

Landscape-level controls on dissolved carbon flux from diverse catchments of the circumboreal

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[1] While much of the dissolved organic carbon (DOC) within rivers is destined for mineralization to CO₂, a substantial fraction of riverine bicarbonate (HCO₃⁻) flux represents a CO₂ sink, as a result of weathering processes that sequester CO₂ as HCO₃⁻. We explored landscape-level controls on DOC and HCO₃⁻ flux in subcatchments of the boreal, with a specific focus on the effect of permafrost on riverine dissolved C flux. To do this, we undertook a multivariate analysis that partitioned the variance attributable to known, key regulators of dissolved C flux (runoff, lithology, and vegetation) prior to examining the effect of permafrost, using riverine biogeochemistry data from a suite of subcatchments drawn from the Mackenzie, Yukon, East, and West Siberian regions of the circumboreal. Across the diverse catchments that we study, controls on HCO₃⁻ flux were near-universal: runoff and an increased carbonate rock contribution to weathering (assessed as riverwater Ca:Na) increased HCO₃⁻ yields, while increasing permafrost extent was associated with decreases in HCO₃⁻. In contrast, permafrost had contrasting and region-specific effects on DOC yield, even after the variation caused by other key drivers of its flux had been accounted for. We used ionic ratios and SO₄ yields to calculate the potential range of CO₂ sequestered via weathering across these boreal subcatchments, and show that decreasing permafrost extent is associated with increases in weathering-mediated CO₂ fixation across broad spatial scales, an effect that could counterbalance some of the organic C mineralization that is predicted with declining permafrost.

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1. Introduction

[2] The riverine flux of dissolved C has important consequences for C cycling at the landscape scale. Dissolved organic carbon (DOC) that is mobilized from soils and transported to rivers is largely a net source of CO₂ to the atmosphere. While some of the terrestrially derived DOC carried by rivers is eventually sequestered in the deep ocean [e.g., Benner *et al.*, 2005], the majority is mineralized as a

result of photochemical or microbial processes – either within the catchment [Cole *et al.*, 2007] or after this organic C has been delivered to the ocean [Degens *et al.*, 1991; Alling *et al.*, 2010]. In contrast, a large fraction of the riverine dissolved inorganic C (DIC; the sum of CO_{2(aq)}/H₂CO₃, HCO₃⁻ and CO₃²⁻) delivered to the ocean is a carbon sink. In particular, bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻; which is minimal at pH < 9) are predominantly derived from chemical weathering, which is one of the primary sinks for CO₂ on land. Thus, the riverine flux of bicarbonate relative to DOC in rivers has important implications for the C balance of catchments and landscapes. Understanding the processes that regulate this flux, and how this regulation may change, is critical to predicting future alterations in C cycling at the landscape scale.

[3] Chemical weathering causes CO₂ – derived either directly from the atmosphere, or indirectly from the mineralization of organic matter or plant autotrophic respiration [Lerman *et al.*, 2007] – to be transformed to bicarbonate (HCO₃⁻). However, the parent material that undergoes the weathering reaction determines the degree to which the bicarbonate produced acts as a CO₂ sink, and thus the implications of a given bicarbonate flux for the larger C cycle. While silicate weathering causes all bicarbonate to be produced from CO₂ fixation, carbonate weathering (in the

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absence of pyrite oxidation; see Section 5) causes half of the bicarbonate to be derived from CO_2 , and the other half directly from the dissolution of carbonate rock. Furthermore, while the weathering of silicates can sequester CO_2 over geologic time scales, carbonate weathering is thought to sequester CO_2 on the scale of thousands to hundreds of thousands of years, as a result of CO_2 release during the biological sequestration of CaCO_3 from Ca^{2+} and HCO_3^- in the oceans [Berner et al., 1983; Sundquist, 1991]. Despite this, both silicate and carbonate weathering deliver sequestered CO_2 (as bicarbonate) from land to the ocean, and the ocean inorganic carbon equilibrium is now greatly perturbed due to the uptake of anthropogenic CO_2 ; thus, both weathering processes are integral components of the terrestrial C sink [Mackenzie and Garrels, 1966; Archer, 2010].

[4] The importance of singular controls on riverine dissolved C flux has been examined in numerous studies. For DOC, the amount of runoff (or the balance of precipitation and evaporation) and the abundance of wetlands, peatlands, or soil C [Ludwig et al., 1996; Frey and Smith, 2005; Raymond et al., 2007; Raymond and Oh, 2007; Townsend-Small et al., 2011; Lauerwald et al., 2012] are often found to be primary drivers of flux, although other factors including land cover, land use, and others [Hope et al., 1994], have been found to be important. For bicarbonate, runoff and lithology are established as primary drivers of concentration and flux [Aminotte Suchet and Probst, 1993; Raymond and Oh, 2007; Hartmann, 2009], while agricultural practices such as liming and fertilization have also recently been shown to increase bicarbonate fluxes at the regional scale [Semhi et al., 2000; Raymond et al., 2008]. In particular, however, because carbonate rocks weather much more quickly than their silicate counterparts [Meybeck, 1987], the relative distribution of these two primary rock types has important implications for bicarbonate flux, in addition to their above-described implications for CO_2 sequestration [Gaillardet et al., 1999; Hartmann et al., 2009].

[5] In northern regions, permafrost is also emerging as a potentially important regulator of dissolved C export from catchments, as a result of its role in inhibiting surface to groundwater interactions [Ge et al., 2011]. While deeper flow paths facilitate interaction between water and mineral components of the soil profile, and thus weathering processes, shallow flow paths can constrain water to organic-rich soil layers (reviewed by Frey and McClelland [2009]). There is also some evidence to support an in situ effect of temperature on the flux of minerals derived from weathering processes [Hartmann, 2009, and references therein], although previous landscape-level comparative studies have found this effect to be relatively weak, only present for some lithological classes, and to not significantly improve the predictive ability of weathering flux models [Hartmann, 2009; Hartmann and Moosdorf, 2011]. Although few studies have directly examined the effect of permafrost on bicarbonate flux, concentrations of non-bicarbonate weathering ions (Ca, Mg, Na) and total inorganic solutes [MacLean et al., 1999; Petrone et al., 2006; Frey et al., 2007b] have been shown to be higher in low-permafrost catchments in West Siberia and northwestern North America, indicating that bicarbonate concentrations should follow the same trends. In Alaska's Yukon River basin, a clear increase in summertime bicarbonate flux between the 1970s and 2000s

[Striegl et al., 2005, 2007] has been attributed to decreases in permafrost extent, as inferred from increasing groundwater flows during this same period [Walvoord and Striegl, 2007]. In contrast, concentrations (and less commonly, fluxes) of DOC have been shown to either increase or decrease across gradients of increasing permafrost extent, depending on the region of study [e.g., MacLean et al., 1999; Striegl et al., 2005; Frey et al., 2007b; Frey and McClelland, 2009].

[6] Less well understood, however, is how various drivers of dissolved C flux might act in concert, and the constancy of their effect across broad spatial scales (but see Ludwig et al. [1996] and Lauerwald et al. [2012] for DOC and Hartmann [2009] for bicarbonate in Japanese watersheds). For permafrost in particular, it is also unclear whether the trends observed to date across permafrost gradients might be confounded or augmented by non-orthogonal variation in other controlling variables. For example, a study examining differences in constituent flux from three neighboring catchments with variable permafrost extent concluded that variations in runoff between catchments partially overwhelmed the ability to discern a permafrost effect [Petrone et al., 2006]. Thus, multivariate analyses are critical for elucidating underlying trends in data, understanding and partitioning the relative importance of various drivers of dissolved C flux, and quantifying how this flux may be altered by ongoing and predicted climate-induced change.

[7] Here, we undertake an examination of the magnitude, direction, and universality of a suite of drivers for controlling bicarbonate and DOC flux throughout the circumboreal region. Although our overarching focus is on the effect of permafrost, we necessarily also assess the co-occurring effect of other primary regulators of dissolved C flux: (1) runoff for both bicarbonate and DOC, which is increasing in northern watersheds in response to climate change [Peterson et al., 2002; Déry et al., 2009]; (2) various facets of lithology for bicarbonate; and (3) wetland (peat) extent for DOC. By undertaking this work using a geographically extensive survey of riverine biogeochemistry (Figure 1) we are able to assess the consistency of these drivers across broad spatial scales. By selecting a suite of study rivers that cover a broad biogeochemical range, with bicarbonate concentrations ranging from dilute ($<1 \text{ mg C L}^{-1}$) to high ($>40 \text{ mg C L}^{-1}$) and DOC concentrations that range almost two orders of magnitude ($0.8\text{--}66 \text{ mg C L}^{-1}$), we are able to draw conclusions that apply across a wide range of boreal landscapes. Across the diverse catchments that we investigate, controls on bicarbonate flux were near-universal. Decreasing permafrost extent was associated with increased bicarbonate flux and thus also increased weathering-mediated CO_2 sequestration. This effect was substantial, and occurred across a broad spatial extent. In contrast, the effect of permafrost extent on riverine DOC flux was not constant across regions, even after the variation attributable to other drivers had been accounted for. Thus, this work suggests that the CO_2 loss that is expected across the terrestrial-aquatic continuum as permafrost thaws should be counterbalanced, in part, by appreciable increases in CO_2 fixation via weathering.

2. Data Sources

[8] We obtained biogeochemical data for 234 sub-watersheds ranging from 19 km^2 to $2.6 \times 10^6 \text{ km}^2$ from the

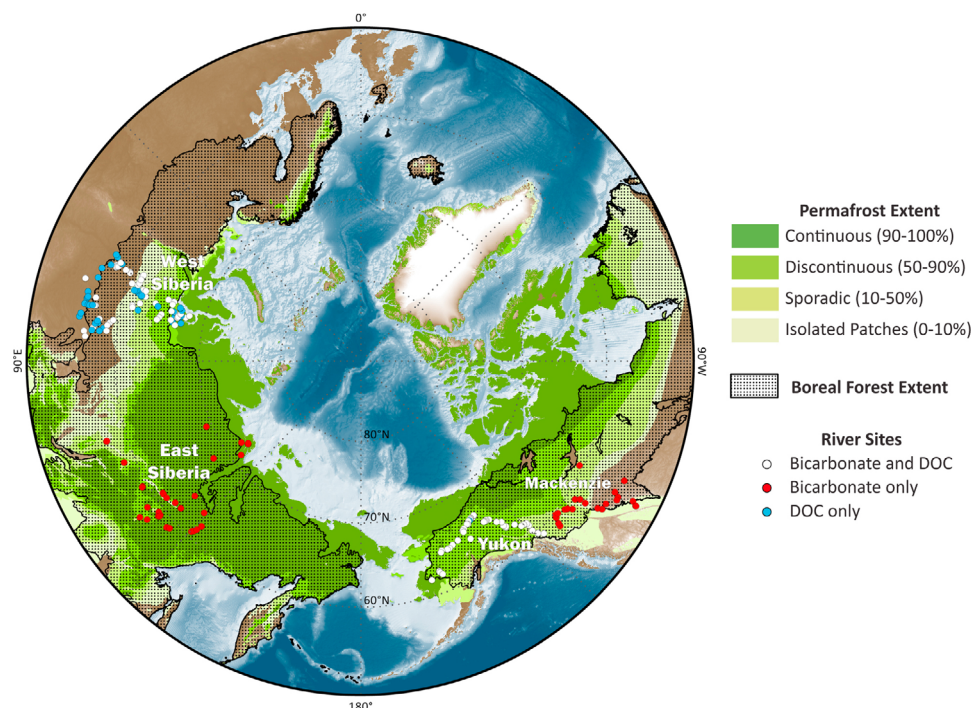


Figure 1. Study catchments of the Yukon, West Siberian, East Siberian, and Mackenzie regions. The global extent of boreal forest [FAO, 2001] and northern permafrost [Brown *et al.*, 1997] are shown.

published literature (Figure 1). Our primary analyses focused on subwatersheds of the Yukon River basin [Dornblaser and Halm, 2006; Halm and Dornblaser, 2007], and West Siberia [Frey and Smith, 2005; Frey *et al.*, 2007b], for which bicarbonate, major anion and cation, and DOC concentration data are available. However, we supplemented our bicarbonate analyses using bicarbonate and major ion data that are available from subwatersheds of the Mackenzie River basin [Milot *et al.*, 2003] and East Siberia [Huh *et al.*, 1998; Huh and Edmond, 1999]. Our study watersheds largely lie within the boreal, with some transition to polar tundra, temperate forest, and temperate mountains at the margins of our study region (Figure 1) [Food and Agriculture Organization of the United Nations (FAO), 2001]. Permafrost underlying these watersheds ranges from continuous to fully absent (Figure 1) [Brown *et al.*, 1997], and the lithologies of the larger regions from which these data are drawn range from carbonate rich (portions of the Mackenzie and Yukon basins) to carbonate and basalt-poor (West Siberia) [Dürr *et al.*, 2005]. A detailed description of the four study regions is provided in the auxiliary material.¹

[9] The Yukon data set has previously been used to estimate annual exports of major solutes from the subwatersheds investigated [Frederick *et al.*, 2011]. The West Siberian data set has been used to quantify the geochemistry of these streams and their potential response to permafrost degradation [Frey *et al.*, 2007b], and to examine how permafrost and peat extent regulate DOC concentration in this region [Frey and Smith, 2005]. Both the Mackenzie and East Siberian data sets have been used to determine region-

specific weathering rates and explore lithologic controls on stream geochemistry [Huh *et al.*, 1998; Huh and Edmond, 1999; Milot *et al.*, 2003]. For the Mackenzie data set, this also included an analysis of the weathering origin of bicarbonate and other weathering constituents. Our aim is to use these previously published data sets to explore the commonality of controls on C constituent flux over disparate regions of the circumboreal.

[10] The Yukon subwatershed data consists of a sample point from the June freshet and a second sample from late summer, although a small number of subwatersheds were only sampled once [Dornblaser and Halm, 2006; Halm and Dornblaser, 2007]. Data for the western and eastern Siberian subwatersheds consists of a single sample point, collected in late summer (July–August) [Huh *et al.*, 1998; Huh and Edmond, 1999; Frey *et al.*, 2007b]. Data for the Mackenzie subwatersheds typically consist of one measurement from early summer (June, post freshet), although there are some late summer measurements (August), and duplicate measurements (June and August) in the data set. Both bicarbonate and DOC concentrations are known to vary across the annual hydrologic cycle: while bicarbonate concentration decreases with increasing discharge, DOC concentrations increase [e.g., Raymond *et al.*, 2007; Raymond and Oh, 2007; S. E. Tank *et al.*, A land-to-ocean perspective on the magnitude, source and implication of DIC flux from major Arctic rivers to the Arctic Ocean, submitted *Global Biogeochemical Cycles*, 2012]. As a result of this disparity we do not use all data for all analyses. A detailed description of data treatment is given in Section 3.1.

[11] Because data were obtained from the published literature, various standard techniques to calculate bicarbonate

¹Auxiliary materials are available in the HTML. doi:10.1029/2012GB004299.

concentration were employed. For the Yukon subwatersheds, bicarbonate was calculated as the difference between measured total DIC and CO_2 concentrations [Dornblaser and Halm, 2006]. For the West Siberian subwatersheds, bicarbonate was calculated by charge balance from major anion and cation data, with a correction for the charge contribution of organic acids [Frey et al., 2007b]. For the eastern Siberian and Mackenzie sub-watersheds, bicarbonate was assumed to be equivalent to alkalinity (in μeq). Thus, we use the term ‘bicarbonate’ to refer to non- CO_2 dissolved inorganic carbon species, and recognize that data for individual sub-watersheds may also contain some carbonate ions (for the Mackenzie and Siberian samples), or be biased because of contributions of non-carbonate species to alkalinity (for the Mackenzie and East Siberian samples). However, because DIC concentrations are relatively high in the Mackenzie and East Siberian sub-watersheds, and all samples are typically circumneutral, both of these effects should be minor. Data from the Mackenzie and Lena main stem (Tank et al., submitted manuscript, 2012; www.arcticgreatrivers.org) indicate that the summertime contribution of non-carbonate species to alkalinity ranges from 1% (Mackenzie) to $\sim 4\%$ (Lena), while measured pH values from the Mackenzie and Siberian tributary data sets indicate that in all but 5 samples, carbonate concentrations were less than 1% of the bicarbonate concentration (remaining samples range from 1 to 5%).

[12] In all cases, watershed areas were obtained from the above-cited publications. Because the Yukon and East and West Siberian sub-watersheds are not gauged, the published values acquired for mean annual discharge from these regions were calculated using known relationships between drainage area and precipitation (West Siberia [Frey et al., 2007b]; Yukon River basin [Frederick et al., 2011]), or published runoff maps (East Siberia) [Huh et al., 1998]. For the Mackenzie River basin, only sub-watersheds gauged by the Water Survey of Canada were selected for our analyses, and gauge data were used to calculate mean annual discharge (www.ec.gc.ca/rhc-wsc). We also made use of instantaneous discharge measured at the time of sampling for the Yukon River basin subcatchments [Dornblaser and Halm, 2006; Halm and Dornblaser, 2007], discharge from the month of sampling for the Mackenzie subcatchments (Water Survey of Canada), and calculated summertime (July, August, September) discharge for West Siberia [Frey et al., 2007a]. Average annual precipitation data were also obtained for the Yukon (Frederick et al. [2011], using data from the isohyetal map in Jones and Fahl [1994]) and western Siberian [New et al., 1999; Frey et al., 2007b] sub-watersheds. For all sub-watersheds, permafrost extent was estimated using the global permafrost data set [Brown et al., 1997] formatted for inclusion in Google Earth (National Snow and Ice Data Center, Boulder, CO), by calculating the percent coverage of each permafrost class within a given sub-watershed multiplied by the median proportion of permafrost in that class. Peat extent for West Siberian sub-watersheds was taken from Frey and Smith [2005], who used the Sheng et al. [2004] data set to determine sub-watershed peat extent. Peat extent for the Yukon sub-watersheds was delineated following Yu et al. [2010], using ESRI ArcGIS 10.0 and sub-watershed shapefiles delineated by the USGS. For the Canadian regions of the basin, we determined the proportion

of each sub-watershed covered by ‘bog’ or ‘fen’ from Tarnocai et al. [2002]. For the Alaskan regions of the basin, we used the Rieger et al. [1979] data set to calculate the percent cover of peat within each peat-containing polygon that had a peat depth greater than 20 cm.

3. Data Analyses

3.1. Preliminary Data Screening and Processing

[13] We screened the bicarbonate data by eliminating all samples with a high Cl:Na ratio (>0.6), which is indicative either of a high proportion of weathering flux from halite rocks, or a significant contribution of saline groundwater to the inorganic constituent flux [e.g., Gaillardet et al., 1999]. We did this to eliminate the possibility of confounding effects caused by elevated Na fluxes from localized halite dissolution, elevated bicarbonate fluxes from bicarbonates embedded in rapidly weathered halite rocks, or saline groundwater inputs that differ regionally in their composition [e.g., Shouakar-Stash et al., 2007]. This resulted in 153 of 224 sub-watersheds with bicarbonate data being input to the bicarbonate analyses (Figure 1).

[14] Because of seasonal variation in constituent concentrations across the hydrograph, we undertake our analyses in three component parts: an assessment of the controls on (1) bicarbonate export (concentration normalized to watershed area and discharge), (2) the proportion of dissolved C exported as bicarbonate (as the bicarbonate:DOC ratio), and (3) DOC export. For our bicarbonate analyses, only annual discharge ($\text{km}^3 \text{ yr}^{-1}$) was available across all four study regions. Thus, we first undertake analyses standardized at this resolution (as $(\text{g m}^{-3}) (\text{km}^3 \text{ yr}^{-1})/(\text{km}^2)$, equivalent to $\text{g C m}^{-2} \text{ yr}^{-1}$) and perform a ‘multiregion’ analysis that includes all sub-watersheds, and region-specific analyses that are directly comparable across the four regions. Bicarbonate dilutes at high flow, and mean annual concentrations in large Arctic rivers compare well to post-freshet summertime point measurements (Tank et al., submitted manuscript, 2012). Therefore, we selectively use summertime (July–August) bicarbonate data for our annually standardized analyses, although some June data are included from the Mackenzie region because of the paucity of late summer measurements in this data set. Despite this inclusion of some June data points, our analyses show controls on bicarbonate flux to be largely universal (see Section 4.1). We also present an analysis of region-specific controls on bicarbonate flux using the most finely resolved discharge data available for the Yukon (single day), Mackenzie (single month), and West Siberian (summer, JAS) subcatchments.

[15] We explored landscape-level controls on bicarbonate:DOC for two reasons. First, because of the opposing C cycle implications of riverine bicarbonate and DOC flux (largely derived from CO_2 fixation by weathering, versus largely destined for remineralization to CO_2 , respectively), analyzing their ratio is a more direct way to assess the magnitude of the controls regulating C flux via riverine biogeochemistry. Second, because these paired data form a unitless ratio of fluxes from equal areas, analyzing controls on sub-catchment bicarbonate:DOC does not require standardization for discharge or watershed area, and thus avoids many of the issues related to seasonal changes in concentration relative to

discharge. Data for DOC are only available for the Yukon and West Siberian sub-watersheds. To look at the universality of controls on bicarbonate:DOC, we first undertake a ‘multiregion’ analysis using annual runoff and precipitation data, with the analysis again limited to summertime data to account for likely seasonal variation in bicarbonate:DOC. We also undertake regional analyses using both annual discharge and the more finely resolved discharge data discussed above, to ensure that the use of coarse-scale data did not skew or invalidate our results.

[16] In large northern watersheds, DOC concentration increases with discharge at a greater than 1:1 ratio, such that the use of post-freshet summertime concentration data to estimate an annual flux leads to a significant underestimate of the true annual flux [Raymond *et al.*, 2007]. Therefore, standardizing point concentration measurements to annual runoff values may be inappropriate, and we analyze controls on DOC flux standardized to single day (Yukon) and summer (West Siberia) discharge data alone.

3.2. Statistical Analyses

[17] For comparability across all of the study regions, we explored controls on dissolved C flux using only variables that were available for all regions. For bicarbonate, this included runoff, variables related to lithology (see below), SO_4 flux normalized to discharge and watershed area, and permafrost extent. For DOC, this included runoff, precipitation, peat coverage, and permafrost extent. We used two primary methods for our analyses. First, the multiregion analyses examined the commonality of controls on patterns in bicarbonate flux and bicarbonate:DOC. These analyses included all available sub-watersheds (Figure 1), and used a stepped, linear regression approach that sequentially partitioned (i.e., parsed out) the variance due to each of the predictor variables, by partitioning variables that are well-established regulators of dissolved C flux before examining the less well-established effect of permafrost. For bicarbonate, we partitioned runoff followed by lithological variables [Bluth and Kump, 1994; Hartmann, 2009]; for bicarbonate:DOC we partitioned peat after lithology [Frey *et al.*, 2007b; Raymond *et al.*, 2007; Raymond and Oh, 2007; Townsend-Small *et al.*, 2011; Lauerwald *et al.*, 2012]. Thus we ensured that variation in fluxes that could be attributed to differences in runoff, lithology, or vegetation did not confound the permafrost effect.

[18] Second, the region-specific analyses employed multiple linear regressions that were assessed for fit using Akaike’s Information Criterion (AIC). For each region, and each C constituent type, all of the predictor variables listed above were considered for input into the regional model, and models with the lowest AIC score were chosen as the best fit model. Models were assessed with and without constants, and variance inflation factors (VIF) were monitored to guard against multicollinearity, with a criteria to discard all models with a VIF > 5. The maximum VIF in our chosen models was 3.4, and thus no models were discarded as a result of their VIF score. In all cases, where multiple models had AIC scores within 4.0 of the best model fit, a combined model was constructed using the multimodel inference approach of Burnham and Anderson [2002]. Combined models that differed significantly from the best model fit are discussed in the text (Section 4.2).

3.3. Assessing the Effect of Lithology on Bicarbonate Flux

[19] Because of the difficulty associated with directly calculating the lithologic composition of these small sub-watersheds, we have instead used weathering constituent ratios to assess the weathering source of bicarbonate in these diverse catchments. First, we use a modification of the inverse modeling approach presented by Gaillardet *et al.* [1999], which is a mixing model of the form (for $\text{X} = \text{Ca}^{2+}$, Mg^{2+} , $[\text{HCO}_3^- + \text{CO}_3^{2-}]$, Sr^{2+} and Cl^-):

$$\left(\frac{\text{X}}{\text{Na}}\right)_{\text{river}} = \sum_i \left(\frac{\text{X}}{\text{Na}}\right)_i \alpha_i (\text{Na}) \quad (1)$$

Where i refers to the various end-member types and α_i are the mixing proportions of Na^+ , which sum to 1. This approach has previously been used by Millot *et al.* [2003] to calculate the lithologic origin of weathering constituents for sub-watersheds of the Mackenzie sub-basin.

[20] We undertook mixing model calculations for the Yukon, East Siberian, and West Siberian data sets as described below. However, because Ca:Na is considerably elevated in streams draining carbonate (as opposed to silicate) rocks, and by the presence of trace carbonates imbedded within the silicate matrix [Hartmann and Moosdorf, 2011], we also used a simple Ca:Na ratio to assess the effects of silicate versus carbonate lithologies on bicarbonate source, following on the Ca:Na ratios presented in Figure 2 and the auxiliary material.

[21] For the mixing model, sub-watershed X:Na ratios were corrected for rainwater inputs using rainwater composition data from the National Atmospheric Deposition Program (nadp.sws.uiuc.edu; Yukon River basin, mean of 2008 concentrations from Poker Creek, Bettles, Denali), Zakharova *et al.* [2005] (Eastern Siberia), and a pan-Arctic mean of rainwater composition developed in Tank *et al.* (submitted manuscript, 2012) (Western Siberia and all Sr estimates). We examined sub-watershed Cl^- concentrations from each of the four study regions to identify tributaries that were not influenced by evaporite weathering, and used these data to estimate region-specific cyclic Cl^- concentrations. Rainwater composition data were then used to estimate ratios of $\text{Cl}^-:\text{Na}^+$ and X:Na ($\text{X} = \text{Ca}^{2+}$, Mg^{2+} , HCO_3^- and Sr^{2+}) for each region, and the cyclic Cl^- concentrations were used to determine a rainwater correction for all constituents.

[22] Models were run using the Bayesian mixing model platform MixSIR [Moore and Semmens, 2008], which allows specification of end-members, end-member standard deviations, and mixture (here, river water) data points, and iteratively generates a distribution to describe the range of possible source contributions to the mixture. End-member configurations were specific to each region. For the Yukon River basin, weathering end-members included carbonate rocks [from Millot *et al.*, 2003], halites (using a pan-Arctic average derived from Siberia [Shouakar-Stash *et al.*, 2007] and the Mackenzie catchment [Millot *et al.*, 2003]), and basaltic silicates (using an average value derived from Dessert *et al.* [2003] and Pokrovsky *et al.* [2005]). Because of the prevalence of basalts in the Yukon River basin and the high susceptibility of basaltic silicates to weathering when compared to felsic silicate rock [e.g., Dessert *et al.*, 2003],

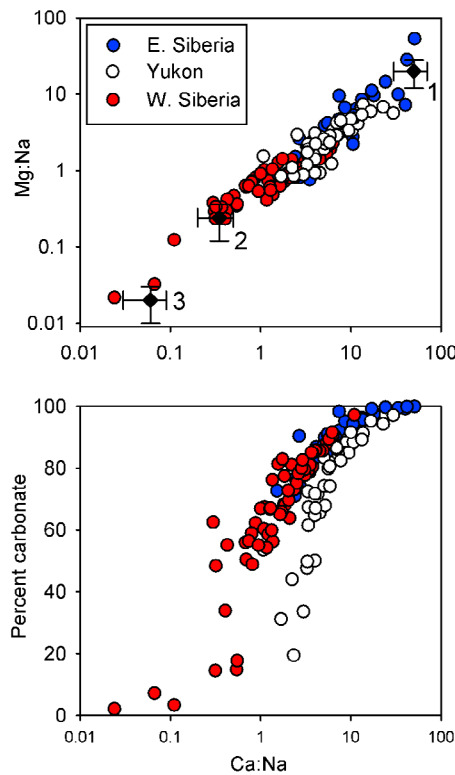


Figure 2. (top) Weathering constituent ratios, shown for Mg:Na and Ca:Na, for subcatchments of the Yukon, East Siberian, and West Siberian sub-watersheds. Weathering end-members are shown for 1, carbonate rock; 2, felsic silicate rock; and 3, halites. (bottom) Mixing model outputs showing the modeled percentage of bicarbonate flux derived from carbonate rock weathering for the three subcatchments regions.

we used a basaltic, rather than felsic, end-member for silicate rocks in the Yukon River basin models (see also auxiliary material for specific values). For West Siberia, end-members included carbonate rocks [Millot *et al.*, 2003],

halites [Millot *et al.*, 2003; Shouakar-Stash *et al.*, 2007], and felsic silicates [Millot *et al.*, 2003]. Although we removed all sub-watersheds with elevated Cl:Na from our analysis, we also included a regionally specific saline groundwater end-member in the West Siberia models [Kurchikov and Plavnik, 2009]. Model outputs indicated that saline groundwater contributed negligibly to our model result. For East Siberia, end-members included carbonate rocks [Millot *et al.*, 2003], halites [Millot *et al.*, 2003; Shouakar-Stash *et al.*, 2007], and felsic silicates [Millot *et al.*, 2003]. Specific end-member values are provided in the auxiliary material.

4. Results

4.1. Controls on Bicarbonate Flux

[23] Ratios of Ca:Na, as an indicator of weathering origin, covered a wide range in the Yukon, East Siberian, and West Siberian sub-watersheds, with West Siberian watersheds tending toward lower values, East Siberian watersheds tending toward higher values, and sub-watershed of the Yukon River basin covering a wide range of Ca:Na (Figure 2). Mackenzie sub-watershed Ca:Na ratios showed a similar range to the Yukon River sub-watersheds (range 2–36), but are not presented in Figure 2 because they have been previously detailed by Millot *et al.* [2003]. Sub-watershed Ca:Na was clearly correlated to the proportion of bicarbonate derived from carbonate rock weathering (Figure 2). The use of a basaltic, rather than felsic, silicate end-member for the Yukon River basin caused the contribution of carbonate rock weathering to the bicarbonate pool to be depressed for a given Ca:Na, relative to sub-watersheds from other regions (Figure 2), underlining the importance of using end-member values specific to the catchment of interest for these analyses. The proportion of bicarbonate derived from carbonate rocks rises rapidly with increasing Ca:Na and quickly reaches an asymptote (Figure 2). Because of the small dispersion in the proportion of bicarbonate derived from carbonate rocks above even modest levels of Ca:Na, we found Ca:Na to be a better predictor of bicarbonate flux in the models below and use this as a predictor variable in the analyses that follow.

Table 1. Sequential, Multiregion Analyses of Controls on the Flux of Bicarbonate and Bicarbonate:DOC Across All Study Catchments^a

| Independent | Dependent | Intercept | Coefficient | p | SS |
|--|--|-----------|-------------|--------|-------|
| HCO_3^- ($\text{g C m}^{-2} \text{ d}^{-1}$); All Regions ($n = 154$) | | | | | |
| HCO_3^- | Runoff (cm yr^{-1}) | 0.433 | 0.142 | <0.001 | 521.4 |
| r1; HCO_3^- | Ca:Na | −1.187 | 0.171 | <0.001 | 267.8 |
| r2; HCO_3^- | SO_4 yield ($\text{g SO}_4 \text{ m}^{-2} \text{ yr}^{-1}$) | −0.436 | 0.130 | <0.001 | 87.6 |
| r3; HCO_3^- | Permafrost (percent) | 0.843 | −0.017 | <0.001 | 57.6 |
| Residual | | | | | |
| HCO_3^- : DOC, Yukon and West Siberia ($n = 99$) | | | | | |
| HCO_3^- : DOC | Runoff ratio | −1.980 | 11.353 | <0.001 | 336.9 |
| r1; HCO_3^- : DOC | Ca:Na | −1.500 | 0.355 | <0.001 | 291.2 |
| r2; HCO_3^- : DOC | Peat (percent cover) | 0.761 | −0.024 | 0.063 | 36.3 |
| r3; HCO_3^- : DOC | SO_4 yield ($\text{g SO}_4 \text{ m}^{-2} \text{ yr}^{-1}$) | −0.380 | 0.149 | 0.025 | 50.4 |
| r4; HCO_3^- : DOC | Permafrost (percent) | 0.684 | −0.016 | 0.083 | 28.4 |
| Residual | | | | | |
| | | | | | 915.9 |

^aAnalyses were conducted by sequentially partitioning variance due to hydrology, followed by lithology and vegetation, and finally permafrost extent as described in the text. Single variables were input in sequence, with the residuals of earlier analyses (r1–r4) used to assess how later variables explained the remaining variance in flux. SS = sums of squares. Shown are the SS explained by each step of the model and the residual SS remaining after the last model step.

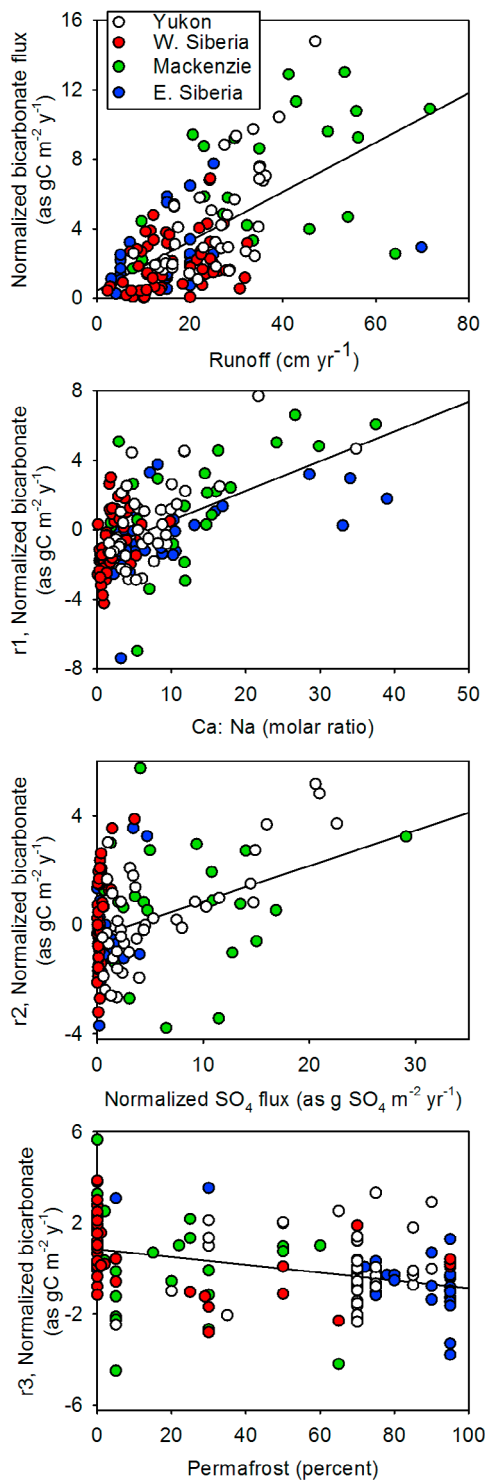


Figure 3. Sequential analysis of controls on bicarbonate flux across diverse boreal catchments. r1–r3: residual 1–residual 3. Regression statistics are given in Table 1. In all panels, $p < 0.001$.

[24] Controls on bicarbonate flux were highly consistent across all temporal and geographic scales of our analyses (Table 1 and Figure 3), with runoff, lithological variables (Ca:Na, SO_4 yield), and permafrost explaining between 60

and 90% of the variation in bicarbonate flux across the diverse boreal regions that we survey (Table 2). In the multiregion analysis, controls on bicarbonate flux varied coherently across the four boreal study regions (Table 1 and Figure 3). Bicarbonate flux showed a strong positive correlation with annual runoff, and the sequential analysis showed further variation in normalized bicarbonate to be positively related to Ca:Na and normalized SO_4 flux, the latter driven largely by the high SO_4 values in the Mackenzie and Yukon tributaries (Table 1 and Figure 3). Even after the variation in bicarbonate flux attributable to runoff and lithology was partitioned, bicarbonate flux declined significantly with increasing permafrost coverage when the four analysis regions were considered in concert (Table 1 and Figure 3).

[25] Results of the regional-scale analyses paralleled those of the global analysis, with runoff, Ca:Na, and SO_4 having a positive influence, and permafrost having a negative influence, on bicarbonate flux (Table 2). However, the relative significance of the various drivers differed between regions. For the annually normalized analyses, weathering source (using the Ca:Na predictor) was a highly significant determinant of bicarbonate flux in all regions, whereas the predictive value of annual runoff ranged from insignificant (Mackenzie; but see more temporally specific analyses below) to highly significant (Yukon and West Siberia, Table 2). Annually normalized SO_4 was a highly significant predictor of bicarbonate flux in the Yukon, Mackenzie and West Siberian regions, but not in East Siberia. Permafrost was insignificant in the Yukon annually normalized analysis (but see below), but significant in all other regions.

[26] Analyses using finer scale discharge measurements also corroborate the multiregion and annually normalized regional results. For the Mackenzie, Ca:Na (estimate = 0.052; $p < 0.001$) and SO_4 (estimate = 0.170; $p < 0.001$) remain significant, positive predictors of bicarbonate flux, whereas the use of finer scale discharge data causes runoff to become significantly, positively related to bicarbonate flux (estimate = 0.040; $p = 0.013$), and permafrost to become a marginal negative predictor of bicarbonate flux (estimate = -0.007 ; $p = 0.078$). For the Yukon River basin, permafrost was a marginal, negative predictor variable in the June single-day normalized analysis, while the August analysis was identical to the annually normalized result (Table 3). For the West Siberian sub-watersheds, the controls on summer-normalized bicarbonate flux are also identical to the annually normalized results (Table 4).

[27] To further explore the effect of permafrost on dissolved C flux in the Yukon River basin, we estimated the groundwater contribution to discharge following *Walvoord and Striegl* [2007]. We use this as a more finely resolved metric of the effect of permafrost on C constituent flux, because permafrost coverage directly influences groundwater contributions to surface flow [*Ge et al.*, 2011], in addition to factors such as geology and topology [*Freeze and Cherry*, 1979]. For all sub-watersheds for which gauge data covering the majority of the basin area were available (19 of the 42 Yukon sub-watersheds), we assumed the average January–March discharge over the period of record (as $\text{m}^3 \text{sec}^{-1}$) to be entirely derived from groundwater and representative of groundwater flow across all months. To estimate the groundwater contribution to total flow we calculated the ratio of this base discharge to the average discharge

Table 2. Region-Specific Controls on Annually Normalized Bicarbonate Flux^a

| | Yukon (n = 40, r ² = 0.936) | | | W. Siberia (n = 55, r ² = 0.657) | | | Mackenzie (n = 24, r ² = 0.762) | | | E. Siberia (n = 33, r ² = 0.615) | | |
|-----------------------|--|-------|-------|---|-------|-------|--|-------|-------|---|-------|-------|
| | Estimate | Error | p | Estimate | Error | p | Estimate | Error | p | Estimate | Error | p |
| Constant | NI | NI | | 0.747 | 0.415 | 0.078 | 3.220 | 0.639 | <.001 | 2.882 | 1.411 | 0.051 |
| Runoff | 0.075 | 0.015 | 0.001 | 0.043 | 0.016 | 0.009 | NI | NI | | 0.038 | 0.020 | 0.068 |
| Ca:Na | 0.146 | 0.037 | <.001 | 0.252 | 0.084 | 0.004 | 0.234 | 0.048 | <.001 | 0.105 | 0.021 | <.001 |
| SO ₄ Yield | 0.271 | 0.042 | <.001 | 1.346 | 0.241 | <.001 | 0.186 | 0.045 | <.001 | 0.480 | 0.282 | 0.100 |
| Permafrost | NI | NI | | −0.015 | 0.005 | 0.001 | −0.038 | 0.018 | 0.047 | −0.033 | 0.016 | 0.041 |

^aWithin each region, multiple linear regression models were assessed for fit using Akaike's Information Criterion, as described in the text. NI = variable not included in the best fit model.

occurring over the 21 day period centered on the day of sampling. We used this long-term average approach because discharge data were not always available for the year of sampling; there was a significant correlation between groundwater contribution calculated using this method, and the sampling-year specific base flow contribution, for years where these data were available ($r^2 = 0.92$, $p < 0.001$). The groundwater contribution to total discharge was significantly, negatively related to permafrost extent in the Yukon River basin sub-watersheds during both sampling periods (June and August; Figure 4 and auxiliary material), consistent with permafrost impeding groundwater flow in this region. For bicarbonate flux, the residuals of the Yukon daily analysis showed a marginal positive relationship with the groundwater contribution to total discharge (Figure 4 and auxiliary material), consistent with high permafrost (and thus, low groundwater) areas having lower rates of bicarbonate export. This occurred even when permafrost was included in the original analysis, indicating that our relatively coarse measure of permafrost extent could not capture the full variability in sub-watershed ground-to-surface water interactions. However, as discussed in Section 5, a similar analysis for the Mackenzie sub-watersheds showed no relationship between either proportion groundwater and permafrost extent, or proportion groundwater and the residuals of the Mackenzie monthly normalized bicarbonate analysis.

4.2. Controls on Bicarbonate:DOC, and DOC Flux

[28] We used the more detailed data available for the Yukon and west Siberian watersheds to examine controls on the flux of bicarbonate relative to DOC. In the multiregion analysis, the runoff ratio (runoff:precipitation, or the proportion of precipitation that is exported as runoff) was better correlated to overall bicarbonate:DOC than either runoff or precipitation alone, and we use this metric as an input variable to our analysis. The runoff ratio was significantly, positively related to bicarbonate:DOC, and the sequential analysis showed further variation in bicarbonate:DOC to be positively related to Ca:Na and SO₄ yield, and inversely related to peat coverage (Table 1). Even after the variation related to this suite of potential predictor variables had been partitioned, permafrost extent was a marginal ($0.10 < p < 0.05$), negative predictor of bicarbonate:DOC (Table 1).

[29] However, examination of the sequential analysis plots indicated that the combined trends exhibit clear regional variation (Figure 5). In particular, the trends for runoff ratio, Ca:Na, and permafrost were significant only within the Yukon sub-watersheds, while trends related to peat extent and SO₄ yield were similar across the two regions (Figure 5). This observation is borne out by the annually normalized

regional analyses, in which controls on bicarbonate:DOC show substantial regional variation. In the Yukon River basin, bicarbonate:DOC is largely predicted by lithologic factors (positive relationship with Ca:Na and SO₄; Table 5), whereas permafrost is a significant, negative predictor variable (Table 5). In contrast, although SO₄ is also a positive predictor of bicarbonate:DOC in western Siberian sub-catchments, peat extent (rather than other lithologic or hydrologic variables) predicts the remaining explained variation in bicarbonate:DOC for this region (Table 5).

[30] Analyses of controls on bicarbonate:DOC using finer scale discharge measurements largely mirror the findings discussed above. For both the Yukon and West Siberian sub-watersheds we calculate runoff and SO₄ yield using the more resolved discharge data, but retain annual precipitation as an input variable for comparison with the annually normalized analyses and because more resolved precipitation data were not available. In the Yukon during both June and August, precipitation and Ca:Na were significant, positive predictors of bicarbonate:DOC (Table 3), while permafrost (in June) and peat (in August) were significant negative predictors of this ratio (Table 3). However, peat and permafrost were positively correlated to one another in the Yukon sub-catchments ($r^2 = 0.347$, $p < 0.001$), and the AIC scores for this analysis show that a second model which substitutes permafrost for peat cannot be excluded as the best fit model ($\Delta AIC < 4.0$). The combined model for the August analysis shows both a significant peat (estimate = 0.115, $p = 0.004$) and permafrost (estimate = −0.078, $p = 0.018$) effect. In addition to the direct permafrost effect, the residuals of the Yukon daily analyses for August show a significant, positive correlation with the estimated groundwater contribution to total discharge (Figure 4 and auxiliary material), consistent with high permafrost sub-watersheds having lower fluxes of bicarbonate:DOC. For the West Siberian sub-watersheds, analyses using summertime discharge are identical to the annually normalized results (Tables 4 and 5).

[31] The lack of coherence in controls on bicarbonate:DOC appears to be driven by underlying differences in regional controls on DOC flux (see below). Given that previous analyses have shown clear differences in how DOC concentration varies with permafrost coverage between these two regions [Frey and Smith, 2005; Striegl et al., 2005; Frey and McClelland, 2009], we did not undertake a multiregion analysis to examine broad-scale controls on DOC flux. Similarly, because of the difficulty of normalizing single DOC measurements using annual discharge (Section 3.1), we also constrain our analyses to the finer-scale discharge data. In West Siberia, summertime DOC yield was positively related to summertime runoff and peat extent, and

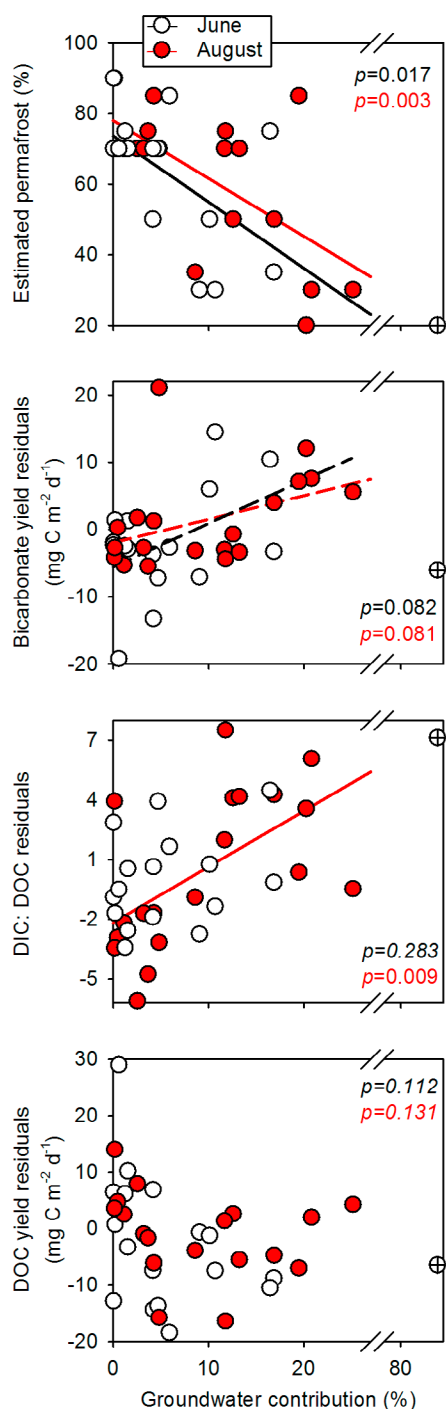


Figure 4. (First panel from top) The relationship between sub-catchment permafrost extent in the Yukon River basin and the contribution of groundwater flux to total discharge during the June and August sample periods. (Second–fourth panels) Relationship between the residuals of the Yukon daily normalized sub-watershed analyses (Table 3) and the contribution of groundwater flux to total discharge. Regressions are shown where significant at the $p < 0.05$ (solid line) and $p < 0.10$ (dotted line) level. Actual p -values are shown, and full statistics are provided in the auxiliary material. The cross-hatched point from the June analyses was excluded from the regressions because sampling occurred prior to the spring freshet.

negatively related to permafrost extent [see also *Frey and Smith*, 2005]. In the Yukon subcatchments, runoff was a significant, and permafrost a marginal, positive predictor of June daily DOC yield (Table 3). In August, runoff and permafrost were positively correlated to DOC yield, whereas annual precipitation was a negative predictor variable – perhaps as a result of the high precipitation modeled for many of the mountainous regions of the basin (Table 3) [Jones and Fahl, 1994]. For both the West Siberian summertime and Yukon August data sets, sequential analyses that partitioned hydrology, followed by peat extent, and finally permafrost, did not differ significantly from the above-described results (data not shown). The residuals of the Yukon DOC analyses show a non-significant negative relationship with the estimated groundwater contribution (Figure 4 and auxiliary material).

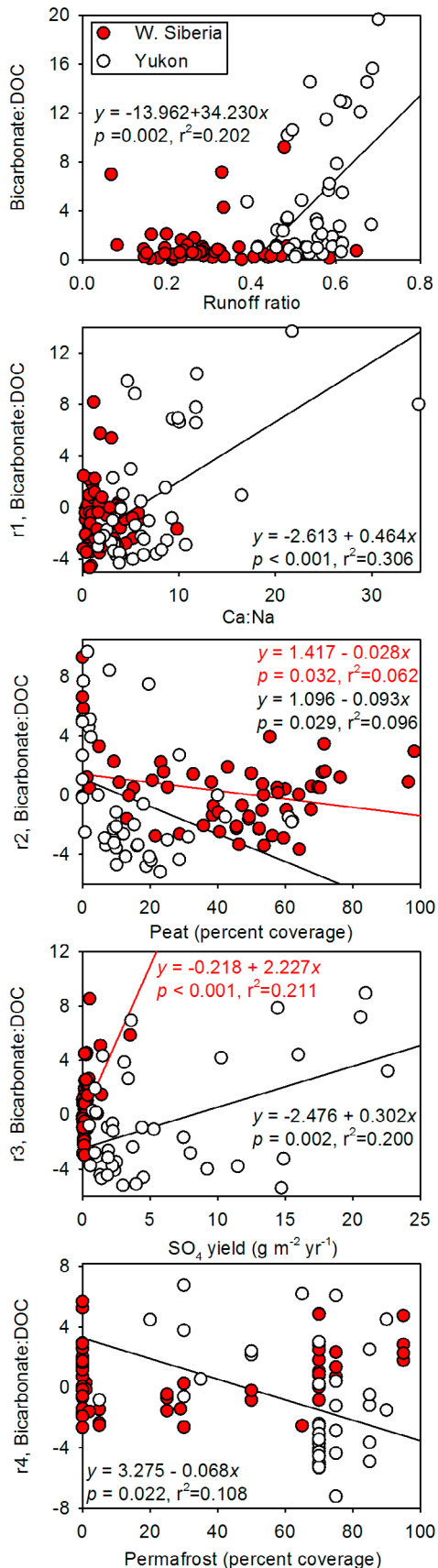
5. Discussion

5.1. Controls on Bicarbonate Flux

[32] Across a suite of study catchments distributed throughout the circumboreal (Figure 1) we were able to explain as much as 90% of variation in bicarbonate flux using just four descriptor variables. While these geographically dispersed catchments do not include representation from the Eastern Canadian or European boreal, they do range in bicarbonate concentration from very dilute ($<1 \text{ mg L}^{-1} \text{ HCO}_3^-$) to bicarbonate-rich ($>40 \text{ mg L}^{-1}$), and thus represent a considerable range of conditions. Similar to previous work conducted primarily in temperate North America [Bluth and Kump, 1994] and Japan [Hartmann, 2009], we found runoff and lithology (in our work, primarily represented as Ca:Na) to be key drivers of bicarbonate flux across the circumboreal. These results are also in line with previous work by Raymond and Oh [2007], who found precipitation and evaporation (of which runoff is the difference) to be strong determinants of interannual variability in bicarbonate flux from large temperate U.S. watersheds.

[33] In addition to carbonate rock extent, SO_4 flux was a second lithological predictor of bicarbonate flux across our study catchments. Work by Hartmann [2009] has similarly found the ratio of bicarbonate to ($\text{SO}_4^{2-} + \text{Cl}^-$) to be significantly correlated with bicarbonate flux in Japanese catchments. In the boreal catchments that we examine, we propose two possible mechanisms to explain the importance of SO_4 for bicarbonate flux. First, the oxidative weathering of pyrite (FeS_2) to sulfuric acid creates a weathering agent that can drive the dissolution of carbonate rock without CO_2 sequestration. In the larger Mackenzie basin, the oxidative weathering of pyrite has been estimated to result in as much as 82% of basin-wide bicarbonate flux [Calmels et al., 2007]. While the importance of pyrite to weathering in the neighboring Yukon River basin has not been investigated, pyrite is known to co-occur with the gold deposits in this region [e.g., Marsh et al., 2003; Verplanck et al., 2008], which contains several active and historical mines [Brabets et al., 2000].

[34] In addition to pyrite, the dissolution of highly weatherable gypsum (CaSO_4) is the second main natural source of SO_4 to river water [e.g., Meybeck, 1987]. Gypsum and carbonate rocks are both sedimentary, and thus commonly co-occur [Flügel, 2004]. Therefore, the high



dissolution rate of gypsum can expose embedded carbonate deposits to increased weathering action, and thus elevate riverine bicarbonate fluxes [Meybeck, 1987]. Similarly, the presence of the products of gypsum dissolution in river water may simply indicate larger co-occurring carbonate rock deposits [Flügel, 2004]. Unlike pyrite oxidation, this mechanism would also result in weathering-mediated CO_2 fixation if the exposed carbonate rock is weathered via carbonic acid. Although pyrite does occur in East Siberia [Meffre et al., 2008], more widespread studies have concluded that gypsum weathering is prevalent in this region [Huh et al., 1998]. In addition, the extensive elevation of riverwater Cl relative to Na throughout Siberia indicates that evaporitic rocks are common in both East and West Siberia (see Section 3.1, Huh et al. [1998], and Frey et al. [2007b]) our exclusion of high Na:Cl (i.e., halite-draining) samples from our analyses would not necessarily have removed waters draining gypsum-type evaporites, particularly where gypsum predominates over halites [e.g., Flügel, 2004]. In general, it is difficult to determine the source of riverine SO_4 over broad scales without detailed analyses of isotopes or other tracers [Meybeck, 1987; Calmels et al., 2007]. Although this study indicates that SO_4 can be an important predictor of bicarbonate flux regardless of mechanism, knowledge of SO_4 source is necessary to assess CO_2 consumption by weathering.

[35] Across these permafrost-influenced boreal catchments, increasing permafrost extent typically limited bicarbonate flux. This was true even after accounting for other important drivers of bicarbonate flux. These quantitative results (see further discussion below) add significant weight to previous studies that strongly indicate that either weathering or bicarbonate flux should increase with decreasing permafrost extent [MacLean et al., 1999; Striegl et al., 2005; Frey et al., 2007b; Petrone et al., 2007; Striegl et al., 2007], but were unable to systematically assess potential co-variance in runoff, lithology, or other variables. While in part this result may have been driven by a direct effect of temperature on weathering [Hartmann, 2009; Hartmann and Moosdorf, 2011], there is ample evidence to suggest an important role for deepening flowpaths with decreasing permafrost extent (Kokelj and Burn [2005], Frey and McClelland [2009], Keller et al. [2010], and see below). Although the Yukon subwatersheds in our analyses showed only a moderate relationship between bicarbonate flux and permafrost extent, we do find bicarbonate yield to be directly related to the contribution of groundwater to total discharge in this region. In accordance with the known inverse relationship between permafrost and groundwater flux [Ge et al., 2011], proportion groundwater decreased significantly with increasing permafrost extent across the Yukon River basin, suggesting that our relatively coarse metric for permafrost extent may not have been finely

Figure 5. Sequential analysis of the controls on bicarbonate:DOC in subcatchments of West Siberia and the Yukon River basin. r1–r4: residual 1–residual 4. The sequential analysis results are given in Table 1. To examine trends within regions, region-specific regression results are also shown, using red text and lines for West Siberia and black text and lines for the Yukon River basin. Regressions are shown where significant at the $p < 0.05$ (solid line) level.

Table 3. Yukon River Basin Subcatchments: Controls on the Single-Day Normalized Flux of Bicarbonate, DOC, and the Bicarbonate:DOC Ratio^a

| | June | | | August | | |
|---|--------------------------------|-------|--------|--------------------------------|-------|--------|
| | Estimate | Error | p | Estimate | Error | p |
| HCO ₃ ⁻ (mg C m ⁻² d ⁻¹) | n = 33, r ² = 0.898 | | | n = 41, r ² = 0.848 | | |
| Constant | NI | NI | | -3.542 | 2.972 | 0.242 |
| Runoff (mm d ⁻¹) | 8.233 | 1.110 | <0.001 | 7.449 | 1.396 | <0.001 |
| Ca:Na | 0.915 | 0.386 | 0.025 | 0.532 | 0.248 | 0.039 |
| SO ₄ (mg m ⁻² d ⁻¹) | 0.244 | 0.076 | 0.003 | 0.331 | 0.038 | <0.001 |
| Permafrost (percent) | -0.085 | 0.051 | 0.106 | NI | NI | |
| HCO ₃ ⁻ :DOC | n = 33, r ² = 0.436 | | | n = 41, r ² = 0.499 | | |
| Constant | 1.554 | 2.303 | 0.505 | -4.806 | 2.509 | 0.063 |
| Runoff (mm d ⁻¹) | -0.404 | 0.271 | 0.147 | NI | NI | |
| Precipitation (cm yr ⁻¹) | 0.118 | 0.047 | 0.017 | 0.194 | 0.058 | 0.002 |
| Ca:Na | 0.273 | 0.084 | 0.003 | 0.452 | 0.098 | <0.001 |
| Peat (percent cover) | NI | NI | | -0.115 | 0.040 | 0.007 |
| SO ₄ (mg m ⁻² d ⁻¹) | NI | NI | | NI | NI | |
| Permafrost (percent) | -0.080 | 0.023 | 0.001 | NI | NI | |
| DOC (mg C m ⁻² d ⁻¹) | n = 37, r ² = 0.649 | | | n = 42, r ² = 0.614 | | |
| Constant | NI | NI | | 2.980 | 8.299 | 0.722 |
| Runoff (mm d ⁻¹) | 5.753 | 1.399 | <0.001 | 9.202 | 1.221 | <0.001 |
| Precipitation (cm yr ⁻¹) | NI | NI | | -0.402 | 0.143 | 0.008 |
| Peat (percent cover) | NI | NI | | NI | NI | |
| Permafrost (percent) | 0.103 | 0.055 | 0.069 | 0.192 | 0.085 | 0.029 |

^aWithin each region, multiple linear regression models were assessed for fit using Akaike's Information Criterion, as described in the text. NI = variable not included in the best fit model.

resolved enough to detect trends at the sub-watershed scale within this basin.

[36] Similar to our Yukon results, groundwater flux has been shown to be strongly negatively correlated with permafrost extent in West Siberian sub-watersheds, as assessed by an end-member mixing analysis of constituent concentrations [Frey *et al.*, 2007b]. In subcatchments of the Mackenzie region, however, we found no significant relationship between permafrost extent and groundwater flux. Instead, this relationship breaks down regionally for the

Mackenzie subcatchments. For June flows, when the majority of Mackenzie measurements were collected, tributaries from the southern Rocky Mountains and Transition to Interior regions have low groundwater contributions to total annual flow (<7%) and low to moderate permafrost coverage (0–25%), while more northerly mountainous subcatchments show moderate to high groundwater contributions (5–40%) over terrains with greater permafrost coverage (30–70%). This overall pattern remained when the contribution of groundwater to total annual (rather than seasonal) flow was considered, suggesting that other common regulators of surface to groundwater interactions, such as topology or geology [Freeze and Cherry, 1979], mask our ability to see a groundwater-permafrost trend in this region. Despite this regional variability, however, there does appear to be a trend of recent increases in base flow across the Mackenzie sub-watersheds in this study, in agreement with the findings of increasing base flow for gauging stations that have been examined across the Mackenzie drainage, northwestern

Table 4. West Siberian Subcatchments: Controls on Seasonally Normalized Flux (July–September) of Bicarbonate, DOC, and the Bicarbonate:DOC Ratio^a

| | Estimate | Error | p |
|--|----------------------------------|--------|--------|
| Bicarbonate (mg C m ⁻² season ⁻¹) | (n = 42, r ² = 0.614) | | |
| Constant | 134.959 | 71.913 | 0.067 |
| Runoff (cm season ⁻¹) | 55.047 | 12.466 | <0.001 |
| Ca:Na | 34.174 | 15.115 | 0.028 |
| SO ₄ (mg m ⁻² season ⁻¹) | 1.331 | 0.213 | <0.001 |
| Permafrost (percent) | -2.948 | 0.869 | 0.001 |
| Bicarbonate:DOC | (n = 54, r ² = 0.549) | | |
| Constant | 1.093 | 0.417 | 0.012 |
| Runoff (cm season ⁻¹) | NI | NI | |
| Precipitation (cm yr ⁻¹) | NI | NI | |
| Ca:Na | NI | NI | |
| Peat (percent cover) | -0.013 | 0.008 | 0.087 |
| SO ₄ (mg m ⁻² season ⁻¹) | 0.011 | 0.002 | 0.012 |
| Permafrost (percent) | NI | NI | |
| DOC (mg C m ⁻² season ⁻¹) | (n = 92, r ² = 0.522) | | |
| Constant | 197.137 | 78.510 | 0.014 |
| Runoff (cm season ⁻¹) | 96.940 | 16.425 | <0.001 |
| Precipitation (cm yr ⁻¹) | NI | NI | |
| Peat (percent cover) | 5.533 | 1.307 | <0.001 |
| Permafrost (percent) | -7.071 | 0.952 | <0.001 |

^aWithin each region, multiple linear regression models were assessed for fit using Akaike's Information Criterion, as described in the text. NI = variable not included in the best fit model.

Table 5. Region-Specific Annual Controls on Bicarbonate:DOC Within Subwatersheds of the Yukon River Basin and West Siberia^a

| | Yukon (n = 40, r ² = 0.604) | | | Western Siberia (n = 59, r ² = 0.575) | | |
|---|---|-------|--------|---|-------|--------|
| | Estimate | Error | p | Estimate | Error | p |
| Constant | 6.272 | 1.955 | 0.003 | 0.919 | 0.350 | 0.011 |
| Runoff ratio | NI | NI | | NI | NI | |
| Ca:Na | 0.343 | 0.094 | 0.001 | NI | NI | |
| Peat (percent cover) | NI | NI | | -0.012 | 0.006 | 0.067 |
| SO ₄ Yield (g m ⁻² yr ⁻¹) | 0.456 | 0.093 | <0.001 | 2.386 | 0.309 | <0.001 |
| Permafrost (percent) | -0.096 | 0.028 | 0.002 | NI | NI | |

^aFor comparison between regions, the runoff ratio and SO₄ yield are calculated using annual data. Within each region, multiple linear regression models were assessed for fit using Akaike's Information Criterion, as described in the text. NI = variable not included in the best fit model.

Canada, and the Yukon basin [Walvoord and Striegl, 2007; St. Jacques and Sauchyn, 2009], and in line with more general observations that active layer depths are increasing throughout the pan-Arctic [Oelke et al., 2004]. Of the 24 unregulated subcatchments that we assess, six show a significant ($p < 0.05$) increasing base flow trend and an additional three show marginal ($0.05 < p < 0.10$) base flow increases (assessed as change in average January–March flow over periods of record ranging from 13 to 55 years, using the Mann-Kendall test statistic) [e.g., Déry and Wood, 2005]. Only one sub-watershed showed a decrease in base flow, which was marginal; the remaining 13 showed no significant trend over time ($p > 0.10$). Subcatchments displaying significant trends were distributed throughout the larger Mackenzie basin.

5.2. Controls on Bicarbonate:DOC, and DOC Flux

[37] In contrast to the relatively consistent effect of permafrost on bicarbonate yields throughout the circumboreal, we found clear regional variation in the effect of permafrost on DOC yield, and thus the bicarbonate:DOC flux ratio. This finding follows those from previous studies [MacLean et al., 1999; Frey and Smith, 2005; Striegl et al., 2005] that show geographically divergent effects of permafrost on riverine DOC. However, we additionally find that this divergent permafrost effect remains even after co-occurring variance owing to runoff and peat extent have been partitioned. Runoff was universally a clear, positive predictor of DOC yield, similar to previous studies that show runoff to control DOC flux (both within and between catchments and in northern watersheds and elsewhere) [Raymond et al., 2007; Raymond and Oh, 2007; Raymond and Saiers, 2010; Townsend-Small et al., 2011]. In the West Siberian subcatchments, and following Frey and Smith [2005], peat extent was a second, positive predictor of DOC.

[38] Peat extent was not always a significant predictor of DOC flux, or the bicarbonate:DOC flux ratio in Yukon River basin. However, we do note a significant relationship between permafrost extent and peat in this region (Section 4.2), suggesting that some of the variation in DOC flux caused by peat extent may have been accounted for by the propensity for peat and permafrost to co-occur [Vitt et al., 1994]. In addition, soils are relatively shallow in the Yukon River basin, indicating that peat occurrence may not influence DOC flux as strongly in this region as elsewhere. Finally, the GIS-compatible data available to assess peat extent in Alaska is somewhat outdated [Rieger et al., 1979; Yu et al., 2010]. Although our peat extent results match well with other assessments of wetland extent in the region (e.g., remotely sensed estimates) [Whitcomb et al., 2009], it may be that our estimates are not as finely tuned as those for West Siberia [Sheng et al., 2004], or wetland estimates from more southern locations.

5.3. Landscape-Scale Implications of Variable Controls on Riverine Dissolved C Flux

[39] The divergence in controls on DOC yield between the Yukon and West Siberian subcatchments has clear implications for the effect of permafrost degradation on C cycling within these regions. In West Siberia, the CO_2 production that follows from an increase in DOC release from thawing permafrost should be offset – to some extent –

by increasing CO_2 fixation as weathering processes and thus bicarbonate flux increase. Based on our summertime calculations, permafrost has a much stronger effect on DOC than bicarbonate yields in West Siberia (regression coefficients in Table 4). For permafrost-affected catchments, our model results indicate that a 10% decrease in permafrost extent (or, allowing catchments with $<10\%$ permafrost to fall to zero) increases DOC yields by 12% and bicarbonate yields by 6.2%. However, because DOC yields in these catchments are greater than those for bicarbonate, the absolute increase in DOC yield is 2.5-fold that of bicarbonate (62 and 24 $\text{mg C m}^{-2} \text{ season}^{-1}$, respectively). These increasing DOC yields likely indicate even greater DOC production and mineralization to CO_2 further up in the catchment [Öquist et al., 2009; Teodoru et al., 2009] and we might conservatively estimate that a minimum of 60% of the DOC measured in-river is converted to CO_2 at some point downstream, based on loss rates of riverine DOC within the Arctic Ocean [Alling et al., 2010; Letscher et al., 2011]. Similarly, approximately 72% of bicarbonate flux can be attributed to weathering-mediated CO_2 fixation in these catchments, based on the relative importance of carbonate versus silicate weathering (Figure 2), and a negligible effect of pyrite oxidation in these sub-watersheds ($\leq 1\%$ effect). Thus, increased CO_2 fixation via weathering appears likely to offset a portion of the effect of increased DOC mobilization if permafrost extent declines in West Siberia.

[40] In contrast, subcatchments of the Yukon River basin experience increased bicarbonate, but decreased DOC yields, when permafrost extent declines. Previous authors have suggested that permafrost-related decreases in DOC yield may be due to an increase in within-catchment microbial degradation as a result of increased water residence times [Striegl et al., 2005], a decreased proportion of water flow through organic-rich surface layers as a result of increasing active layer depths [MacLean et al., 1999; Carey, 2003; Petrone et al., 2006; O'Donnell et al., 2010], or some combination thereof. These two processes have fundamentally different C cycling implications: the first implies increased DOC mobilization from soils that is degraded to CO_2 before it reaches downstream locations, while the second implies an overall decrease in the mobilization of DOC, or increased adsorption of DOC within mineral-rich soil horizons. The uncertainty about the relative importance of these two processes, and the time scales over which processes such as DOM adsorption might operate, makes it difficult to assess the overall implications of our model results. For example, if the second process for DOC flux dominates, increasing bicarbonate flux and decreasing DOC mobilization could both act to increase CO_2 sequestration with decreasing permafrost extent. Based on our calculated relationship between permafrost and bicarbonate:DOC (Table 3, where the June and August permafrost coefficient averages -0.08 , as described in Section 4.2), a 10% decrease in permafrost extent would increase bicarbonate:DOC by ~ 0.8 ; a significant increase given that flow-weighted bicarbonate:DOC ranges from 2.0 (June) to 3.0 (August) in the Yukon subcatchments. Although only 48–60% of the flow-weighted bicarbonate flux originates from CO_2 fixation in these catchments (depending on season and the importance of pyrite oxidation; Figure 2), this change still represents a considerable potential increase in CO_2 sequestration (or decrease in CO_2 loss) measured

upstream for bicarbonate and downstream from the point of measurement for DOC.

[41] As expected, runoff was universally a positive predictor of bicarbonate and DOC flux. On the surface, therefore, and given the increase in discharge documented for much of the Arctic [Peterson *et al.*, 2002; Déry *et al.*, 2009], it seems that climate-induced changes in runoff and permafrost should reinforce each other universally for bicarbonate and in West Siberia for DOC, but work antagonistically for DOC in the Yukon River basin. However, the true effect of increasing runoff will likely depend on the mechanistic underpinning of the change. For example, increases in annual runoff that occur as a result of increasing base flow may simply be a symptom of decreasing permafrost extent [Ge *et al.*, 2011]; an increased contribution from deeper flowpaths to total runoff [e.g., Walvoord and Striegl, 2007] would have a very different effect on C cycling than increases in runoff that occur across the hydrograph as a result of an intensification of the hydrologic cycle [Rawlins *et al.*, 2010]. While our model results indicate that increases in spring to summertime runoff will increase dissolved C flux in these regions, they do not provide a prediction for the effect of increases in base flow-associated discharge.

6. Summary and Conclusions

[42] The flux of DIC across all of the boreal-to-arctic catchments that drain northward to the Arctic Ocean represents between 13 and 15% of global DIC flux (Tank *et al.*, submitted manuscript, 2012). Throughout the circumboreal catchments that we studied, controls on bicarbonate yields were near-universal. Runoff, the extent of carbonate rocks (as Ca:Na), and SO₄ yield were significant, positive predictors of bicarbonate yield, while increasing permafrost extent was associated with clear decreases in bicarbonate. In contrast, while runoff was also universally a positive predictor of DOC yield, the effect of peat and permafrost was not consistent across regions for DOC. For peat, this may have been due to our inability to properly assess peat extent and its effects in the Yukon River basin. For permafrost, however, there was a significant, but opposite, effect of permafrost extent on DOC yield in the two regions we studied, after the effect of variations in runoff and peat had been accounted for. Our results indicate that weathering-mediated CO₂ sequestration should increase with permafrost thaw over a broad geographic range, while the movement of DOC from thawing soils to rivers may be more region-specific. Because the increase in weathering-mediated CO₂ sequestration that we document with decreases in permafrost is substantial, it can be expected to counterbalance some of the organic C mineralization that is predicted as permafrost soils thaw. Specific to bicarbonate, while more southern regions of the globe are not affected by permafrost, they are experiencing increasing temperatures – albeit at a lower rate of change than in the Arctic – and changes in flowpath as the seasonal freezing and thawing of soils is affected by changing climate [Intergovernmental Panel on Climate Change, 2007]. Thus, while the weathering effect that we document is likely much more pronounced in permafrost-influenced regions, it may also occur elsewhere.

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