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Key Points:
- Antarctic streams exhibit chemostatic concentration-discharge relationships for weathering-derived solutes
- Hydrologic transit times are short (less than four months), yet solute export is predominantly transport limited because equilibrium time scales are also short (<13 days)
- Hydrologic transit time explains between-stream variability in the shape of concentration-discharge relationships

Supporting Information:
- Supporting Information S1

Correspondence to:
A. N. Wlostowski,
adam.wlostowski@colorado.edu

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Transit Times and Rapid Chemical Equilibrium Explain Chemostasis in Glacial Meltwater Streams in the McMurdo Dry Valleys, Antarctica

A. N. Wlostowski[1], **M. N. Gooseff**[1,2], **D. M. McKnight**[1,2], and **W. B. Lyons**[3]

[1]Institute of Arctic and Alpine Research, University of Colorado Boulder, Boulder, Colorado, USA, [2]Department of Civil, Environmental, and Architectural Engineering, University of Colorado Boulder, Boulder, Colorado, USA, [3]School of Earth Sciences and the Byrd Polar and Climate Research Center, Ohio State University, Columbus, Ohio, USA

Abstract Fluid transit time is understood to be an important control on the shape of concentration-discharge (*C-q*) relationships, yet empirical evidence supporting this linkage is limited. We investigated *C-q* relationships for weathering-derived solutes across seven Antarctic glacial meltwater streams. We hypothesized that (H1) solute fluxes in McMurdo Dry Valley streams are reaction limited so that *C-q* relationships are characterized by dilution and that (H2) transit time explains between-stream variability in the degree of *C-q* dilution. Results show that *C-q* relationships are chemostatic because solute equilibrium times are shorter than stream corridor fluid transit times. Between-stream variability in the efficiency of solute production is positively correlated with transit time, suggesting that transit time is an important control on the solute export regime. These results provide empirical evidence for the controls on weathering-derived *C-q* relationships and have important implications for Antarctic ecosystems and solute export regimes of watersheds worldwide.

Plain Language Summary Relationships between solute concentration and stream discharge (i.e., streamflow) rates in rivers contain important information regarding how water moves through a watershed. In this research, we use a combination of observations and mathematical modeling to show that the shape of concentration-discharge relationships is related to hydrologic transit time, the duration of time a parcel of water spends moving through the watershed. Because the time scales of chemical reactions are shorter than hydrologic transit times, solute concentration is invariant with discharge. Results of this work empirically corroborate previous theoretical work regarding the physical controls on concentration-discharge relationships, and have important implications for understanding chemical concentration patterns in rivers worldwide.

1. Introduction

Relationships between stream solute concentration and discharge (*C-q*) result from reaction and transport processes occurring across scales within a catchment (Godsey et al., 2009; Maher, 2011), and are useful for discerning patterns of source water connectivity and flow paths (Chanat et al., 2002; Evans & Davies, 1998; McGlynn & McDonnell, 2003). Concentrations of weathering-derived (geogenic) solutes typically exhibit either little variation with *q* (chemostasis), or declining concentrations with increasing *q* (dilution; Godsey et al., 2009).

It is generally understood that the shape of *C-q* relationships depends on flow path transit times, chemical reaction rates, and equilibrium concentrations (Ameli et al., 2017; Clow & Mast, 2010). One hypothesis for chemostasis (i.e., minimal change in *C* across many orders of magnitude of *q*) is that water discharging to streams is always in chemical equilibrium with catchment mineral surfaces, resulting in transport-limited solute fluxes. In catchments where stormflow is mostly composed of “old” water, equilibrated water from long flow paths is displaced to the stream during storm events, maintaining chemostasis (Clow & Mast, 2010; Kirchner, 2003). On the other hand, in catchments where stormflow is mainly composed of “new” water, brief transit times prevent solute concentrations from reaching equilibrium during storm events, resulting in dilution (Shanley et al., 2011). However, if reaction rates are sufficiently high and/or equilibrium concentrations are sufficiently low, chemostasis can arise regardless of transit time (Ameli et al., 2017).

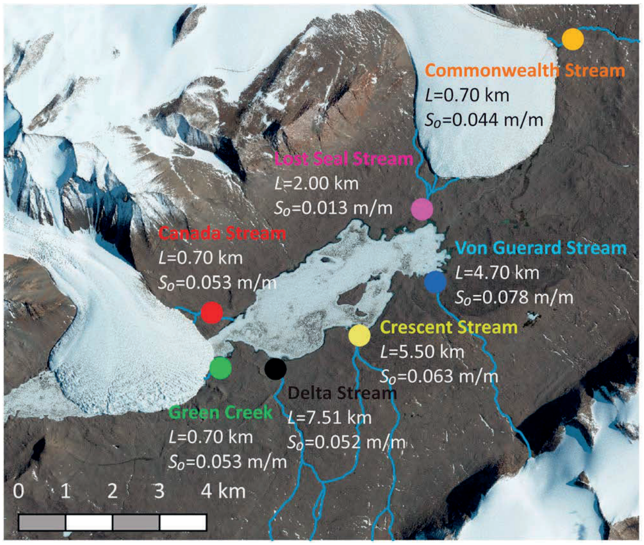

Figure 1. Seven glacial meltwater streams in the Taylor Valley, Antarctica, are considered in this study. Stream gauge locations are shown as colored circles. Colored text adjacent to circles indicates stream names, longest stream length from glacier to gauge (L), and average stream slope (S_0).

Modeling studies have developed generalizable theories for the physical and chemical factors controlling *C-q* relationship shape (Ameli et al., 2017; Maher, 2010, 2011). However, the evaluation of these theories to explain *between*-catchment variations in *C-q* shape has been limited. Godsey et al. (2009) synthesized *C-q* relationships from many catchments across North America, yet could not find a suitable explanation for observed variability among catchments. Overall, unquantified catchment heterogeneity seems to complicate the validation of these controls by catchment comparison. Here we use a unique natural system as a laboratory for disentangling physical and chemical controls on *C-q* relationships.

Because of the extremely cold and dry climatic setting, glacial meltwater streams of the McMurdo Dry Valleys (MDV) are model systems for investigating hydrologic and geochemical controls on *C-q* relationships. In this environment, precipitation is minimal and nearly all streamflow is derived from glacial melt (Fountain et al., 2010; Wlostowski et al., 2016). Streams are physically short, ranging in length from 1 to 10 km. Surface water-groundwater interactions are limited to shallow hyporheic zones (Gooseff et al., 2003; Runkel et al., 1998), which are important incubators for chemical weathering in an otherwise parched landscape (Maurice et al., 2002; Nezat et al., 2001).

To provide insight toward the controls on *C-q* relationships globally, the goals of this research are to (1) characterize the shape of *C-q* relationships in MDV streams and (2) offer a mechanistic explanation for the observed shapes. We pose two hypotheses:

H1: The production and mobilization of weathering-derived solutes (Si, K^+, Ca^{+2}, HCO_3^-) is reaction limited in MDV streams because mean transit times are shorter than equilibrium time scales. We expect *C-q* relationships to be characterized by dilution, whereby stream water chemistry becomes similar to glacier ice chemistry at increasingly high flows.

H2: The degree of *C-q* dilution (or chemostasis) depends on stream length. Solute fluxes in longer streams will be more transport-limited than in shorter streams because longer streams exhibit lower average flows (Wlostowski et al., 2016), have more hyporheic storage volume, and thereby sustain longer water transit times.

To test H1, we first quantitatively characterize the shape of *C-q* relationships using a power law model and a statistical metric of *C-q* variation. In addition, *C-q* data are fit with a simple advection-reaction model and results are interpreted in terms of the Damköhler number (*Da*). We expect quantitative metrics of *C-q* shape to be characteristic of a diluting system and solute fluxes to be reaction limited ($Da < 1$). To test H2, we calculate mean fluid transit times for each stream, expecting between stream variability in *Da* to be positively correlated with transit time.

2. Study Site

This study considers seven streams in the Taylor Valley, Antarctica (Figure 1). Nearly all streamflow is derived from glacial melt, which fluctuates on a subdaily basis due to diel changes in solar aspect (Conovitz et al., 1998; Wlostowski et al., 2016). Daily meltwater pulses are routed from glaciers along the stream corridor to closed-basin ice-covered lakes. Stream channels are surrounded by hyporheic zones that are bounded at depth by permafrost, and typically thaw <1 m (Conovitz et al., 2006). The connectivity of surface water and groundwater is limited to hyporheic exchange. Continuous permafrost precludes any mixing between near-surface water and deep (subpermafrost) groundwater. Also, extreme aridity limits hydrologic connections between stream channels and adjacent, soil-mantled, hillslopes.

While streams differ by slope (S_0), length from glacier to gauge (L), and glacier source, all streams have common geomorphic and geologic properties. All streams flow through similar sandy soils interspersed with cobbles and boulders. Soils were deposited by the Ross Sea drift and show evidence of strong cryoturbation

(Bockheim & McLeod, 2008). Parent material is a mixture of granite, gneiss, dolerite, volcanics, and sandstone (Bockheim, 1997; Doran et al., 1994; Péwé, 1960). Primary and secondary minerals in hyporheic sediments are believed to a significant source of geogenic solutes (Lyons et al., 1998). X-ray diffraction analysis shows that hyporheic mineral assemblages are dominated by plagioclase, quarts, and muscovite/illite/smectite (Gooseff et al., 2002).

3. Data and Methods

3.1. Data Sets Used

As part of the McMurdo Long-Term Ecological Research Project, a network of stream gauges was established and is maintained throughout the MDVs (Figure 1). Gauges measure stage, water temperature, and specific conductance at 15-min intervals, and a rating curve is used to estimate volumetric discharge, Q (m^3/day; see Wlostowski et al., 2016 for details). The stream corridor Darcy velocity, q (m/day), is calculated as

$$q = \frac{Q}{A_x} = \frac{Q}{[(w_c + 2w_{HZ})z_{\text{thaw}}]} \tag{1}$$

where A_x is the cross-sectional area of the stream corridor (m^2), w_c is the channel width (m), w_{HZ} is the half-width of the hyporheic zone (m), and z_{thaw} is the thawed active layer depth (m). We assume w_c and w_{HZ} to be 4 and 5 m, respectively, based on observations of channel and wetted margin widths (Northcott et al., 2009). Thaw depth (z_{thaw}) is set to 1 m, which is approximately the maximum annual thaw depth observed beneath stream channels (Wlostowski et al., 2018).

Between 1993 and 2014, 75–124 stream water samples were collected near each gauge location. We focus on dissolved Ca^{2+}, K^+, HCO_3^-, and Si, because these solutes are mainly produced by chemical weathering of mineral surfaces along the stream corridor. Within 24 hr of collection, samples are filtered through 0.4-μm Nuclepore polycarbonate membrane filters into HDPE bottles prerinsed with deionized water. Samples were stored at 4 °C until analysis, following the methods of Welch et al. (2010). Alkalinity was determined by titration, and titration alkalinities are assumed to be primarily bicarbonate (Welch et al., 2010). Dissolved Si is measured colorimetrically following the methods of Mullin and Riley (1955). Hereinafter, we will use "Si" in reference to colorimetrically detected dissolved silicon species, H_4SiO_4. Dissolved Ca^{2+} and K^+ were quantified using the ion chromatographic techniques outlined in Welch et al. (2010).

3.2. Data Analysis

In order to test our hypotheses, we quantitatively characterize *C*-*q* shapes and mechanistically interpret *C*-*q* data under a Damköhler framework; first, by fitting a power law model to *C*-*q* observations:

$$C = aq^b \tag{2}$$

where C is the concentration (ppm), b is a scaling parameter and the slope of the *C*-*q* relationship on a logarithmic axis, and a is a constant. Following Godsey et al. (2009), best fitting b values indicate the degree of dilution, where $b = -1$ indicates pure dilution and $b = 0$ indicates chemostasis (i.e., constant C for all q). In addition, we calculate the ratio of coefficients of variation for C and q (CV_C/CV_q), whereby $CV_C/CV_q << 1$ is characteristic of chemostatic *C*-*q* relationships (Thompson et al., 2011).

To provide a process-based interpretation of observations, *C*-*q* data are also fit with a quasi steady state advection-reaction model with an exponential fluid transit time distribution (Maher, 2011; Maher & Chamberlain, 2014).

$$C = C_{\text{eq}} \frac{\gamma Dw/q}{1 + \gamma Dw/q} \tag{3}$$

where γ is a dimensionless constant (=e^2), C_{eq} is the solute equilibrium concentration (ppm), and Dw is the "Damköhler coefficient" (m/day). This model assumes that concentrations of aqueous geogenic species increase with distance along the river corridor until a thermodynamic equilibrium is reached (Maher, 2010). The implicit spatial pattern of increasing solute concentration with distance is in-line with previous synoptic water quality observations in MDV streams, which clearly show increasing weathering-derived solute concentrations with distance from glaciers (Gooseff et al., 2002; Nezat et al., 2001; Wlostowski et al., 2016). Equation (3) is fit to *C*-*q* observations by optimizing *Dw* and C_{eq} with the method of least squares. By determining C_{eq} through model calibration, we assume that solute concentrations are near equilibrium at the low end of the observed *q* range.

Contrary to a power law model (equation (2)), parameters in equation (3) are physically meaningful. The Damköhler coefficient, *Dw*, is the slope of a negative linear relationship between the dimensionless Damköhler number (*Da*) and *q* (Maher & Chamberlain, 2014).

$$Da = \frac{Dw}{q} = \frac{\tau_f}{\tau_{\text{eq}}} \tag{4}$$

Da is equal to the ratio of mean fluid transit time (τ_f) to equilibrium time scale (τ_{eq}; equation (4)) and describes the efficiency of solute production. The model assumes an exponential distribution of fluid transit times along an idealize flow path, with a mean fluid transit time approximated as the ratio of channel length to seepage velocity (q/ϕ)

$$\tau_f = \frac{L\phi}{q} \tag{5}$$

where *L* is the length of the stream corridor and ϕ is the porosity of hyporheic sediments (m^3/m^3). This simple approximation of transit time is warranted by the relatively simplicity of Antarctic “catchments,” which can be idealized as natural flumes: meltwater enters the channel head, is routed along the length of the stream with minimal lateral inflows. After rearranging equation (3), inserting equation (4), and simplifying, τ_{eq} is calculated as

$$\tau_{\text{eq}} = \frac{\tau_f}{Da} = \frac{L\phi}{qDa} = \frac{L\phi}{Dw} \tag{6}$$

Alternatively, τ_{eq} can be expressed as the ratio of C_{eq} and the bulk reaction rate, *R* (g/m^3/day; Maher, 2010), leading to the following equation for *R*.

$$R = \frac{C_{\text{eq}} Da}{\tau_f} \tag{7}$$

4. Results

Visual inspection of *C*-*q* relationships reveals that Si, Ca^{2+}, K^+, and HCO_3^- concentrations vary only slightly across 4 orders of magnitude of discharge (Figure 2). The ratio of coefficients of variation of *C* and *q* (CV_C/CV_q) ranges from 0.09 to 0.73 with a mean value of 0.26 (Table S1), quantitatively confirming that solute concentration is relatively invariant compared to discharge. Additionally, best fit power law exponent values, *b* (equation (2)), range from −0.2 (Canada Stream, Si) to 0.0 (Crescent Stream, K^+; Table S1). Exponent values are all greater than −0.2, indicating that MDV streams are chemostatic according to the Godsey et al. (2009) criteria.

Advection-reaction and power law models produced similar quality fits to *C*-*q* observations (Table S1 and Figures S1–S7). *R*-squared statistics from each model are linearly correlated with a slope of 0.94 (Figure S8), suggesting that the power law model produces slightly better fits than the advection-reaction model.

Damköhler Number exceedence probability (*P* (*Da*)) curves (Supplemental Text) summarize advection-reaction model results and the transport regime of weathering-derived solutes (Figure 3). When $Da > 1$, $\tau_f > \tau_{\text{eq}}$ and solute flux is transport-limited. On the other hand, when $Da < 1$, $\tau_{\text{eq}} > \tau_f$ and solute flux is reaction-limited. Across all streams and solutes, $P(Da > 1)$ ranges from 0.5 to 1 and median *Da* (Da_{med}) ranges from 1.1 to 219.1, suggesting that solute fluxes are predominantly transport-limited. Longer

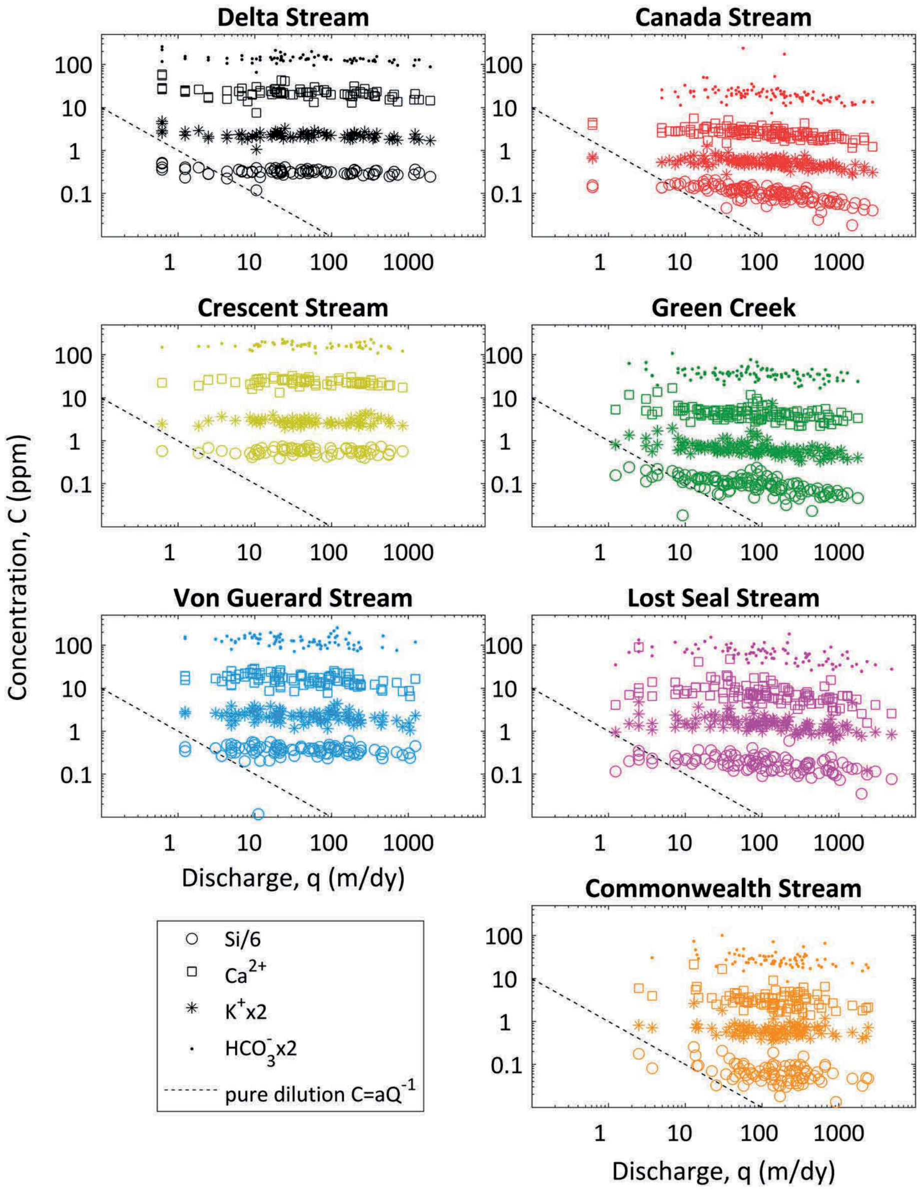

Figure 2. Concentration-discharge relationships for Si, K$^+$, Ca^{2+}, and HCO$_3^-$ for seven MDV streams. Concentration magnitudes are scaled to improve visualization (see legend).

streams (Crescent, Delta, and Von Guerard) exhibit a greater frequency of transport-limitation and have higher Da_{med}, compared to shorter streams (Canada, Green, Lost Seal, and Commonwealth).

While all streams exhibit chemostatic C-q relationships and predominantly transport-limited flux regimes, between-stream variations in C-q shape (Figure 2) and P(Da) (Figure 3) are apparent. Median flow τ_f explains between-stream variability in C-q shape and Da_{med} (Figure 4). As median flow τ_f increases, CV_C/CV_q and b approach zero. This shows that the degree of C-q chemostasis increases with transit time. Additionally, Da_{med} is positively correlated with median flow τ_f, suggesting that residence time is a key control on a stream's solute flux regime. On the other hand, between-stream variation in C-q shape (CV_C/CV_q and b) and Da_{med} does not seem to depend on between-stream differences in τ_{eq} (Figures 4b, 4d, and 4f). Only results for Si-q relationships are shown in Figure 4 to improve presentation clarity. Other weathering-derived solutes (K$^+$, Ca^{2+}, and HCO$_3^-$) exhibit similar relationships as those for Si (Figures S9–S11).

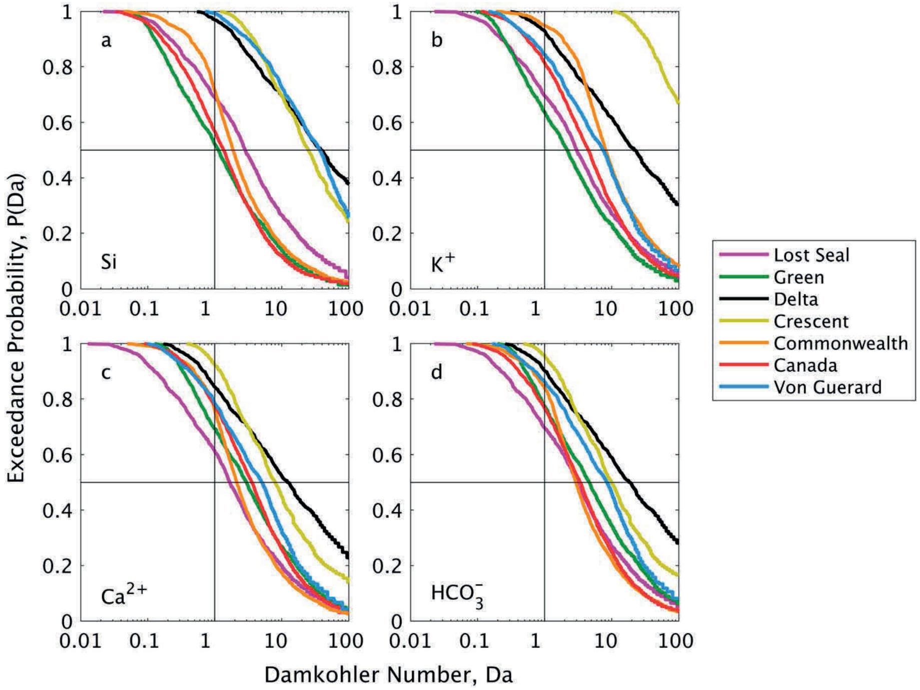

Figure 3. Damköhler exceedance probability curves for Si, K$^+$, Ca^{2+}, and HCO$_3$$^-$. When $Da > 1$ solute flux is transport limited, and when $Da < 1$, solute flux is reaction limited. Curves are derived by evaluating Da across the range of flows at each stream, per equation (3).

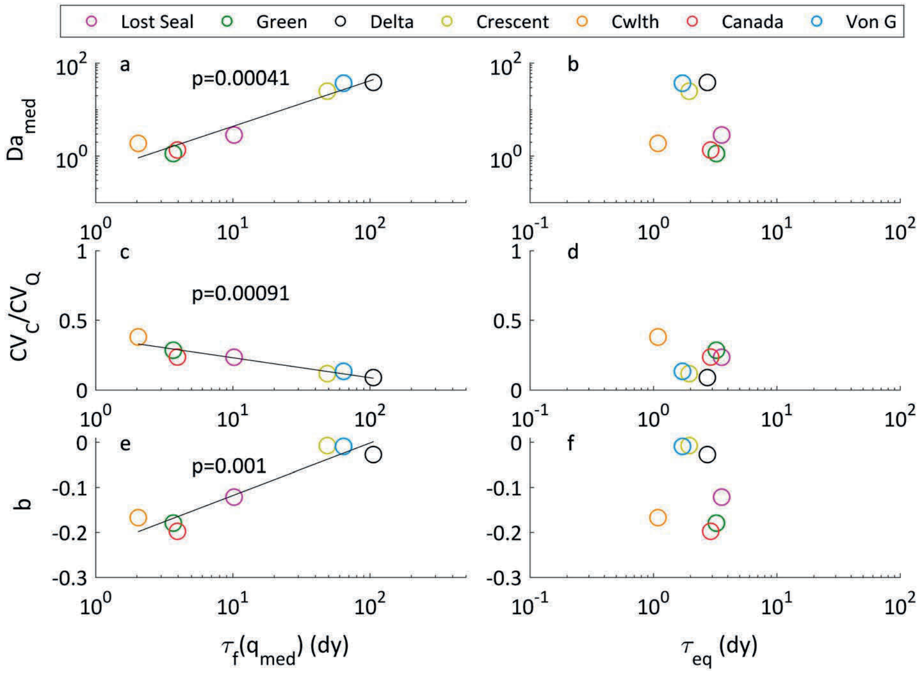

Figure 4. Relationships between Si-q shape parameters and (a, c, and e) median flow mean transit time, $\tau_f\,(q_{\text{med}})$, and (b, d, and f) equilibrium time scale, τ_{eq}.

5. Discussion

5.1. Ubiquity of Near-Chemostatic *C-q* Relationships in Antarctic Streams

Contrary to H1, weathering-derived *C-q* relationships are resoundingly chemostatic (Figure 2). Additionally, a quasi steady state advection-reaction model (equation (3)) suggests that solute fluxes are predominantly transport-limited (Figure 3). Together, this is sufficient evidence to refute H1. Instead, model results argue that chemostasis occurs as result of the geochemical evolution of meltwater along the stream corridor, such that weathering-derived solutes are near equilibrium with mineral surfaces near stream outlets, regardless of flow rate.

This result is somewhat surprising because fluid transit times under median flow conditions are short in MDV streams, less than four months (Figure 4). MDV streams are conceptually comparable to a laboratory flume. Like a flume, flow is generated at the channel head by glacial melt. Meltwater is then routed down the stream corridor through surface (in-channel) and subsurface (hyporheic) flow paths. Unlike many temperate midlatitude catchments, continuous permafrost and near absent stream-hillslope hydrologic connectivity precludes the development of long and deep flow paths. As a result, we estimate that fluid transit time distributions range from hours to months in MDV streams (Supplemental Text and Figures S13 and S14), compared to hours to centuries typical for midlatitude catchments (Jasechko et al., 2016). In order for meltwater to be near chemical equilibrium ($Da \geq 1$) at the stream outlet, equilibrium time scales (τ_{eq}) must be equal to or shorter than the transit times (τ_f; equation (4)).

Model-inferred τ_{eq} ranges from 0.2 to 12 days, with a mean value of 3.5 days (Table S1). For comparison, Maher (2010) argues that τ_{eq} in six midlatitude catchments from the U.S. Geological Survey Hydrologic Benchmark Network (HBN; Murdoch et al., 2005) could range from 30 days (0.08 year) to 365 days (1 year). Relatively low C_{eq} in MDV stream waters could explain the disparity in τ_{eq}. For example, C_{eq} (Si) ranges from 0.4 to 3.5 ppm with a mean value of 1.52 ppm in MDV streams (Table S1). These values are much lower than C_{eq} (Si) observed in HBN catchments, which range from 4 to 16 ppm with a mean value of 8.5 ppm (Table S2; Maher, 2010). Assuming similar chemical weathering rates, τ_{eq} will tend to be shorter in MDV streams than HBN streams, simply because C_{eq} is lower.

High rates of chemical weathering might also contribute to short τ_{eq}. Numerous investigations have shown that chemical weathering rates are high in MDV streams because mineral faces are relatively fresh and dilute meltwater is charged with CO_2 (Gooseff et al., 2002; Green et al., 1988, 2005; Lyons et al., 1997; Maurice et al., 2002; Nezat et al., 2001). For example, Maurice et al. (2002) observed the development of etch pits on mica surfaces buried in hyporheic sediments along Green Creek after only 39 days. Separately, Gooseff et al. (2002) calculated catchment-wide weathering rates to be an order of magnitude greater than those observed in warmer and wetter temperate watersheds. Model-derived bulk silicon dissolution rates (*R*; equation (7) and Table S1) range from 0.2 to 24.1 g $Si{\cdot}m^3{\cdot}day$. These rates are equal to or greater than *R* at HBN catchments inferred from Maher's (2010) results, which span from 0.01 to 0.5 g $Si{\cdot}m^3{\cdot}day$ (Table S2). Based on this single comparison, it is possible to argue that weathering rates are relatively high in MDV streams; however, a more robust comparison of catchment weathering rates is needed to strengthen this claim.

While the advection-reaction model provides a single plausible hypothesis for the ubiquity of chemostasis in MDV streams, factors not considered by the model may also be important. For example, structured spatial heterogeneity of solute sources can control *C-q* shape (Basu et al., 2010; Herndon et al., 2015; Musolff et al., 2017). Specifically, homogenously distributed solute sources give rise to chemostatic *C-q* patterns. The apparent geologic homogeneity of stream corridor sediments may also control the observed chemostasis of weathering-derived solutes in MDV streams. Along these lines, temporal changes in reactive surface area have also been hypothesized to control *C-q* dynamics (Godsey et al., 2009). In MDV streams, highly unsteady flows can influence the connectivity of hyporheic flow paths and storage/flushing of solutes (Koch et al., 2011; Singley et al., 2017). Similarly, expansion and contraction of the wetted perimeter between high and low flows may cause the dissolution and precipitation of channel-margin salt crusts. Additionally, periodic freezing and thawing of stream corridor waters can alter solute concentrations (Anderson, 1967; Wlostowski et al., 2018). Incrementally more complex, yet parametrically constrained, models will be needed to assess the influence of additional physiochemical processes on *C-q* relationships.

5.2. Residence Time Controls Between-Stream Variability of *C-q* Relationships

We find that median flow τ_f explains between-stream variability in *C-q* shape and transport regime, and this evidence supports H2. Other studies have observed relationships between *C* and τ_f. For example, Zapata-Rios et al. (2015) and Rademacher et al. (2001) found positive relationships between τ_f and major ion concentrations in spring waters. Similarly, Wolock et al. (1997) found a positive correlation between basin size to and acid-neutralizing capacity, which was attributed to between catchment differences in τ_f. However, there is little empirical evidence relating τ_f to the shape of *C-q* relationships, likely because measuring and/or predicting catchment-scale transit time distributions is challenging. By leveraging the relative simplicity of Antarctic "catchments," the findings of this study show that τ_f is a key factor affecting the variability in *C-q* shape observed across MDV streams (Figure 2).

5.3. Ecosystem Implications

Future climate warming in the MDVs is likely to increase glacial melt and streamflow rates (Doran et al., 2002). Higher streamflow rates will decrease τ_f, assuming that changes in channel geometry and z_{thaw} are less pronounced. Consequently, results of this study suggest that warming could shift weathering-derived solute flux regimes from transport- to reaction-limited, provided sufficient increases in streamflow rates. For example, Green Creek experiences a lognormal distribution of flows with q_{med} = 76 m/day (Figure S15). Currently, Da_{med} (Si) = 1.14, suggesting a predominantly transport-limited Si flux regime. In order for Da_{med} (Si) to equal 1, median flows would have to increase to 122 m/day, a 60% increase.

The productivity of lentic and lotic ecosystems depends on fluxes of weathering-derived solutes, particularly P and Si. Bioavailable P is primarily sourced from apatite weathering (Heindel et al., 2017) and can be the limiting nutrient for lake phytoplankton (Lizotte et al., 1996; Priscu, 1995) and stream cyanobacteria communities (Kohler et al., 2015). Similarly, Si is required for diatom growth and dissolved Si may influence diatom species composition in benthic microbial mats. Predicting future aquatic ecosystem dynamics in the MDVs will benefit from consideration of hydrologically mediated shifts in stream solute export regimes.

6. Conclusions

This study investigated *C-q* relationships for weathering-derived solutes in seven glacial meltwater streams in order to better understand the physical and chemical controls on *C-q* orientation. It was hypothesized (H1) that solute fluxes in MDV streams are reaction limited, and *C-q* relationships would indicate dilution. Contrary to H1, *C-q* relationships are objectively chemostatic, despite exceedingly short water residence times. It was hypothesized (H2) that residence time could explain between-stream variability in the degree of *C-q* dilution. Supporting H2, between-stream variability of *C-q* shape parameters and Da_{med} is explained by median flow transit time, suggesting that transit time is an important control on the variability of *C-q* shapes observed between MDV streams. The results of this study provide important empirical evidence for the controls on *C-q* relationships and may have implications for ecosystem dynamics in Antarctic and temperate watersheds.

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