.

The high Arctic polar semidesert has recently gained attention as a notable atmospheric sink of CH₄ (-0.001 g C-CH₄ m⁻² d⁻¹; Emmerton et al., 2014), which has since been observed in studies at other high Arctic locations (e.g., Jorgensen et al., 2015). These uptake fluxes coupled with its expansive coverage made the polar semidesert the key landscape controlling net CH₄ exchange throughout the Lake Hazen watershed (-412 Mg C-CH₄; 94% of total exchange; Table 4). Surprisingly, a productive meadow wetland in the watershed was a weaker emitter of CH₄ to the atmosphere (+0.001 g C-CH₄ m⁻² d⁻¹) compared to other high Arctic wetlands (Emmerton et al., 2014), releasing only 10 Mg C-CH₄ (2%) to the atmosphere during the growing season. All upland freshwater systems (Evaporative and Meltwater systems) had low emissions of CH₄ to the atmosphere (11 Mg C-CH₄; 2%), as did Lake Hazen itself (+6 Mg C-CH₄; 1%). All measured ecosystems had statistically-similar CH₄ fluxes except for the strong CH₄-producing Shoreline ponds (Table 4). However, poor areal coverage of these dynamic systems in the watershed (0.6 km²; <1%) resulted in contributions of <<1% (+0.4 Mg C-CH₄) of all CH₄ exchange in the Lake Hazen watershed (-385 Mg C-CH₄; -0.052 g C-CH₄ m⁻²).

4 Discussion

4.1 Dissolved concentrations and net atmospheric exchange of CO2 and CH4 of high Arctic freshwaters

4.1.1 CO₂

Dissolved CO₂ was likely being produced effectively in all Evaporative ponds by ecosystem metabolism because of their high concentrations of DOC. These, another other, isolated systems concentrate many solutes in their waters including degraded allochthonous and fresh autochthonous DOC (Tank et al., 2009), which would be available as a source of energy to heterotrophs. Accumulation and dissociation of weathered carbonates and evaporates in these moderately warm, high alkalinity environments (2-5 mEq L⁻¹) may have also been important (Trettin, 1994; Marcé et al., 2015). However, differences in pond volumes likely controlled the ultimate concentrations of CO₂ found in Evaporative ponds. Small and shallow Evaporative ponds (Ponds 03, 07) showed much higher concentrations compared with those that were larger and deeper (Ponds 10, 12) and were therefore more susceptible to wind-related turbulence and gas exchange with the atmosphere.

The biogeochemistry of Meltwater systems was steady and similar between sites, possibly related to stream flushing, but they ultimately had similar CO₂ concentrations and fluxes as other freshwater types. This occurred despite inclusion of early summer sampling at Skeleton Lake (2007, 2010) when CO₂ concentrations were higher as post-ice-covered waters were re-equilibrating with the atmosphere (Kling et al., 1992; Karlsson et al., 2013). However, fluxes of CO₂ to the atmosphere from these systems did not correspond closely with early season venting, but rather to the frequency of episodic releases of CO₂ to the atmosphere (Figure S5). This may have been related to their greater mean depths, which promoted stratification in at least one of our sampled Meltwater systems (Skeleton Lake; Figure S6). Stratification would confine decomposition products (e.g., CO₂, CH₄) to near their sites of origin in bottom sediments and extensive benthic mat communities, which would then be released most readily during and just after wind mixing events. We observed evidence of this process via strong positive correlations between CO₂ and CH₄ concentrations in surface waters (Table S4). Results from our automated systems supported this argument as mean diurnal CO₂ and O₂ concentrations in surface waters of Skeleton Lake associated poorly together, rather than oppositely if metabolic processes (i.e., primary productivity or decomposition of organic matter; see Pond 01 below) were dominant drivers in surface waters. Mixing-related releases of CO₂ would be offset by calmer, lowerflux conditions when DOC concentrations may have been higher in upper layers. Meltwater streams flushing

through marginal wetlands before entry into the Meltwater systems, but then not mixing with the entire lake, may explain the negative correlation observed between CO₂ and DOC concentrations.

Shoreline ponds changed drastically in size and chemistry in response to seasonal flooding by Lake Hazen shoreline water (Table 1, 3). During pre-flooding conditions, CO₂ concentrations were low which could be attributed to DIC use by autotrophic plankton (pre-flooding: 1.2 µg L⁻¹ chl-a; post-flooding:to 0.4 µg L⁻¹ chl-a), but more likely by observed dense benthic and macrophytic communities along the margins of the ponds (Tank et al., 2009). When inundated by flood waters, CO₂ concentrations rose sharply which is typically observed in flooded wetlands (Kelly et al., 1997). This occurs because widespread inundation of plants and soils typically prompts rapid decomposition (Table S4). Although negatively correlated diurnal CO₂ and O₂ concentrations suggest that primary productivity was consistently occurring in Shoreline pond surface waters, flooding of the ponds was ultimately the more important process controlling seasonal CO₂ concentrations.

CO₂ concentrations in Lake Hazen shoreline water were near atmospheric equilibrium and only weakly consumed atmospheric CO₂. These results along the shoreline appear to be similar to other locations offshore (unpublished, 2015) and were reflective of most deep lakes with extremely low nutrient, organic matter and chl-*a* concentrations (0.20 μg L⁻¹; Keatley et al., 2007; Babaluk et al., 2009). CO₂ gas exchange between the lake and the atmosphere correlated well with DIC, alkalinity and other ions, which are considerable in glacial rivers draining to the lake (Babaluk et al., 2009). These rivers were also strongly undersaturated in CO₂, as observed elsewhere in glacial environments (Meire et al., 2015), and may explain the slight CO₂ uptake observed by the lake, especially later in summer.

4.1.2 CH₄

Evaporative and Meltwater systems were typically weak producers and emitters of CH₄, which was possibly related to concurrently high SO₄²⁻ concentrations in these systems due to additions of water draining evaporite geologies (Table 3; Trettin, 1994). This may have given competitive advantage to SO₄²⁻-reducing bacterial communities in sediments, which typically outcompete methanogenic bacteria for hydrogen. This hypothesis was supported by the prevalence of H₂S gas in collected sediment cores from Skeleton Lake (unpublished, 2013) and by the trivial fluxes of CH₄ in bubbles measured emerging from sediments (+0.00 to +0.01 mg m⁻² d⁻¹; Table S5; see Supporting Information). Stratification in Meltwater systems and the only periodic wind-related releases of CH₄, similar to CO₂, likely also limited CH₄ emissions (Table S4). Low production and exchange of CH₄ in Lake Hazen,

alternatively, was most likely associated with the lake's ultra-oligotrophic standing (Keatley et al., 2007), well-oxygenated water, and little accumulation of littoral organic matter where anoxia could prevail and CH₄ be produced. Only during periods of strong wind mixing of surface waters, or when Shoreline ponds breached and mixed organic particles (Table S4) across its shoreline, did the near shore waters of Lake Hazen release CH₄ to the atmosphere above near-zero values.

Shoreline ponds were regional "hot-spots" of CH₄ exchange, which was clearly driven by seasonal flooding, and releases of organic matter and nutrients (Table S4). Pre-flooding conditions in the ponds were characterized by dry and oxygenated wetland soils which were exposed to the atmosphere and not connected to the central pond where we sampled. Flooding induced saturation of organic soils surrounding the wetland and perhaps provided advantageous conditions for anaerobic metabolism, including methanogenesis. This may have been further supported by the flushing of the ponds with SO₄²⁻-poor Lake Hazen water, therefore potentially favouring metabolism of methanogens over SO₄²⁻-reducers in the flooded soils.

4.2 Net atmospheric exchange of CO₂ and CH₄ of a large high Arctic watershed

Studies from the southern Arctic have estimated that fluxes of CO₂ (e.g., -1.55 to +1.10 g C-CO₂ m⁻² d⁻¹, Tank et al., 2009, Abnizova 2012) and CH₃ (+0.01 to +0.09 g C-CH₄ m⁻² d⁻¹, Walter 2006, Sachs 2010) from ponds and lakes can contribute a strong majority of a region's total exchange of CO₂ and CH₃ with the atmosphere (Sachs et al., 2010; Abnizova et al., 2012). Carbon and nutrient-rich soils, longer growing seasons, and high densities of aquatic and wetland ecosystems are likely key characteristics responsible for these strong signals. To our knowledge, concurrent measurement of freshwater and terrestrial carbon GHG exchange at a high Arctic location has not occurred previous to this study. We found that in a large high Arctic watershed, a size range from small ponds up to one of the world's largest high-latitude lakes, together contributed only an estimated 9% (CO₂; -0.01 to +0.05 g C-CO₂ m⁻² d⁻¹ and 3% (CH₄; +0.00 to +0.01 g C-CH₄ m⁻² d⁻¹ of all carbon GHG exchanges (Table 4). Several reasons may explain the limited role of aquatic systems there. First, pond and lake coverage in the high Arctic is typically very low (<10% of Lake Hazen watershed; Table 4) compared to the southern Arctic (Lehner and Doll, 2004). Well-drained soils, a semi-arid climate and continuous evaporation throughout a 24-hour daylight growing season all contribute to negative pond and lake water balances often observed across the high Arctic (Woo and Guan, 2006). Second, growing seasons of high Arctic freshwaters are very short as ice-cover can remain perennially on some lakes, or may vacate for only three months (Rautio et al., 2011). Though ponds in the Lake

Hazen watershed can warm to moderate levels compared to other Arctic locations (Table 3, Rautio 2011), time exposure to these temperatures is short and likely limits growing season autotrophic and heterotrophic activity and their contributions to freshwater carbon gas exchange. Geochemical production of CO₂ in high-alkalinity ponds and lakes is also lessened in only moderately warm environments (Marcé et al., 2015). Third, runoff delivered to high Arctic freshwaters is typically dilute, nutrient-poor and low in quality organic matter because it drains among the most unproductive and desiccated soils anywhere on Earth (ACIA, 2004). Therefore, neither important nutrients key for aquatic photosynthesis (Markager et al., 1999), nor labile carbon for heterotrophic activities are supplied to many high Arctic lakes in great quantities, thus limiting potential biological carbon GHG uptake or emission. These constraints on aquatic productivity were visible at our sites as few were dominated by productive emergent plants, but rather by barren lake beds or submerged benthic mats of weaker productivity.

Despite a challenging climate and poor-quality substrates, our results suggest that the degree of moisture availability in high Arctic ecosystems was an overarching control on CO₂ exchanges. Running water environments are the most productive landscapes in the Lake Hazen watershed (Table 4) because they are consistently wet, but not starved of (e.g., polar semidesert) or inundated by (e.g., ponds, lakes) water. These ideal conditions support productive emergent plant communities, which typically outgrow other vegetation types along the terrestrial-aquatic watershed gradient (Wetzel, 2001). This occurred despite low soil temperatures in these wetlands because of shallow permafrost tables. Productive standing water environments were rare in the Lake Hazen watershed, except for Shoreline ponds during their drier wetland phase. However, the flooding hydrology of Lake Hazen promoted a near balance of net autotrophy and heterotrophy in these systems. For CH_{4s} the spatial coverage of ecosystem types was the most important factor controlling its exchange at the watershed scale. Only Shoreline ponds, due to the flooding of its wetland vegetation, were substantially higher in per-unit CH₄ gas exchange than other ecosystems (Table 4). However, net uptake of CH₄ by methanotrophs in polar semidesert soils was ultimately of greatest importance at the watershed scale because of the landscape's extensive spatial coverage relative to other ecosystem types. This finding supports other recent studies which highlight the potential global importance of this substantial high Arctic CH₄ sink (Jorgensen et al., 2015).

Modification of moisture availability in high Arctic regions is likely in a changing climate. High Arctic latitudes are expected to endure considerable warming and increased precipitation, resulting in shifting snow and ice phonologies, greater contributions to runoff from subsurface ice and glaciers, and greater evaporation rates (ACIA,

2004). These changes will affect the distribution and sustainability of water across high Arctic landscapes. Smol and Douglas (2007) have suggested that negative water balances and the drying of small and shallow aquatic systems will become a more frequent response to rapidly increasing temperatures and enhanced evaporation. Others have suggested that site-specific hydrological conditions have important controls on the ultimate sustainability of high Arctic waters, including substrate characteristics, snowpack accumulation, and connection to water sources (Abnizova and Young, 2010). In the Lake Hazen watershed, expected increases in nearby coastal evaporation and landward precipitation (Bintanja and Selten, 2014) may deliver larger snowpacks, recharges of subsurface ice or water storage, and increases in summertime runoff to aquatic systems. Increased temperatures, however, should also work to sustain wet areas in the watershed. Increased glacial melt would continue to deliver more water to Lake Hazen and flood Shoreline Lakes for longer periods. Higher temperatures should also improve water delivery to Meltwater systems and meadow wetlands supplied by thawing subsurface ice. Only shallow Evaporative ponds, which endure a precarious existence based on net balances in snowmelt and evaporation, have a less certain future. We suspect that these Evaporative systems may be susceptible to drying over the shorter term as air temperatures increase, but the weak water storage capacity of well-drained polar semidesert soils continues. Only until long-term improvements in productivity and organic matter content in soils occurs, would we expect more consistent sources of runoff to shallow systems. Well-drained polar semideserts, similarly, may also be expected to remain relatively dry until water holding capacity of the soils improves (Emmerton et al., 2016).

With expected sustainability of water delivery to most wet systems in the Lake Hazen watershed over the longer term, future carbon GHG exchange there and other high Arctic regions, is likely dependant on the trajectory of landscape change of polar semideserts (Sitch et al., 2007). Low CO₂ and CH₄ exchange in upland systems and Lake Hazen will likely continue until water and nutrient conditions in polar semidesert soils draining to them improves over the longer term. Shoreline ponds may be flooded earlier and for longer periods as Lake Hazen receives increased glacial melt water, possibly amplifying carbon GHG emissions over the short term. However, supply of decomposable organic carbon may decrease as periods when these systems are in a productive wetland-state becomes less frequent. Regardless, Shoreline ponds likely have little role in regional carbon GHG exchange due to minimal abundances. Consequently, changes in the terrestrial ecosystems, over the longer term, should continue to define the direction and intensity of GHG exchanges in the high Arctic. Meadow wetlands are key high Arctic regions due to substantial growing season productivity and CO₂ consumption, despite their low abundance.

Notable spatial expansion of these very productive systems, though, is unlikely due to topographical constraints. The potential of dry polar semideserts to change, however, is great over the long term (ACIA, 2004). As plant growth, organic matter production and soil water retention improve as expected in the polar semidesert, its CO₂ sink strength during the growing season should also improve. However, this may also work to perturb atmospheric oxygen and methane infiltration into polar semidesert soils and perhaps decrease the magnitude of its globally-important atmospheric CH₄ sink (Jorgensen et al., 2015). Ultimately, terrestrial ecosystems and their future climate-related changes, rather than those in lakes and ponds, will likely control future carbon cycling at high Arctic latitudes.

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Tables

Table 1 Morphometry and hydrology of ponds and lakes sampled for <u>dissolved</u> greenhouse gases concentrations and general chemistry in the Lake Hazen (LH) watershed during the growing seasons <u>(June-August)</u> of 2005, and 2007-2012.

Lake or I	Pond (location)	Surface area (ha)	Mean depth (m)	Max. depth (m)	Elevation (m asl)	Primary water sources
Pond 01	(N81.822 W71.352)	0.1-0.7	0.2-0.6	0.5-1.3	166	LH, snowmelt
Pond 02	(N81.811W71.453)	0.2-3.4	0.1-0.4	0.3-1.2	165	LH, snowmelt
Pond 03	(N81.829 W71.462)	0.04	0.3	0.8	338	Snowmelt
Pond 07	(N81.835 W71.305)	0.4	0.1	0.3	184	Snowmelt
Pond 10	(N81.838 W71.343)	2.5	1.1	2.4	222	Snowmelt
Pond 11	(N81.832W71.466)	0.2	1.1	2.5	291	Snowmelt, ground ice
Pond 12	(N81.831W71.529)	0.2	0.8	1.9	370	Snowmelt
Pond 16	(N81.850W71.392)	0.7	1.1	2.1	434	Snowmelt, ground ice
Skeleton l	L. (N81.829W71.480)	1.9	1.9	4.7	299	Snowmelt, ground ice
LH-shore	(N81.821 W71.352)	54,200	95 ^a	267 ^a	158	Glacial, snowmelt

^aKock et al., 2012

Table 2 Number of samples collected for both dissolved greenhouse gases and general chemical analyses within freshwater systems of the Lake Hazen watershed during the growing seasons (June-August) of 2005, and 2007 to 2012. All calculated gas fluxes were based on samples collected for concentration analyses.

Water body	2005	2007	2008	2009	2010	2011	2012
CO ₂ , CH ₄ (chemistry)							
Pond 01	16	25	30(5)	24(5)	35(5)	3	-
Pond 02	16	1	5(5)	-	2(2)	3	-
Pond 03	1	1	1	-	1(1)	3	-
Pond 07	1	1	1	-	2(2)	3	-
Pond 10	1	-	-	-	2(2)	3	-
Pond 11	1	-	-	-	2(2)	6	3
Pond 12	1	1	1	-	2(2)	-	-
Pond 16	-	-	-	-	2(2)	3	-
Skeleton Lake	-	19	16(5)	23(5)	29(4)	6	3
Lake Hazen shoreline	17	27	30(6)	24(5)	29(4)	3	-

Table 3 Mean ($\pm 1SD$) water temperature and general chemistry of different freshwater types, and other selected locations and periodsb in the Lake Hazen watershed during the growing seasons (June-Aguust) of 2005, 2007-2012. All measurements are in μ mol L⁻¹ except for water temperature (°C), total dissolved solids (mg L⁻¹) and chlorophyll-a (μ g L⁻¹).

	<u>W</u> _T	TDS	<u>PC</u>	DIC	DOC	<u>NO₃-+NO₂-</u>	<u>NH4</u> ±	TDN	TDP	<u>Fe</u>	<u>SO₄²⁻</u>	Chl-a
Evaporative												
<u>Pond 03</u>	<u>8</u>	<u>485</u>	<u>44</u>	<u>2,308</u>	<u>1,848</u>	<u>0.01</u>	<u>0.1</u>	<u>113</u>	0.4	0.9	<u>1,720</u>	<u>0.9</u>
<u>Pond 07</u>	<u>12±6</u>	1,336±32	<u>62±6</u>	2,574±93	$3,859\pm88$	0.01±0.00	1.1±1.0	125±40	<u>0.4±0.0</u>	3.2±1.0	6,628±186	0.5 ± 0.2
<u>Pond 10</u>	<u>12±6</u>	934±32	<u>47±15</u>	<u>2,248±4</u>	1,982±106	0.01±0.00	0.5 ± 0.6	<u>121±35</u>	0.2 ± 0.0	0.0±0.0	4,676±113	2.4±0.8
Pond 12	<u>11±3</u>	1,060±15	<u>41±3</u>	1,450±97	<u>1,544±29</u>	0.03 ± 0.02	0.1 ± 0.1	<u>86±1</u>	0.3 ± 0.0	0.2 ± 0.1	6,454±118	1.1±0.1
Mean±SD	<u>10±2</u>	953±355	<u>49±9</u>	2,145±484	2,308±1,050	0.01 ± 0.01	$\underline{0.5 \pm 0.5}$	<u>111±18</u>	0.3±0.1	1.1±1.5	4,870±2278	1.2±0.8
Meltwater												
<u>Pond 11</u>	<u>12±2</u>	451±24	29±11	1,453±30	383±12	0.03±0.02	0.3±0.4	<u>20±2</u>	0.2±0.0	0.0±0.0	2,232±52	0.6±0.2
<u>Pond 16</u>	<u>11±5</u>	328±12	<u>18±3</u>	939±4	<u>554±18</u>	0.01±0.00	0.3±0.3	<u>24±0</u>	0.2 ± 0.0	0.1±0.1	1,885±49	0.3±0.1
Skeleton L.	<u>11±4</u>	317±115	<u>23±9</u>	1,533±241	<u>447±63</u>	0.02±0.01	2.4 ± 2.3	<u>22±2</u>	0.2 ± 0.0	0.0 ± 0.0	1,669±392	0.5 ± 0.4
<u>Mean±SD</u>	<u>11±0</u>	$\underline{365 \pm 75}$	<u>24±6</u>	1,308±323	<u>461±86</u>	0.02 ± 0.01	1.0±1.2	<u>22±2</u>	<u>0.2±0.0</u>	<u>0.1±0.0</u>	1,928±284	0.5 ± 0.1
Melt. streams	<u>3</u>	<u>653</u>	Ξ	<u>769</u>	<u>67</u>	<u>7.70</u>	<u>0.1</u>	<u>35</u>	<u>0.0</u>	<u>0.6</u>	<u>3,318</u>	<u>2.1</u>
Shoreline												
Pond 01	<u>12±3</u>	192±31	34±17	1,848±443	409±124	0.11±0.18	2.8±2.8	24±11	0.2±0.1	2.1±1.6	407±129	0.5±1.1
<u>Pond 02</u>	<u>10±2</u>	<u>131±26</u>	27±15	1,356±198	<u>103±25</u>	0.11±0.19	0.5 ± 0.7	<u>6±1</u>	0.1±0.0	0.3±0.3	273±107	0.2 ± 0.1
Mean±SD	<u>11±2</u>	<u>162±43</u>	<u>31±5</u>	1,602±348	256±216	<u>0.11±0.00</u>	1.6±1.6	<u>15±13</u>	<u>0.2±0.1</u>	1.2±1.3	340±95	<u>0.4±0.3</u>
<u>Pre-flood</u>	<u>14±3</u>	<u>216±56</u>	<u>34±4</u>	1,740±243	<u>497±115</u>	<u>0.01±0.00</u>	2.2±2.8	<u>27±4</u>	<u>0.3±0.0</u>	1.7±0.7	<u>608±231</u>	<u>0.4±0.2</u>
Post-flood	<u>11±2</u>	<u>164±40</u>	<u>32±18</u>	<u>1,681±470</u>	<u>270±172</u>	<u>0.13±0.19</u>	2.0±2.5	<u>16±13</u>	<u>0.2±0.1</u>	<u>1.5±1.7</u>	<u>311±102</u>	<u>0.5±1.0</u>
Lake Hazen s	<u>horeline</u>											
<u>Mean±SD</u>	<u>5±3</u>	<u>59±68</u>	<u>10±5</u>	<u>524±301</u>	<u>51±123</u>	0.24±0.18	1.8±2.3	<u>2±1</u>	0.1±0.0	0.0±0.0	<u>69±42</u>	0.1±0.1

 W_T : water temperature; TDS: total dissolved solids; PC: particulate carbon; DIC: dissolved inorganic carbon; DOC: dissolved organic carbon; $NO_3 + NO_2$: dissolved nitrate + nitrite; NH_4^+ : dissolved ammonium; TDN: total dissolved nitrogen; TDP: total dissolved phosphorus; Fe: dissolved iron; SO_4^2 : dissolved sulfate; chl-a: chlorophyll-a

Table 4 Comparison of the daily net exchange of carbon dioxide (CO_2) and methane (CH_4) between high Arctic terrestrial and freshwater ecosystems and the atmosphere in the Lake Hazen watershed during the growing seasons (June-August) of 2005 and 2007-2012. Positive values represent net emission of a gas to the atmosphere. Underlined values denote statistical differences of daily fluxes from other ecosystem types for each gas (linear mixed model; α =0.05; see Methods). The total and percent growing season exchange of each gas and ecosystem is also shown, as is the surface area of each ecosystem.

	CC	O ₂ flux		CI	Area			
Ecosystem	g C-CO ₂ m ⁻² d ⁻¹	Mg C-CO ₂ season ⁻¹	%	g C-CH ₄ m ⁻² d ⁻¹	Mg C-CH ₄ season ⁻¹	%	km ²	%
Aquatic								
Upland	$+0.045\pm0.180$	+598	4	$+0.001\pm0.001$	+11	2	144	2
Shoreline	$+0.031\pm0.218$	+2	0	$\pm 0.008 \pm 0.001$	+0	0	1	0
Lake Hazen	-0.014±0.269	-721	5	$+0.000\pm0.002$	+6	1	542	7
Terrestrial ^a								
P. semidesert	+0.004+0.223	+1,253	9	-0.001±0.003	-412	94	3,819	51
M. wetland	-0.955±0.291	-11,368	82	$+0.001\pm0.002$	+10	2	129	2
Glacial ice	n/a	n/a	n/a	n/a	n/a	n/a	2,809	38
Totals		-10,236	100		-385	100	7,443	100

a from Emmerton et al. 2014, 2016

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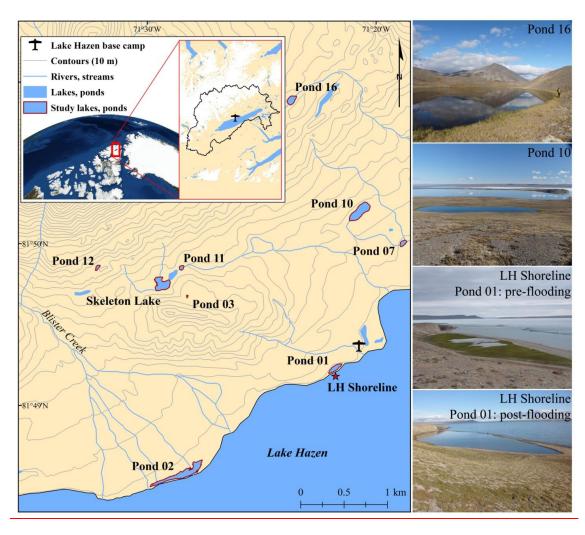


Figure 1 Map of the Lake Hazen base camp in Quttinirpaaq National Park, Nunavut, Canada. Ponds and lakes investigated in this study are indicated on the map and <u>selected sites are</u> shown in photographs. Shown inset are the general locators of the Lake Hazen watershed.

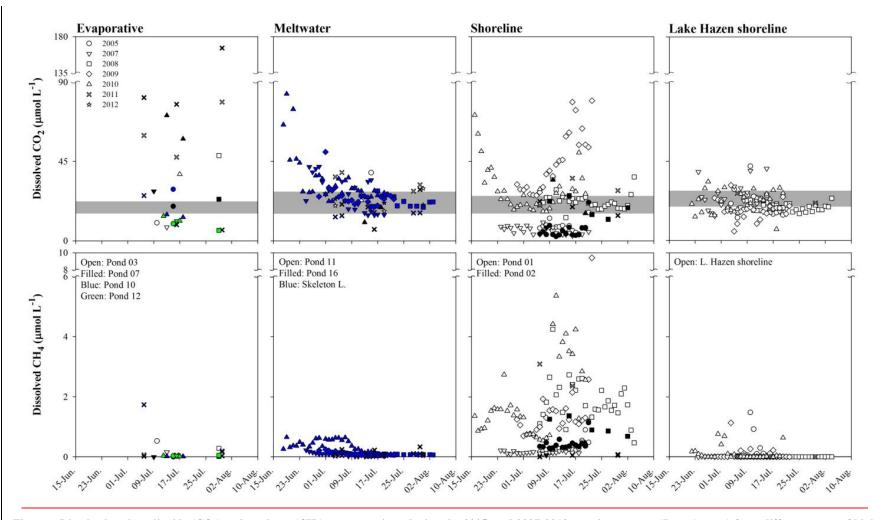


Figure 2 Dissolved carbon dioxide (CO_2) and methane (CH_4) concentrations during the 2005, and 2007-2012 growing seasons (June-August) from different types of high Arctic freshwater systems in the Lake Hazen watershed. Inset text shows site names within each freshwater type. Grey areas indicate the range of atmospheric equilibrium concentrations $\underline{CO_2}$ and $\underline{CH_4}$ during the sampling period.

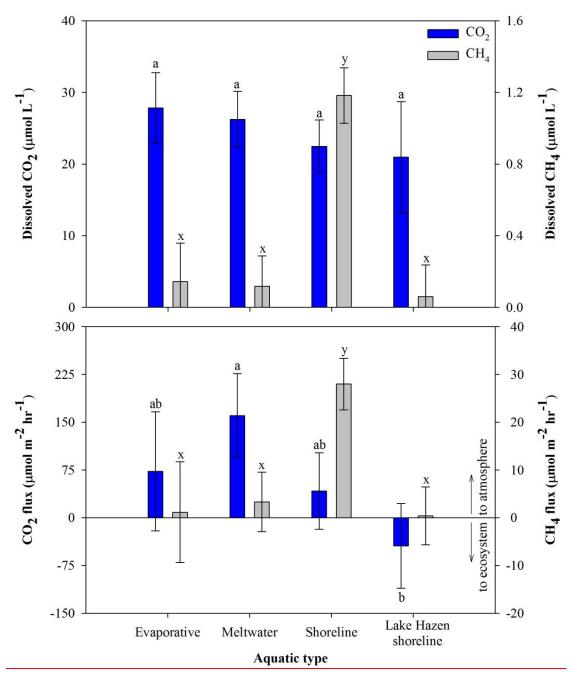


Figure 3 Mean (\pm SE) dissolved carbon dioxide (CO₂) and methane (CH₄) concentrations and fluxes during the 2005, and 2007-2012 growing seasons (June-August) from four different freshwater types in the Lake Hazen watershed. Letters denote statistical differences between ecosystem types for each gas (linear mixed model; α =0.05; see Methods).

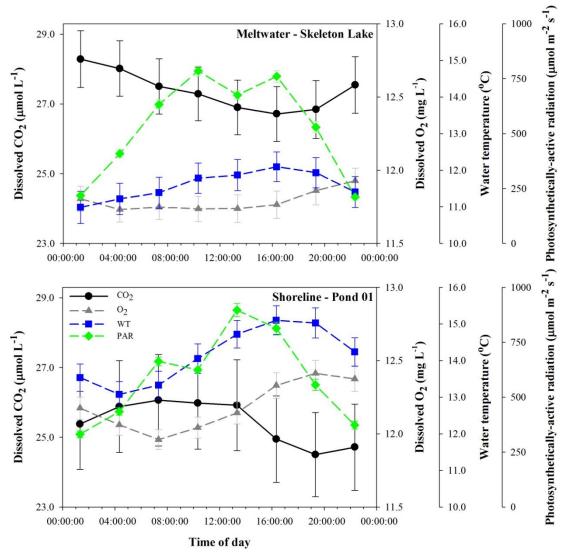


Figure $\underline{4}$ Three-hour diel dissolved carbon dioxide (CO₂) concentration, oxygen (O₂) concentration, water temperature and photosynthetically-active radiation (PAR) data measured by automated systems deployed at the shorelines of Skeleton Lake (2008-10) and Pond 01 (2008-10) during the high Arctic growing season (June-August) in the Lake Hazen watershed.