

21 **Acknowledgments**

22 This work was supported by the UK Natural Environment Research Council (grant numbers
23 NE/K000217/1, NE/K000225/1, NE/K000268/1 and NE/K000284/1). We would like to thank
24 the Aurora Research Institute in Inuvik, Prof Philip Marsh of Wilfrid Laurier University, Dr
25 Oliver Sonnentag of Université de Montréal and Dr Mark Cooper of the University of Exeter
26 for their support during the field campaigns, and Dr James Weedon of Vrije Universiteit
27 Amsterdam for support with the statistical analyses. We would also like to thank the associate
28 editor for this manuscript – Dr Breck Bowden – and three anonymous reviewers whose
29 comments have substantially improved this paper. The authors declare that they have no
30 conflicts of interest.

31

32 **Abstract**

33 Climate change poses a substantial threat to the stability of the Arctic terrestrial carbon (C)
34 pool as warmer air temperatures thaw permafrost and deepen the seasonally-thawed active
35 layer of soils and sediments. Enhanced water flow through this layer may accelerate the
36 transport of C and major cations and anions to streams and lakes. These act as important
37 conduits and reactors for dissolved C within the terrestrial C cycle. It is important for studies
38 to consider these processes in small headwater catchments, which have been identified as
39 hotspots of rapid mineralisation of C sourced from ancient permafrost thaw. In order to better
40 understand the role of inland waters in terrestrial C cycling we characterised the
41 biogeochemistry of the freshwater systems in a *c.* 14 km² study area in the western Canadian
42 Arctic. Sampling took place during the snow-free seasons of 2013 and 2014 for major
43 inorganic solutes, dissolved organic and inorganic C (DOC and DIC, respectively), carbon
44 dioxide (CO₂) and methane (CH₄) concentrations from three water type groups: lakes,

45 polygonal pools and streams. These groups displayed differing biogeochemical signatures,
46 indicative of contrasting biogeochemical controls. However, none of the groups showed
47 strong signals of enhanced permafrost thaw during the study seasons. The mean annual air
48 temperature in the region has increased by more than 2.5 °C since 1970, and continued
49 warming will likely affect the aquatic biogeochemistry. This study provides important
50 baseline data for comparison with future studies in a warming Arctic.

51 **Keywords:** Arctic catchments; inland waters; freshwater biogeochemistry; pristine
52 environment; baseline study; permafrost thaw; climate change.

53

54 **1. Introduction**

55 Climate change predictions for the Arctic regions cover a number of scenarios: warming
56 only, wetting only and warming and wetting (Zhang et al. 2013). Each of these scenarios
57 indicates intensification of Arctic hydrological regimes, creating more extreme droughts and
58 floods (Déry et al. 2009; Rawlins et al. 2010); this is expected to have a profound influence
59 on subsurface C pools and rates of permafrost loss (Hinzman et al. 2013). Modelled warming
60 scenarios predict that there will be a large (53-66 %) reduction in the areal extent of the upper
61 2-3 m of permafrost by 2100 (Schuur et al. 2013), albeit with a large range of uncertainty
62 (Jiang et al. 2016), which is expected to result in considerable loss of C from permafrost soils
63 (Schuur et al. 2015; Jiang et al. 2016). Warming conditions in the Arctic are also expected to
64 alter the areal extent of thaw ponds and lakes as seasonal permafrost subsidence increases
65 (Karlsson et al. 2014; Smith et al. 2005; van Huissteden et al. 2011; Liljedahl et al. 2016);
66 these water bodies are associated with high CO₂ and CH₄ release to the atmosphere
67 (Negandhi et al. 2013; Tan and Zhuang 2015). Intensification of the hydrological cycle, to
68 which the Arctic is predicted to be more sensitive than other areas of the globe (Bintanja and

69 Selten 2014), is thought to have begun to manifest itself in measurable changes in the C cycle
70 in some Arctic catchments (Vonk et al. 2013), although more studies focusing on both large
71 river systems and small headwater catchments are needed to predict and model long-term
72 change (Holmes et al. 2012; Wrona et al. 2016).

73 Hydrological and C cycles in the Arctic are closely linked, with surface water accessing
74 contemporary C pools, and groundwater potentially accessing older, deeper C pools as
75 permafrost thaws (Neff et al. 2006; Raymond et al. 2007). There is a general assumption that
76 warming in Arctic regions will increase dissolved organic C (DOC) export to the Arctic
77 Ocean as terrestrial biomass production and hydrological connectivity (both vertical and
78 lateral) increases (e.g. Amon et al. 2012; Tank et al., 2016). In sub-Arctic Sweden for
79 example, permafrost peatland plateaus are associated with low annual DOC export (2-3 g C
80 m⁻² yr⁻¹) dominated by the snow melt period (c. 70%), and non-permafrost fens are
81 characterized by much higher DOC export (7 g C m⁻² yr⁻¹) due to more sustained annual flow
82 through deeper soil layers that then discharges to streams (Olefeldt & Roulet 2014).
83 However, Striegl et al. (2005) showed that growing season export of DOC decreased
84 significantly between 1978-1980 and 2001-2003 in the Yukon River, Alaska. This was likely
85 caused by the combined effect of increased active layer depth, longer residence times in the
86 subsurface, and microbial mineralisation of DOC in the unfrozen soil and groundwater zone.
87 Hence a large fraction of soil-derived DOC would be either retained or mineralised within the
88 subsurface horizons, reducing DOC transport to the drainage network. This is supported by a
89 controlled leaching experiment that found (regardless of temperature and leaching time) that
90 only small amounts of DOC could be released from tundra soils, and that mobilisation of C
91 occurred largely in the particulate phase (Guo et al. 2007). Hydrological processes controlled
92 by active layer depth in permafrost zones therefore play a key role in mobilising and
93 exporting terrestrial C, but there is limited understanding of these processes at local scales,

94 particularly in headwater catchments (Drake et al. 2015; Holmes et al. 2012). Furthermore,
95 few freshwater biogeochemistry studies in the Arctic include all dissolved C species,
96 generally focusing on DOC, DIC, CO₂ or CH₄ individually. Permafrost thaw has, however,
97 been linked to increased aquatic C concentrations and fluxes in all forms: DOC (Olefeldt and
98 Roulet 2014), DIC (Dornblaser and Striegl 2015), CO₂ (Shirokova et al. 2013), and CH₄
99 (Walter et al. 2006; Shirokova et al. 2013). These examples from studies in Northern
100 America and Northern Europe therefore show that there is currently not a consensus on
101 whether progressive deepening of the active layer will lead to an increase or a decrease in
102 riverine DOC concentrations and fluxes.

103 The major ion biogeochemistry of aquatic systems can provide insight into the source(s),
104 extent and rate of the mobilisation of thawed soil material, and it has been hypothesized that
105 concentrations of weathering-derived ions will increase as thaw depth and thermokarst
106 slumping increases, exposing previously frozen mineral soils (Frey and McClelland 2009;
107 Vonk et al. 2015a). There is already some evidence for this from Alaska (Keller et al. 2010)
108 and Siberia (Frey et al. 2007; Tank et al. 2012).

109 We carried out a study of specific surface water types in a small catchment area of the
110 western Canadian Arctic to identify spatial patterns and distinctive biogeochemical signatures
111 in all forms of aquatic C and major ions. Previous work in the Siksik Creek catchment found
112 that mineral earth hummocks slow runoff rates to the stream channel by increasing surface
113 roughness, but this is overridden by the higher hydraulic conductivity of the organic-rich inter
114 hummocks during high water-table periods; these processes drive site hydrology in the
115 months following the freshet (Quinton and Marsh 1998; 1999; Quinton et al. 2000). Quinton
116 and Pomeroy (2006) also found that snowmelt dominated surface water chemistry early in the
117 thaw season, but that inputs from soil and decomposing vegetation in the conductive inter-

118 hummocks became more important as the season progressed, coupled with inputs from the
119 more calcareous streambed material during low flows. It is not known whether the
120 hydrological influence of the hummock/inter-hummock geomorphology extends to the lake
121 systems in the region. Furthermore, the vegetation in this area has altered substantially in the
122 last three decades through "shrubification" (increases in tall shrub tundra and alder density of
123 68% and 35% respectively; Lantz et al. 2013), and there are few (if any) studies linking
124 shrubification to C export in the hydrological system.

125 In this study we hypothesise that hydrologically distinct water types will differ geochemically
126 on the basis of biogeochemical processes and hydrological connections – which control
127 aquatic C (CO₂, CH₄, DOC and DIC) and major ion concentrations – that are likely to be
128 sensitive to future climate change. We aim to test this hypothesis by (1) describing the
129 geochemistry of the water types sampled in the study area and (2) linking the differences
130 observed to specific biogeochemical processes in the terrestrial-aquatic continuum,
131 particularly the presence or absence of enhanced seasonal permafrost thaw. Apart from some
132 earlier research in Siksik Creek (Quinton and Marsh 1998; 1999; Quinton et al. 2000;
133 Quinton and Pomeroy 2006) this is the first time that the biogeochemistry of the wider
134 aquatic system has been characterised in this part of the western Canadian Arctic. Hence this
135 study forms an important platform for future research; this might include the potential
136 impacts of the new Inuvik-Tuktoyaktuk road, which runs within 500 m of the study area and
137 construction of which is currently taking place in part of the study watershed.

138

139 **2. Study site**

140 *2.1 Location and climate*

141 The study area (68° 44' 54.5" N, 133° 29' 41.7" W) is located east of the Mackenzie River
142 Delta, *c.* 45 km north of the town of Inuvik, Northwest Territories, Canada, and north of the
143 shrub-tundra transition zone. The total study area covers approximately 14 km², including the
144 0.94 km² Siksik Creek catchment (Fig. 1), with an elevation range of approximately 50-110
145 m above sea level. Within this area are six lakes (ranging from 0.006 to 0.34 km²) among
146 gently rolling hills with Siksik Creek draining into a larger stream system, Trail Valley Creek
147 (Fig. 1). Trail Valley Creek, a 68.3 km² catchment, flows east, through a relict glacial
148 meltwater channel incised into the Arctic plateau and drains into the saline Husky Lakes,
149 which are connected to the Beaufort Sea (Teare 1998). Climate in the study area and the
150 discharge of Trail Valley Creek have been monitored by Environment Canada since 1977
151 (Endrizzi and Marsh 2010; Quinton and Marsh 1998; 1999; Quinton et al. 2000; Quinton and
152 Pomeroy 2006); the Trail Valley Creek gauging station is just upstream of the Siksik
153 confluence (Fig. 1). The discharge towards the bottom of Siksik Creek catchment was
154 monitored during the 2013-14 sampling seasons, but there was some equipment failure
155 resulting in a patchy record, while the Trail Valley Creek discharge data was more
156 consistently available (Fig. 2).

157 The study area is in the continuous permafrost zone of the western Canadian Arctic, with an
158 average end of season active layer thickness (ALT) in Siksik catchment of *c.* 0.5 m in both
159 2013 and 2014 (see section 5.1). Mean air temperatures were -24.9°C for January to April
160 and 6.7°C for May to September in 2013, -16.7°C for October 2013 to April 2014, and 7.1°C
161 for May to September 2014 (Fig. 2). These fall close to the mean monthly temperatures in the
162 region of 7.7°C ($\pm 1.1 \sigma$) from May to September, and -20.9°C ($\pm 2.1 \sigma$) from October to
163 April (Teare 1998; Environment Canada, accessed May 2015). However, the annual average
164 air temperature in Inuvik has increased by 2.5 °C since 1970, and active layer depths at

165 Illisarvik on Richards Island, c. 120 km north-northwest of the site, have increased by around
166 8 cm since 1983 (Burn and Kokelj 2009).

167 Precipitation during the study period was 162 mm in 2013 and 277 mm in 2014 (Fig. 2),
168 bracketing mean annual precipitation from 1960 to 2005 ($253 \text{ mm} \pm 49 \sigma$, of which $38\% \pm 18$
169 σ fell as rainfall – note, however, that winter precipitation data in this area can be unreliable;
170 Environment Canada, accessed May 2015; Marsh et al. 2000). The hydrology of the area is
171 dominated by spring snowmelt (c. 90% of annual flow; Quinton and Marsh 1999) following
172 an eight-month snow covered season, while the growing season is limited to June through
173 August (Quinton et al. 2000). The freshet commenced in late May (Fig. 2) with deep snow
174 beds remaining until mid-June in both 2013 and 2014. Average daily streamflow during the
175 growing season for 2013 and 2014 was 1.3 and 1.2 mm day^{-1} , respectively, in Trail Valley
176 Creek, and 2.3 mm day^{-1} in Siksik for 2014, however both miss the major freshet event (Fig.
177 2). Average annual streamflow in Trail Valley Creek for the same period (June to October)
178 from 1979-2011 was $0.6 \text{ mm} (\pm 0.2 \sigma)$.

179 The vegetation of the area consists predominantly of ericaceous shrubs, sedges (*Eriophorum*
180 and *Carex* spp.), bryophytes and lichens, with patches of tall shrubs on hillslopes (*Alnus*
181 *viridis* and *Betula* spp.). The riparian areas are characterized by *Betula glandulosa* and *Salix*
182 spp.).

183 2.2 Geology

184 The underlying geology of the Siksik Creek catchment and surrounding lakes system is
185 Miocene/Pliocene in age and comprises unconsolidated chert, quartzitic sandstone and
186 siltstone alluvial gravel that makes up the Tertiary Beaufort Formation (Rampton 1987; Teare
187 1999). This is overlain by a one-metre thick Quaternary Pleistocene till, deposited following
188 the early (c. 100,000 years BP) and late (c. 21,000-25,000 years BP) Wisconsin glaciation

189 (Rampton 1987). The surface topography overlying this till layer is dominated by organic-
190 rich topsoil, between 0.05 and 0.5 m thick, underlain by mineral soils in a heterogeneous
191 hummock/inter-hummock morphology. The hummocks are on average 0.4 to 1 m wide and
192 0.1 to 0.4 m high, consisting of mainly mineral soils, while the inter-hummocks are filled
193 with 0.2 to 0.5 m of loose peat, moss and vascular plant litter, which may contain 5 to 10 cm
194 wide soil pipes; these are thought to be the primary controls of site hydrology (Quinton and
195 Marsh 1998; 1999; Quinton et al. 2000; Quinton and Pomeroy 2006). The organic-rich peat
196 layers consist of weak to strongly decomposed plant material, accumulated during the last *c.*
197 1,000 to *c.* 30,000 years (Rampton 1987). Physical weathering along the main branch of
198 Trail Valley Creek has caused the deposition of some fine-silt to coarse-pebbled colluvial
199 material within the system. Cryoturbation is common in the region, resulting in periglacial
200 structures such as mud boils and ice-wedge polygons. There are relatively few thermokarst
201 features in the study area; what few there are include thaw lakes and several active layer
202 detachments (Rampton 1987; Quinton and Marsh 1998).

203 *2.3 Sampling strategy*

204 Water was collected for analysis of bulk chemistry and dissolved C species from 27 different
205 sites throughout the study area (Fig. 1). Sampling sites were selected to represent the
206 contrasting types of surface water bodies and geomorphological settings that can be found in
207 this part of the western Canadian Arctic tundra, including lakes, pools and streams of
208 different size. The sampling sites were then grouped together into water types based on their
209 hydrological and geomorphological setting: multiple lakes and their outlets, polygonal pools
210 associated with ice-wedge polygons, and streams including Siksik Creek, lake inlets and Trail
211 Valley Creek (a larger, 68.3 km² catchment, regional stream system; Fig. 1).

212 These three geomorphologically distinct water types were sampled on 6 to 18 occasions
213 during the snow-free seasons in 2013 and 2014 (Fig. 2). The lake samples (“Lake”) were
214 taken from shore-side at the mid-point and outlet of six lakes (Fig. 1); the combined total area
215 of these lakes was 0.73 km². The polygonal pool samples (“Polygon”) were collected from
216 pools ranging in surface area from 0.5 to 3.0 m² that form in between the ice-wedges;
217 samples were collected from three different polygonal areas totalling 0.04 km², including
218 polygons that feed Siksik Creek and a lake (Fig. 1). The stream samples (“Stream”) were
219 collected from four points along the 3.1 km long Siksik Creek channel, three points along
220 Trail Valley Creek immediately above and below the Siksik confluence, and five lake inlet
221 locations (Fig. 1; note that these sites are part of a larger study, hence the reason why site
222 names are not in strict numerical order).

223

224 **3. Methods**

225 Sampling campaigns took place during the period between spring snowmelt (early June) and
226 autumn (early September) of 2013 and 2014 (Fig. 2). Surface water samples ($n = 238$) were
227 collected using a 60 ml syringe from approximately 5 cm depth in the water column and the
228 sample injected through 0.45 µm Millipore syringe-driven filters and stored without
229 headspace in 30 or 60 ml bottles that were first rinsed with the filtered sample. In situ field
230 parameters (pH, electrical conductivity – EC, and temperature) were measured at the same
231 time as sampling using Hanna Instruments[®] HI-9033 and HI-9124 meters. Samples were kept
232 cool (< 6°C) and dark in the field prior to refrigeration in the laboratory. The filtrate from one
233 sample bottle was analysed for DOC and DIC at the Centre for Ecology and Hydrology (CEH
234 – Edinburgh, UK) on a PPM LABTOC Analyser (detection range of 0.1–4000 mg l⁻¹);
235 concentrations were calculated based on a three point calibration curve with a maximum of

236 50 mg l⁻¹. The filtrate from the second sample bottle was analysed for major ions at the
237 University of Stirling (Stirling, UK) using a DX-120 IC (Dionex Corp. – Cl⁻, NO₃⁻, and SO₄²⁻
238 ; minimum detection limit of 0.03 mg l⁻¹) and an iCAP 6000 ICP-OES (Thermo Fisher
239 Scientific Inc. – Al³⁺, Ca²⁺, total Fe, K⁺, Mg²⁺, total Mn, Na⁺, P and Si; minimum detection
240 limit of 0.05 mg l⁻¹).

241 Dissolved CO₂ and CH₄ gas samples (*n* = 219) were collected using the headspace technique
242 (Kling et al. 1992a; Dinsmore et al. 2013), where a 20 ml headspace of ambient air was
243 equilibrated with a 40 ml water sample (collected from between 2 and 10 cm water depth) in
244 a 60 ml syringe at natural stream temperature by shaking the syringe for 1 min vigorously
245 underwater at the sampling point. Sampling depth was noted and used to calculate total (air
246 plus water) system pressure. The equilibrated headspace (20 ml) was then injected into a pre-
247 evacuated gas-tight borosilicate Exetainer[®] tube (Labco, UK) and transported back to the UK.
248 Multiple ambient samples were collected and stored in Exetainer[®] tubes throughout each
249 day's sampling trip. Both headspace and ambient samples were analysed at CEH, Edinburgh
250 on an HP5890 Series II gas chromatograph (Hewlett–Packard) with flame ionization detector
251 and attached methaniser for CH₄ and CO₂, respectively. Detection limits for CO₂ and CH₄
252 were 7 ppmv and 84 ppbv, respectively. Concentrations of CO₂ and CH₄ dissolved in the
253 stream water were calculated from the headspace and ambient concentrations using Henry's
254 Law (e.g. Hope et al. 1995).

255 Active layer depths were measured in June, July and September in both years at randomly
256 located points along 3 transects crossing Siksik catchment (*n* = 10 points per transect).
257 Depths were measured at 4 random spots within *c.* 1 m of each measurement point in both
258 hummock and inter-hummock areas using a long steel rod marked with measurement
259 graduations (i.e., *n* = 8 measurements per point, *n* = 30 points in total across the catchment).

260 Significant differences between the measured variables' means for each group were analysed
261 by applying an ANOVA in R (version 3.1.1) using a linear model, then testing the differences
262 using the Tukey's Honest Significant Differences test ($P < 0.05$; Table 1).

263 Principal components analysis (PCA) was carried out on the hydrochemical dataset to
264 simplify the description of variability (Filella et al. 2014). Samples with missing values for
265 the variables included in the PCA (DOC, DIC, $\text{CO}_2\text{-C}$, $\text{CH}_4\text{-C}$, Al^{3+} , Ca^{2+} , Cl^- , total Fe, K^+ ,
266 Mg^{2+} , total Mn, Na^+ , Si, and $\text{SO}_4^{2-}\text{-S}$), were first removed and the PCA was then applied to
267 the remaining dataset ($n = 181$) using the "prcomp" function in R. The principal components
268 (PCs) that best described the variability in the dataset were identified, and compared with the
269 biogeochemical variables used to define the PCs (plus the descriptive variables pH,
270 temperature, electrical conductivity, total dissolved solids – TDS, the sum of all measured
271 chemical constituents of a water sample in mg l^{-1}) using a Pearson pair-wise correlation
272 ("rcorr" function, "Hmisc" package in R). This was done for the entire dataset, as well as the
273 three water types individually.

274 To test if there was significant spatial connectivity between sites, Pearson pair-wise
275 correlations (method as above) were carried out to determine "synchrony" between sites for
276 each chemical species (after Kling et al. 2000). Aquatic synchrony analyses are intended to
277 highlight the co-variance of geochemistry at sites that are well connected physically (e.g.
278 stream sites upstream or downstream from one another), in comparison to those that are
279 physically separated (e.g. two disconnected lakes). This was carried out for two groups; those
280 sites outside Siksik catchment (sampled less regularly), and those within (sampled more
281 regularly; Fig. 2). For each chemical species, correlation coefficients were determined for
282 every possible pair of sites within a group, and the percentage of correlations that were
283 significant ($P < 0.05$) was then calculated; we term this "spatial synchrony." Conversely, to

284 test for linkages between specific pairs of sites, the correlations were isolated by site and the
285 average correlation was taken for all the C species and all the ions for each site pair (see
286 section 4.3); we term this “temporal synchrony.” Finally, we also analysed for “synchrony-
287 through-time,” i.e. whether the variability of specific variables across all sites was correlated
288 to the time of sampling. This was done using Pearson pair-wise correlations between each
289 variable at each site and the day of year (DOY; i.e. day 1-365); this was also split based on
290 whether sites were within or outside Siksik catchment. This method treats the sampling date
291 as a variable, just like DOC concentration for example, and hence we test for whether a
292 change in DOY is reflected in changes of chemical species concentrations. We further test for
293 trends through time graphically, see section 5.1.

294 To explore the potential influence of weathering inputs on dissolved C concentrations at the
295 study site we examined the Ca^{2+} and Si ratios to Cl^- . Si and Ca^{2+} are the most likely inputs
296 from the underlying glacial geology, and their ratio to Cl^- accounts for the influence of
297 element concentration due to evapotranspiration (Dean et al. 2014; Moulton et al. 2000). Cl^-
298 at the study site is assumed to have a dominantly wet and dry airborne deposition source
299 because the late Holocene marine transgression is unlikely to have reached the elevations of
300 the study region (Hill et al. 1992; Campeau et al. 2000).

301

302 **4. Results**

303 *4.1 Bulk Chemistry*

304 Electrical conductivity (EC) was similar across the water types, with Stream having the
305 lowest (50.4 ± 2.0 [standard error – SE] $\mu\text{S cm}^{-1}$), and Lake the highest ($63.7 \pm 3.4 \mu\text{S cm}^{-1}$);
306 variability was relatively low, with coefficients of variation (CVs) ranging from 0.36 to 0.49

307 (Table 1). Water temperature varied from $4.8^{\circ}\text{C} \pm 0.3$ to $8.6^{\circ}\text{C} \pm 0.6$ across the groups, with
308 Stream the coldest and Lake the warmest, and CVs of 0.45 to 0.75 (Table 1). Mean pH of the
309 water types (Table 1; Fig. 3) varied between $5.74 (\pm 0.15)$ and $6.69 (\pm 0.05)$ with Polygon
310 samples the most acidic (5.74 ± 0.15), but most variable (CV = 0.16), and Lake the least
311 acidic (6.69 ± 0.05).

312 Calcium (Ca^{2+}) was the dominant cation in the waters (average $6.13 \pm 0.19 \text{ mg l}^{-1}$ across all
313 samples), with the greatest variability observed in the Polygon samples (CV = 0.61; Fig. 3).
314 Magnesium (Mg^{2+}) was the next dominant cation (average $2.79 \pm 0.09 \text{ mg l}^{-1}$ across all
315 samples), followed by sodium (Na^{+} ; average $1.57 \pm 0.05 \text{ mg l}^{-1}$ across all samples); both
316 Mg^{2+} and Na^{+} had similar concentrations in all water types (CVs of *c.* 0.50 for both ions
317 across all samples; Table 1). The Polygon samples again had the highest variability in Mg^{2+}
318 (CV = 0.65), but the Lake samples had the most variability in Na^{+} concentrations (CV = 0.56;
319 Fig. 3). Silica (Si) was lower in the Lake samples ($1.04 \pm 0.11 \text{ mg l}^{-1}$) compared to Stream
320 ($2.84 \pm 0.15 \text{ mg l}^{-1}$) and Polygon samples ($2.79 \pm 0.25 \text{ mg l}^{-1}$; Fig. 3). The dominant metal
321 was (total) Fe (0.28 ± 0.03 to $0.54 \pm 0.05 \text{ mg l}^{-1}$), with lowest and highest concentrations in
322 the Polygon and Stream samples, respectively (Fig. 3).

323 Sulphate ($\text{SO}_4^{2-}\text{-S}$) was the dominant anion in the Lake samples ($3.85 \pm 0.39 \text{ mg l}^{-1}$; Fig. 3),
324 but was lower in Polygon ($0.73 \pm 0.32 \text{ mg l}^{-1}$) and Stream ($1.82 \pm 0.24 \text{ mg l}^{-1}$) samples, where
325 DIC (a proxy for HCO_3^{-} , which was not measured directly in this system; see section 4.2; Fig.
326 4) was the dominant anion.

327 Nitrate ($\text{NO}_3^{-}\text{-N}$) was not analysed in 2013, and was only detectable in one Lake sample in
328 2014 (0.26 mg l^{-1}), so was not considered important in the aquatic system. Phosphorous (P)
329 was only present in very low concentrations in a few samples, being generally below the
330 detection limit. Potassium (K^{+}), however, was present in most samples: higher in the Lake

331 samples ($0.63 \pm 0.05 \text{ mg l}^{-1}$) compared to the Polygon and Stream samples (0.15 ± 0.05 and
332 $0.22 \pm 0.05 \text{ mg l}^{-1}$ respectively; Fig. 3).

333 *4.2 Carbon Species*

334 DOC concentrations were highest in the Polygon group ($32.6 \pm 1.0 \text{ mg C l}^{-1}$), higher than
335 both the Stream ($23.0 \pm 0.6 \text{ mg C l}^{-1}$) and Lake ($16.6 \pm 0.7 \text{ mg C l}^{-1}$). DOC concentrations did
336 not vary substantially within the groups (CVs of 0.21 to 0.32; Table 1; Fig. 4).

337 DIC concentrations followed a similar pattern to DOC, with the highest concentrations
338 observed in the Polygon ($4.16 \pm 0.53 \text{ mg C l}^{-1}$), followed by the Stream ($2.93 \pm 0.20 \text{ mg C l}^{-1}$)
339 and Lake ($2.51 \pm 0.28 \text{ mg C l}^{-1}$) groups. DIC variability was consistently greater than DOC,
340 with CVs of 0.79 to 0.86 (Table 1; Fig. 4).

341 The highest CO_2 concentrations were again in the Polygon group ($4.13 \pm 0.42 \text{ mg C l}^{-1}$); the
342 Stream and Lake concentrations were at least 50% lower (2.01 ± 0.10 and 1.19 ± 0.10
343 mg C l^{-1} , respectively); variability in CO_2 concentration (CVs 0.56 to 0.62) was in between
344 that of DIC and DOC (Fig. 4). CH_4 concentrations in comparison were consistently low
345 compared to the other C species across all groups (generally $<0.05 \text{ mg C l}^{-1}$; Table 1), but
346 were highly variable (CVs of 1.35 to 4.05; Fig. 4).

347 Total C concentrations were highest in the Polygon group (40.9 mg C l^{-1}), followed by
348 Stream (27.9 mg C l^{-1}) and Lake (20.3 mg C l^{-1} ; Fig. 5). The Polygon samples were
349 characterised by higher concentrations of all C species compared to the other water types,
350 with the exception of CH_4 , which was slightly higher in the Lake samples (Fig. 4). The
351 relative proportion of the different C species to each other was similar across all water types
352 (Fig. 5), although the total C concentrations varied significantly. DOC accounted for 80% or
353 more of total C concentrations, followed by DIC (c. 10-15%) and CO_2 (5-10%); CH_4 was less

354 than 0.1% (Fig. 5). DIC concentrations in the Polygon samples were comparable to CO₂; in
355 the other groups DIC was greater.

356 To explore the potential influence of weathering inputs on dissolved C concentrations at the
357 study site we examined the relationship between Ca²⁺ and Si concentrations, and Ca²⁺/Cl⁻ and
358 Si/Cl⁻ ratios with aquatic C species. The Ca²⁺ and Si concentrations, and Ca²⁺/Cl⁻ and Si/Cl⁻
359 ratios correlated poorly with DOC (maximum R² < 0.08), DIC (maximum R² < 0.05), CO₂
360 (maximum R² < 0.01) and CH₄ concentrations (maximum R² < 0.01).

361 *4.3 Statistical Analysis*

362 The differing geochemistry of the water types is described in the previous two sections, and is
363 highlighted by the Tukey's Honest Significant Differences test (Table 1). The mean values
364 for the Polygon and Stream samples were significantly different for three variables (pH, DOC
365 and CO₂), contrasting with the mean values for the Lake and Polygon samples which were
366 significantly different for all variables except EC, CH₄, Ca²⁺ and Mg²⁺; Mg²⁺ was the only
367 variable for which the means of all the water types were indistinguishable.

368 In order to simplify the variability inherent in the dataset, we first carried out principal
369 components analysis (PCA) on the entire dataset. The first six principal components (PCs)
370 each explained at least 5% of the variability within the entire dataset (and also for each of the
371 three water types), and cumulatively explained 79%; all other PCs were omitted from further
372 analysis. The PCs were then correlated with the measured variables (Table 2). PCs 1 and 2
373 described almost half the variability within the data and are both highly correlated with
374 virtually all the variables in the dataset (Table 2). The rest of the PCs correlated with at least
375 half of the variables, but only total Mn is significantly correlated with all PCs for the entire
376 dataset.

377 PCAs were also carried out for the each of the individual water types. The first six PCs were
378 again selected (describing cumulatively between 79 and 91% of variability in each group),
379 and the number of times a variable was correlated with a PC across all three of the water
380 types was collated (Table 2). This demonstrates how often a variable was significant in
381 describing the variability in each PC across the PCAs for each group, and therefore how
382 important it was in defining the overall water geochemistry, in comparison with the overall
383 PCA. In this case total Mn was the least significant, along with temperature, Ca^{2+} , TDS, EC
384 and pH (Table 2); the most consistently significant variables were $\text{CO}_2\text{-C}$, DOC, $\text{CH}_4\text{-C}$ and
385 Na^+ (Table 2). This indicates that the latter variables are key to differentiating/grouping the
386 water types by biogeochemical processes.

387 To determine the level of geochemical connectivity we estimated the spatial synchrony of
388 chemical species across the different sampling points (Kling et al. 2000). The percentage of
389 significant correlations (Table 3) shows, for each chemical species, how often the
390 concentrations co-varied across the different sampling sites. Ca^{2+} and Mg^{2+} , the major cations
391 in the system (see Section 4.1), were the most synchronised species across the sites outside
392 Siksik catchment, along with TDS and Si (Table 3). In the sites within Siksik catchment Ca^{2+} ,
393 Mg^{2+} and TDS were again highly synchronised, but Si and K^+ were the most synchronised
394 (Table 3).

395 The temporal synchrony between specific site pairs (all possible pairs of sites either within or
396 outside Siksik catchment; Fig. 1) is shown in Tables 4 and 5. The mean synchrony in the sites
397 outside Siksik catchment is 0.34 ± 0.25 for the C species, and 0.52 ± 0.19 for the ions (error
398 ranges are one standard deviation; Table 4). The mean synchrony in the sites within Siksik
399 catchment is 0.38 ± 0.18 for the C species, and 0.48 ± 0.14 for the ions (Table 5).

400 Synchrony-through-time is more important for the ions compared to the C species for the
401 sites within as well as outside Siksik catchment (Table 6). For sites within Siksik catchment,
402 Si, K⁺, TDS, Ca²⁺, Mg²⁺, SO₄²⁻-S and Cl⁻ were all significantly correlated with the sampling
403 day of year for the majority of samples. For the sites outside Siksik catchment, Na⁺, SO₄²⁻-S,
404 Ca²⁺, Mg²⁺ and TDS were also correlated with sampling day. The C-species in both site
405 groups were only significantly correlated with the sampling day of year for less than 30% of
406 samples (Table 6).

407

408 **5. Discussion**

409 This study aimed to describe the geochemical signatures of the study waters across both
410 space and time, and in turn identify the key biogeochemical controls on the aquatic chemistry
411 at the study site. This is firstly addressed from the perspective of the geochemistry and then
412 secondly, aquatic C concentrations.

413 *5.1 Controls on aquatic geochemistry*

414 The neutral to acidic pH across all groups (7.27 to 3.89; Fig. 3) likely reflects its origin in the
415 organic-rich, upper soil layer of the study region through which much of the soil water flows
416 due to the shallow active layer (Quinton and Pomeroy 2006; Fig. 6). This acidifies the water
417 to a degree similar to that observed in temperate peatlands (pH 4.5 to 7.0; Billett and Moore
418 2007; Billett et al. 2007) and organic rich Western Siberian lowlands (pH 3.0 to 7.0;
419 Shirokova et al. 2013), as opposed to the more buffered waters observed in the Alaskan,
420 Eastern Canadian, Far East Siberian and Svalbard Arctic regions (pH 6.5 to 9.0; Crawford et
421 al. 2013; Kling et al. 1992b; Mann et al. 2012; Negandhi et al. 2013 and 2014; Stutter and
422 Billett 2003). The slightly higher pH in the Stream and Lake groups relative to the polygons

423 may indicate a lesser influence of this organic layer, or CO₂ degassing (evasion) losses when
424 soil water enters the lakes and streams, or even a greater carbonate input; however, Ca²⁺
425 concentrations in these groups do not support the latter conclusion (Fig. 3).

426 Electrical conductivity in the sampled waters was consistently low across all water samples
427 ($55.7 \pm 1.7 \mu\text{S cm}^{-1}$; Table 1), in the lower range of reported values from other Alaskan,
428 Canadian and Siberian Arctic sites (7 to 843 $\mu\text{S cm}^{-1}$; Kling et al. 1992b; Kokelj et al. 2005;
429 Mann et al. 2012; Shirokova et al. 2013). The low conductivity and pH of the sampled waters
430 could also indicate that precipitation is important in defining the water chemistry, as rainfall
431 in the region generally has a pH of *c.* 5.5 (Kling et al. 1992b) and a low conductivity of
432 between 2.9 $\mu\text{S cm}^{-1}$ (Kling et al. 1992b) and *c.* 8 $\mu\text{S cm}^{-1}$ (median of 5 samples, unpublished
433 data). However, the PCA highlights DOC and CO₂ as significant in defining the different
434 water groups' biogeochemical signatures (Table 2), neither of which are likely to be derived
435 from precipitation. The relatively high spatial synchrony of TDS (for which electrical
436 conductivity is a proxy; Table 3) in the sites outside Siksik catchment may indicate that
437 evapotranspiration plays an important role in defining the freshwater biogeochemistry.
438 However, TDS was also significant in the sites within Siksik catchment where
439 evapotranspiration is unlikely to be a controlling factor given the lower surface water area,
440 unless the concentration of solutes by evapotranspiration is occurring primarily in the soil
441 solution prior to entering the stream. This confirms that, despite precipitation being the
442 principal direct source of surface water in the study area (deep groundwater contributions are
443 negligible due to the shallow active layer), localised soil, fluvial and lacustrine processes are
444 more important in defining the water chemistry (Quinton and Pomeroy 2006).

445 Previous studies have used water chemistry as an indicator of enhanced permafrost thaw and
446 thermokarst processes (e.g. TIS, the total concentration of inorganic solutes; Frey and

447 McClelland 2009; Kokelj et al. 2005). Degrading permafrost is expected to increase the
448 concentration of inorganic solutes as subsurface water flow is able to interact with, and
449 weather, deeper, newly thawed mineral soils and sediments (Kokelj et al. 2005). Depending
450 on the geochemical composition of the frozen material, different chemical species may be
451 leached into the aquatic system during thawing, such as Ca^{2+} , K^+ , Mg^{2+} , Na^+ , S and Si (Kling
452 et al. 1992b; Kokelj et al. 2005; Stutter and Billett 2003; Frey et al. 2007; Keller et al. 2007;
453 Frey and McClelland 2009). The synchrony-through-time analysis suggests that the time of
454 sampling is important for sample biogeochemistry. Fig. 6 explores this further, showing the
455 time series of key chemical species identified in the PCA and synchrony analyses through the
456 thaw seasons of both 2013 and 2014, along with the active layer depth. While there is some
457 indication of an increase in TIS during 2013 (alongside DOC, Si and K^+), this was not seen in
458 2014 where larger fluctuations than the 2013 seasonal increase were seen on much shorter
459 time scales (Fig. 6). In 2014 in general, where the temporal resolution is higher, this
460 increasing trend is only apparent at the first few sampling points of the year, with
461 concentrations dropping towards the end of the measurement period (Fig. 6). This highlights
462 the need for high resolution sampling when seeking to identify geochemical signatures in
463 streams in these environments.

464 Ca^{2+} and Si are the most likely elements to be derived from mineral weathering of thawing
465 permafrost material in the study area, particularly the addition of Ca^{2+} from calcareous
466 material in parts of the system (Quinton and Pomeroy 2006). Ca^{2+} and Mg^{2+} were well
467 correlated ($R^2 = 0.91$), were the dominant cations in the system, and were both significant in
468 the spatial synchrony analysis with positive Pearson r values (0.67 to 0.76), suggesting that
469 these ions behave relatively conservatively within the system (Table 3). Furthermore, there is
470 no relationship between $\text{Ca}^{2+}/\text{Cl}^-$ ratios and Cl^- ($R^2 = 0.27$) which would indicate the
471 introduction of Ca^{2+} to the system relative to (Cl^-) inputs from wet and dry deposition. Ca^{2+}

472 (and Mg^{2+}) does not show a seasonal trend in either 2013 or 2014 (Fig. 6), indicating that the
473 concentrations of these ions were not controlled by increasing weathering inputs as the active
474 layer deepened through the thaw season. Ca^{2+} and Mg^{2+} are therefore important to the
475 freshwater geochemistry of the site, but more likely derived from rainfall and/or dry
476 deposition rather than weathering.

477 SO_4^{2-} -S was significantly higher in the lakes than in the Polygon and Stream samples
478 (Table 1), although there was considerable variability in the latter two (Fig. 3). Increased
479 SO_4^{2-} -S concentrations have been linked to permafrost thaw (Frey and McClelland 2009),
480 suggesting that there may be more thawing in the lakes, releasing SO_4^{2-} , compared to the
481 stream and polygon samples. However, such responses are not consistent (e.g. Parham et al.
482 2013), and the values measured here (0.73 ± 0.32 to $3.85 \pm 0.39 \text{ mg l}^{-1}$) are not especially
483 high compared to similar systems in Alaska and Siberia (0.03 to 2.58 mg l^{-1} ; Petrone et al.
484 2006; Parham et al. 2013). The lower SO_4^{2-} -S in the polygons and stream maybe also be due
485 to increased sulphate reduction, linked to methane oxidation, in these waters or associated
486 sediments, and this may help explain the low CH_4 concentrations in these samples (Fig. 4).

487 There are higher Si concentrations in the Polygon and Stream samples compared to the Lake
488 samples, and this may be due to weathering inputs from the mineral soils in the region. Si/Cl
489 ratios showed a slight relationship with Cl^- ($R^2 = 0.46$), suggesting that inputs of Si from
490 weathering (altering its relationship to the conservative ion, Cl^-) may be an important process
491 across the study area. Si is strongly correlated with the sampling day of year, particularly in
492 sites within Siksik catchment, suggesting that it behaved conservatively in both site groups
493 (Pearson's r of 0.76 and 0.79 for sites outside and within Siksik catchment, respectively;
494 Table 6). However, like Ca^{2+} , an increasing seasonal trend is not evident in Fig. 6. The lower
495 Si concentrations in the Lake samples compared to the Polygon and Stream samples are more

496 likely explained by assimilation of Si by diatoms in the lake waters (Conley 2002), rather
497 than greater weathering inputs of Si (relative to other ions) within the Siksik catchment.

498 The system presented here is relatively undisturbed, physically, compared to other parts of
499 the Arctic, with relatively little visible evidence of recent thermokarst features and enhanced
500 permafrost thaw, over and above seasonal thawing, with the exception of some few thaw
501 lakes and several active layer detachments. At Toolik Lake in Alaska, for example, there is
502 considerable evidence of enhanced permafrost thaw, and as a result increased contributions of
503 inorganic solutes to the aquatic system have been reported (Hobbie et al. 1999). N, P and K⁺
504 are often the most noticeable elements derived from this increase in thawing, as Arctic
505 regions are generally nutrient poor (Keller et al. 2007), and this was also observed at Toolik
506 Lake (Bowden et al. 2012). Dissolved N₂O and NO₃⁻ were generally undetectable in this
507 study; P was also generally undetectable in the water samples from our site, comparable to
508 low concentrations observed at Toolik Lake (Kling et al. 1992b). Potassium (K⁺) was present
509 at our study sites in low concentrations ($0.31 \pm 0.05 \text{ mg l}^{-1}$; Fig. 2), overlapping the low end
510 of concentrations at Toolik Lake (0.01 to 3.0 mg l⁻¹; Kling et al. 1992b; Keller et al. 2007).
511 Potassium was particularly low in the Polygon ($0.15 \pm 0.05 \text{ mg l}^{-1}$) and Stream (0.22 ± 0.05
512 mg l⁻¹) samples compared to the Lake group ($0.63 \pm 0.05 \text{ mg l}^{-1}$; Fig. 3). This contradicts
513 what might be expected, given that the Polygon samples are from the pools located between
514 permafrost ice-wedges where the water has the greatest chance to interact directly with
515 thawing permafrost, and that much of the Stream site waters originate from polygons (Fig. 1).
516 K⁺ did correlate significantly in the synchrony-through-time analysis at sites within Siksik
517 catchment, with a negative trend in time (Pearson's $r = -0.72$; Table 6), but showed clear
518 spatial synchrony with a positive spatial trend (Pearson's $r = 0.80$; Table 3). This could
519 suggest that, as the growing season progresses, K⁺ is taken up by plants, but also that K⁺ may
520 be added to the stream from the decay of organic matter, possibly resulting from enhanced

521 permafrost thaw. This pattern is not clear in Fig. 6, however, and is hard to separate from the
522 overall variability at the site.

523 *5.2 Aquatic carbon biogeochemical controls*

524 Rates of permafrost thaw are important in controlling DOC and DIC concentrations in Arctic
525 streams and lakes (Olefeldt and Roulet 2014; Abbott et al. 2015). Aquatic DOC
526 concentrations in this study ranged widely from 3.04 to 46.9 mg C l⁻¹ across all groups (mean
527 = 23.4 ± 0.54 mg C l⁻¹; Table 1), falling in the mid-range of 2-55 mg C l⁻¹ observed elsewhere
528 in Arctic and sub-Arctic catchments (Dornblaser and Striegl 2015; Mann et al. 2012; Olefeldt
529 and Roulet 2012; Olefeldt et al. 2014; Petrone et al. 2006; Prokushkin et al. 2011; Striegl et
530 al. 2005). Areas undergoing elevated permafrost thaw have recorded values as high as 164
531 mg C l⁻¹ (Shirokova et al. 2013), although thermokarst processes do not necessarily result in
532 increased DOC concentrations in the current study region (Kokelj et al. 2005). Conversely,
533 DIC in the study waters (0.00 to 12.4 mg C l⁻¹, mean = 3.07 ± 0.17) was predominantly at the
534 lower end of the range observed elsewhere in the Arctic (generally 2-50 mg C l⁻¹, using
535 HCO₃⁻ as a proxy for DIC where DIC values were not given; Dornblaser and Striegl 2015;
536 Parham et al. 2013; Prokushkin et al. 2011; Tank et al. 2012), although some sites had much
537 higher concentrations (50 to 391 mg C l⁻¹; Kling et al. 1992a and 1992b; Striegl et al. 2007),
538 especially where carbonate was present in soil profiles (e.g. Frey et al. 2007). The low DIC
539 concentrations in the waters presented here suggest that there is minimal input from
540 carbonate weathering at the study site.

541 Active layer deepening and thermokarst features can increase DOC and CO₂ concentrations
542 when the active layer is shallow, channelling water through organic layers, and increase DIC
543 concentrations where the active layer is deep enough to allow water to pass through mineral
544 soils (Abbott et al. 2015; Dornblaser and Striegl 2015). DOC concentrations are consistently

545 eight times greater than DIC (and CO₂) in all water samples (Fig 5), suggesting that flow
546 paths were predominantly focused in the upper organic layer, rather than the mineral soils
547 below. DOC concentrations did not show a significant trend through time (Fig. 6), indicating
548 these flow paths did not alter much through the study seasons. DOC concentrations were
549 highest in the Polygon group (Fig. 4), indicating that DOC contributions to the water in the
550 ice-wedge pools were higher than in the other water types as a result of the longer residence
551 times of these waters in the organic-rich layer and/or increased contact times with organic
552 pool margins.

553 Dissolved CO₂ concentrations ranged from 0.36 to 23.8 mg C l⁻¹ (mean = 2.20 ± 0.12
554 mg C l⁻¹; Fig 4), comparable to 0.1 to 6.8 mg C l⁻¹ for other Arctic aquatic studies (Crawford
555 et al. 2013; Kling et al. 1992; Negandhi et al. 2013; 2014; Shirokova et al. 2013; Striegl et al.
556 2012). The lower values of the Lake and Stream samples were similar to other stream and
557 river values (0.1 to 2.0 mg C l⁻¹; Crawford et al. 2013; Kling et al. 1992a; Striegl et al. 2012),
558 and the Polygon samples more closely match values from other Arctic polygonal ponds and
559 thermokarst features (0.4 to 6.8 mg C l⁻¹; Negandhi et al. 2013; 2014; Shirokova et al. 2013).
560 The highest CO₂ concentrations observed in the Polygon samples were possibly due to
561 increased contributions from/interactions with the soil zone, as observed in the DOC
562 concentrations in the same waters.

563 Dissolved CH₄ is present only in very low concentrations in the study waters, generally
564 below 0.05 mg C l⁻¹ (Fig. 4), similar to the 0.0002 to 0.21 mg C l⁻¹ range observed in the
565 Siberian Arctic (Shirokova et al. 2013). Although CH₄ is generally below 0.1% of total
566 carbon concentrations in the sampled waters (Fig. 5) and is not considered an important form
567 of aquatic C in this system, this could partly be due to the rapid transfer of this gas to the
568 atmosphere meaning that aquatic CH₄ may be more important in the study area than these

569 observations suggest. Evasion rates were not assessed in this study. In addition, the low CH₄
570 values in the stream and polygon samples could also be related to sulphate reduction (see
571 section 5.1). Much of the CH₄ release in Arctic aquatic environments is thought to occur
572 through ebullition from the streambed and lake sediments (Walter et al. 2006; Tan et al.
573 2015), which was not measured in this study. It should also be noted that direct
574 measurements of CH₄ concentrations in soils and sediments across a transect from the Siksik
575 Creek streambed upslope towards the edge of an alder thicket showed potentially very high
576 *in-situ* values (up to 16% CH₄) in 2014 (Street et al. in press).

577 All C species were also poorly correlated with Ca²⁺/Cl⁻ and Si/Cl⁻ ratios, with R² values all
578 below 0.8 (see section 4.2). A stronger correlation with DIC in particular would be expected
579 if the mineral soils were markedly contributing to DIC concentrations; this was not evident.

580 *5.3 Biogeochemical implications*

581 The C species CO₂, DIC and DOC were consistently significant in defining the variability in
582 the data set, along with Na⁺, Cl⁻ and total Fe (Table 2). This suggests that C concentrations
583 were important for defining the geochemical variability in the system along with a minority
584 of the inorganic solutes. Given that the total C concentrations in the samples (20.3 to 40.9 mg
585 l⁻¹; Fig. 5) were equal to or greater than TDS (21.3 to 27.1 mg l⁻¹), they therefore comprise a
586 key characteristic of the study site's freshwater biogeochemistry.

587 This is supported by the synchrony analysis, where the mean temporal synchrony values of
588 all the specific site pairs were lower for C species than for the inorganic solutes (both within
589 and outside Siksik catchment; Tables 4 and 5), showing that C species are less well conserved
590 in the system than the inorganic solutes. When we look specifically at the lake sites that
591 appear to be physically well connected (L7 to L15; Fig. 1) the mean synchrony for these sites
592 is 0.40 ± 0.26 and 0.63 ± 0.18 for the C species and ions, respectively (Table 4). These values

593 are slightly higher than the subset (sites outside Siksik catchment) mean, but are within one
594 standard deviation (Table 4). This again indicates that despite extracting sites that appear to
595 be well connected spatially, there is less conservation of C species than the inorganic solutes;
596 this suggests that many neighbouring sites are not well connected. The synchrony-through-
597 time analysis further highlights the differences between the ions and the C species’
598 synchrony, with the most significant correlations with sampling day of year occurring
599 primarily with the inorganic solutes, showing that that these species are more synchronous
600 (i.e. co-vary more) in time than the C species (Table 6). This could be because of the
601 conservative nature of the inorganic solutes in the site waters, and/or because of the spatially
602 heterogeneous operation of processes such as degassing of gaseous C species (Raymond et al.
603 2013), or the microbial and photochemical degradation of DOC leading to degassing of its
604 breakdown products (Vonk et al. 2015b).

605 The apparent conservative nature of the inorganic solutes as highlighted by the synchrony
606 analyses, along with the lack of evidence of enhanced deepening of the active layer during
607 the study period, suggests that the organic-rich inter-hummocks currently dominate the
608 biogeochemistry of all the waters studied here. This shows that the importance of the
609 hummock/inter-hummock topography to the Siksik hydrology as identified by Quinton and
610 Pomeroy (2006), also extends to the lakes as well.

611 Thawing permafrost can increase nutrient concentrations (N, P and K; Keller et al. 2007), and
612 the “priming” ability of these nutrients may enhance allochthonous DOC and DIC
613 respiration, and subsequent CO₂ and CH₄ production (Bianchi 2011; Marcé et al. 2015).
614 Priming may render less labile organic C vulnerable to mineralisation if it is circulated
615 through multiple lake systems and subjected to photo-oxidation and microbial respiration
616 (Bianchi 2011; Cory et al. 2014). In our study, the relative proportion of different C species

617 to each other remained consistent throughout the different water types (Fig. 5). There are,
618 however, much lower total C concentrations in the Stream and Lake samples compared to the
619 Polygon samples, and it is therefore possible that C is being sequestered, via plant uptake
620 and/or burial in sediments, in the lakes (Walter Anthony et al. 2014) and stream beds, and
621 subsequently released by CH₄ ebullition (Walter et al. 2006; Street et al. in press), which was
622 not measured in this study. Alternatively, DOC may be lost in the Lake and Stream waters via
623 microbial respiration (Spencer et al. 2015) and photo-oxidation (Cory et al. 2014), which is
624 rapidly degassed to the atmosphere (Billett and Moore 2007; Long et al. 2015; Raymond et
625 al. 2013), or diluted by water from other sources (e.g. precipitation, runoff and snowmelt).
626 The vulnerability of DOC to mineralisation to CO₂ means that pristine catchments with large
627 DOC loads have the potential to be high CO₂ sources. Whether one or a combination of these
628 processes is occurring in these systems needs to be explored further using a C mass balance
629 approach in order to contextualise the results presented here.

630

631 **6. Conclusions**

632 The waters in this study were slightly acidic and of low salinity, dominated by Ca²⁺, Mg²⁺
633 and Na⁺; Lake samples were SO₄²⁻-S rich and Si poor, while the Polygon and Stream samples
634 were Si rich and SO₄²⁻-S poor (Table 1). Although the synchrony-through-time analysis
635 indicates that time of sampling can be important in defining a given sample's
636 biogeochemistry, there were no strong seasonal trends in the aquatic biogeochemistry in
637 either 2013 or 2014, or between years. The study waters did not show clear evidence of
638 enhanced permafrost thaw of the mineral sub-soils, or of thermokarst activity (i.e. thermal
639 detachment slides) delivering mineral-derived solutes to the aquatic system, during the two
640 study seasons (2013 and 2014).

641 Dissolved organic C is the dominant C species across all water types, followed by dissolved
642 inorganic C and then dissolved CO₂-C; dissolved CH₄-C, whilst highly variable, generally
643 only occurred at very low concentrations in the study waters. Total C concentrations were
644 present in the following order of decreasing magnitude across the water types: Polygon >
645 Stream > Lake, suggesting that different water types carry and process significantly different
646 C loads. As such, it is important to consider all forms of C that may be stored or released
647 from the region, given that C may be rapidly transformed from one form to another, and that
648 C measurements in far downstream locations are unlikely to be representative of C
649 processing in the upper catchment.

650 The analyses presented here support our original hypothesis, demonstrating the geochemical
651 uniqueness of the water types identified as controlled by both hydrological and
652 biogeochemical processing. However, further studies on small catchments similar to the one
653 presented here are vital to analyse and detect change in these biogeochemical processes in
654 vulnerable and disturbed systems. While there are several existing small catchment studies in
655 the Arctic, they are generally associated with regions that are currently undergoing
656 considerable change (e.g. Abbott et al. 2015; Vonk et al. 2013). The dataset presented here,
657 however, shows no significant biogeochemical evidence of a shift to deeper water sources
658 linked to enhanced summer active layer deepening, with most biogeochemical variables
659 remaining relatively stable throughout the two study seasons despite substantial (seasonal)
660 deepening of the active layer during the snow free season. This suggests that in the absence
661 of enhanced permafrost thaw, the aquatic biogeochemistry of the study area (and similar
662 regions elsewhere in the Arctic) could be expected to remain relatively stable.

663 Although there has been marked warming and shrubification in the region in the last three
664 decades, this study appears, nonetheless, to provide a “baseline” surface water analysis for

665 the western Canadian Arctic from which to consider potential future changes to the region
666 under predicted climate change. These might include (1) increased CO₂ concentrations
667 relative to DOC as a result of aquatic mineralisation of organic matter, (2) increased DIC
668 relative to DOC as a result of substantial deepening of the active layer such that flow paths
669 develop within the mineral layers, and (3) a change in the total C balance of the catchments.
670 With the caveat that we only report two years of data (2013 and 2014), this study appears to
671 provide a good example of an Arctic system in a state of relative biogeochemical equilibrium
672 compared to many other research sites.

673

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891

892 **Figure Captions**

893 Figure 1. The study region (68° 44' 54.5" N, 133° 29' 41.7" W) and sampling sites for the
894 water types identified in this study. Siksik catchment, flow gauging stations and areas of sub-
895 sampled polygonal ice wedges are also shown (Note: For clarity, not all areas of polygonal
896 tundra are identified here). Inset: location of the study site in the Northwest Territories,
897 Canada.

898 Figure 2. Daily discharge (Trail Valley Creek), precipitation and mean air temperature
899 (Environment Canada meteorological station 220N005) during the sampling years 2013 and
900 2014; sampling dates are shown by the vertical lines, solid lines represent when all locations
901 were sampled, and the dashed lines represent when only the Siksik catchment sites were
902 sampled.

903 Figure 3. Boxplots of pH and primary ion concentrations in water samples collected during
904 both the 2013 and 2014 field campaigns, grouped by water type (Lake = Lake, Poly =
905 Polygon, Strm = Stream). The thick horizontal lines represent the median, the upper and
906 lower limits of the boxes represent the upper and lower quartiles, and the whiskers extend to
907 1.5 times the group's interquartile range for the displayed variable; the circles represent
908 outliers.

909 Figure 4. Boxplots of dissolved C species concentrations in water samples collected during
910 both the 2013 and 2014 field campaigns, grouped by water type (see legend to Fig. 3); the
911 format of the boxplots is also the same as in Fig. 3.

912 Figure 5. Exploded pie charts of the relative proportions of dissolved C species
913 concentrations in water samples collected during both the 2013 and 2014 field campaigns,
914 grouped by water type (see legend in Fig. 3). The average total C content of for each group is
915 given next to the group labels; CH₄ concentrations were < 0.1% of the total C content for all
916 groups.

917 Figure 6. Seasonal active layer depth in hummock and inter-hummock areas (top figures) and
918 selected species mean concentrations for each sampling period (bottom ten figures; see Fig.
919 2) for the 2013 and 2014 snow-free seasons (left and right figures, respectively); the x-axes
920 are the same for each figure, only the year differs. *TIS is the sum of total inorganic solutes
921 in the samples (Ca^{2+} , K^+ , Mg^{2+} , Si, Cl^- , DIC [HCO_3^-], SO_4^{2-} ; Frey and McClelland 2009).

922