Dissolved Organic Carbon Chemostasis in Antarctic Polar Desert Streams

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Abstract

The relationship between dissolved solute concentration (C) and discharge (q) in streams, i.e., the C-q relationship, is a useful diagnostic tool for understanding biogeochemical processes in watersheds. In the ephemeral glacial meltwater streams of the McMurdo Dry Valleys [MDVs], Antarctica, studies show significant chemostatic relationships for weathering solutes and NO₃⁻. Dissolved organic carbon (DOC) concentrations here are low compared to temperate streams, in the range of 0.1 to 2 mg C L⁻¹, and their chemical signal clearly indicates derivation from microbial biomass. Many MDV streams support abundant microbial mats, which are also a source of organic matter to underlying hyporheic sediments. We investigated whether the DOC generation rate from these autochthonous organic matter pools was sufficient to maintain chemostasis for DOC despite these streams' large diel and interannual fluctuations in discharge. To evaluate the DOC-q relationship, we fit the long-term DOC-q data to two models: a power law and an advection-reaction model. By using model outputs and other common metrics to characterize the DOC-q relationship, we found that this relationship is chemostatic in several MDV streams. We propose a conceptual model in which hyporheic carbon storage, hyporheic exchange rates, and net DOC generation rates are key interacting components that enable chemostatic DOC-q behavior in MDV streams. This model clarifies the role of autochthonous carbon stores in maintaining DOC-q chemostasis and may be useful for examining these relationships in temperate systems, where autochthonous organic carbon is readily bioavailable but where its signal is masked by a larger allochthonous signal.

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Key Points:
• Although DOC concentrations in McMurdo Dry Valleys streams are very low, DOC-flow relationships are chemostatic
• Biogeochemical processes in microbial mats and the hyporheic zone support chemostasis for DOC in Dry Valleys streams
• Autochthonous organic matter pools in the hyporheic zone may also influence DOC concentrations in temperate streams
Index terms 0414: Biogeochemical cycles, processes, and modeling; 0744: Rivers; 0428: Carbon cycling; 0456: Life in extreme environments; ephemeral streams, Antarctica, DOC, concentration-

25 discharge, chemostasis, LTER

26 Abstract

27 The relationship between dissolved solute concentration (C) and discharge (q) in streams, i.e., 28 the C-q relationship, is a useful diagnostic tool for understanding biogeochemical processes in 29 watersheds. In the ephemeral glacial meltwater streams of the McMurdo Dry Valleys [MDVs], 30 Antarctica, studies show significant chemostatic relationships for weathering solutes and NO₃⁻. 31 Dissolved organic carbon (DOC) concentrations here are low compared to temperate streams, in 32 the range of 0.1 to 2 mg C L^{-1} , and their chemical signal clearly indicates derivation from 33 microbial biomass. Many MDV streams support abundant microbial mats, which are also a 34 source of organic matter to underlying hyporheic sediments. We investigated whether the DOC 35 generation rate from these autochthonous organic matter pools was sufficient to maintain 36 chemostasis for DOC despite these streams' large diel and interannual fluctuations in discharge. 37 To evaluate the DOC-q relationship, we fit the long-term DOC-q data to two models: a power 38 law and an advection-reaction model. By using model outputs and other common metrics to 39 characterize the DOC-q relationship, we found that this relationship is chemostatic in several 40 MDV streams. We propose a conceptual model in which hyporheic carbon storage, hyporheic 41 exchange rates, and net DOC generation rates are key interacting components that enable 42 chemostatic DOC-q behavior in MDV streams. This model clarifies the role of autochthonous 43 carbon stores in maintaining DOC-q chemostasis and may be useful for examining these 44 relationships in temperate systems, where autochthonous organic carbon is readily bioavailable 45 but where its signal is masked by a larger allochthonous signal.

46

47 Plain Language Summary

48 This study assesses the relationship between instream dissolved organic carbon [DOC] 49 concentrations and streamflow in the McMurdo Dry Valleys, Antarctica [MDVs]. DOC comes 50 from the breakdown of organic matter (e.g., plants, microbes and soil). In temperate streams, 51 DOC mostly comes from plants and soil outside of the stream. MDV streamflow is derived 52 entirely from glacial melt in summer and varies on a daily and interannual basis. Although there 53 are no vascular plants, some streams have abundant microbial mats composed of cyanobacteria 54 and diatoms. Organic material from these mats is stored in the underlying streambed sediments, which are saturated with streamwater. We used two different models to evaluate whether and 55 56 how DOC changed with changing streamflow. Both models indicated that stream DOC

57 concentrations are relatively stable over large changes in streamflow. We developed a new

58 conceptual model that emphasizes the role of the saturated streambed sediments in DOC

59 generation and storage. This streambed storage zone is key to maintaining DOC concentrations

60 in spite of the highly variable MDV streamflow. We believe this model also provides insight into

61 the role that DOC from this saturated zone plays in other systems.

62 1 Introduction

63 Stream concentration-discharge (C-q) relationships are the result of reaction and fluvial 64 transport processes at various scales along the catchment. Fluid transit times, solute reaction 65 rates, and equilibrium concentrations all impact the shape of C-q relationships (Godsey et al., 66 2009) and capture both surface and subsurface flow paths and processes. Channel subsurface 67 (hyporheic) processes can impact the C-q shape via the transient storage and flow-mediated 68 release of both geogenic and biogenic solutes (Castro & Hornberger, 1991; Singley et al., 2021). 69 Understanding the C-q dynamics of a system helps us understand the relative controls of these 70 surface and sub-surface processes on stream solute variability.

71 Possible C-q relationships include chemostasis (little variation in C with changes in q), 72 flushing (increasing C with increasing q), and dilution (decreasing C with increasing q) (Evans & 73 Davies, 1998; Godsey et al., 2009; Singley et al., 2017). Chemostasis can occur, for example, if 74 high discharges transport "old" water with higher solute concentrations into the catchment, thus 75 maintaining a relatively stable C values when q increases. Flushing occurs when the solute 76 concentrations in this "old" water are high enough to elevate C in spite of the increased q. 77 Dilution occurs if the water transported into the stream is "new", with relatively short transit time 78 and lower solute concentrations.

79 *C-q* relationships in the McMurdo Dry Valleys [MDVs] are shaped by the region's 80 distinctive and relatively simple biology and hydrology. Intermittent glacial meltwater streams 81 flow for 4-8 weeks during the austral summer. Most are first or second order streams from 82 glacier to terminal lake. They are fed only by glacial melt: precipitation and hillslope inputs are 83 negligible, and there is no deep groundwater interaction (Gooseff et al., 2004; McKnight et al., 84 2004). As a result, stream discharge is characterized by strong diel pulses that are generated as 85 the sun's movement around the horizon changes the angle and intensity of insolation to the 86 source glaciers. These pulses can increase streamflow up to an order of magnitude in a single day 87 (Conovitz et al., 1998). Interannual streamflow varies widely based on seasonal differences in

cloud cover and glacial albedo, which also impact the rate of melt (Gooseff et al., 2017; Obryk etal., 2018).

90 These streams flow through unconsolidated, highly porous glacial alluvium (Cozzetto et 91 al., 2013). They are well-connected to their hyporheic zones (Gooseff et al., 2004), which are 92 key sites for weathering and microbial activity (Kohler et al., 2018; Lyons et al., 1997). Isotopic 93 analysis shows that the hyporheic zone is an important source of autochthonous, remineralized 94 nitrogen to MDV stream channels, via the processing and retention of N from sloughed black 95 microbial mats (Nostoc) (Kohler et al., 2018). Hyporheic zone extent is determined by the thaw 96 depth, which increases throughout the summer flow season (Gooseff et al., 2002; McKnight et 97 al., 2004; Runkel et al., 1998). Typically, the seasonal maximum thaw depth is < 1 m (Conovitz 98 et al., 2006).

99 One outcome of the extensive hyporheic exchange is that MDV streams are chemostatic 100 for weathering-derived ions such as Si (Wlostowski et al., 2018b). This behavior reflects the low 101 equilibrium concentrations of weathering solutes (C_{eq}) and the relatively fast weathering rates 102 that are characteristic of MDV streams (Gooseff et al., 2002; Lyons et al., 1997; Wlostowski et 103 al., 2018b). Experiments in Von Guerard stream found that it is also chemostatic for dissolved 104 inorganic nitrogen, which reflects both the low ambient dissolved N concentrations and the 105 increasing release of hyporheic N stores with increasing discharge (Kohler et al., 2018; Singley 106 et al., 2021).

107 The landscape is poor in organic carbon: there are no vascular plants, and the riparian 108 vegetation is sparse and comprised of mosses. Thick, perennial microbial mats are present in the 109 channel and wetted margins of streams and represent sources of both dissolved and particulate 110 organic matter in the stream ecosystem (Aiken et al., 1996; Cullis et al., 2014). DOC is a 111 biologically-derived solute and would not be influenced by the same reaction processes as 112 weathering solutes but may be influenced by processes controlling N-cycling. The instream 113 concentrations of dissolved organic carbon (DOC) are generally low compared to temperate 114 streams and the source of the DOC from microbial biomass is reflected in the low humic content 115 and spectroscopic properties (less than 10%, Aiken et al., 1996). At daily high flow conditions, 116 some mat material from the black mats in the stream margins is scoured and flushed downstream 117 (Cullis et al., 2014), as well as into the hyporheic zone (Barrett et al., 2007; Hawes & Howard-118 Williams, 1998; Heindel et al., 2021). In addition, the hyporheic zones contain microbial

biofilms (Maurice et al., 2002) and particulate organic matter (POM) (Heindel et al., 2021) that
may contribute dissolved organic carbon to the stream.

121 In temperate and boreal streams, allochthonous DOC from upstream and upland sources 122 typically dominates the instream DOC fluxes, especially in lower-order streams (Burns et al., 123 2016; Hale & Godsey, 2019, Vannote et al., 1980). These inputs can either support chemostasis 124 as they are mobilized by higher flows, buffering the increase in discharge (Hale & Godsey, 2019; 125 Jantze et al., 2013; Mulholland & Hill, 1997) or can lead to greater variability or 'flashiness' of 126 DOC-q responses in small or low-flow streams (Creed et al., 2015; Rue et al., 2017). The tendency towards DOC-q chemostasis generally increases as stream order increases because each 127 128 allochthonous input contributes a smaller portion of the total load (Creed et al., 2015).

129 The goal of this research is to characterize the dynamics of autochthonous DOC in these 130 polar desert streams and elucidate the controlling processes. To do this we seek 1) to establish 131 whether the DOC-q relationship in MDV streams is characterized by chemostasis, flushing, or 132 dilution (i.e., whether it is limited by the DOC transport or generation rate), and 2) to identify 133 key factors controlling the DOC-q relationship. We compare DOC-q dynamics to those of silica 134 (Si)-q, to assess differences in biological vs physical controls. It is expected that the DOC-q 135 dynamics will not correlate to the same controls as those of weathering solutes because DOC is 136 generated from biomass rather than from interactions with mineral surfaces. To quantitatively 137 characterize the DOC-q relationship in MDV streams, we chose three common metrics for 138 characterizing C-q relationships. One metric assesses the relative variance in concentration and 139 discharge data, the second was generated by a power-law model, and the third by an advection-140 reaction model. To assess potential controls on this relationship, we ran multiple regression 141 analyses exploring the influence of instream biomass (ash-free dry mass [AFDM]) and stream 142 length on DOC concentrations, as well as the influence of the three the DOC-q shape parameters 143 vs. both fluid transit time (a transport parameter) and vs. the net generation time scale (a reaction 144 parameter that describes the timescale of net DOC generation and transport from source to 145 stream water). Given the low levels of organic carbon and the highly variable discharge in these 146 streams, we expected to find a reaction- (or generation-) limited, diluting DOC-q relationship. 147 Surprisingly, we find that these streams are chemostatic for DOC.

148 2 Study Site

149 The abundance and distribution of MDV microbial mats are dependent upon mat type, 150 streambed substrate, and discharge (Kohler et al., 2015; McKnight et al., 1998). The mats are 151 commonly divided into three categories for biomass assessments, based on dominant color and 152 community composition: orange, green and black (Alger et al., 1997; McKnight et al., 1998). 153 Each type of mat has a different habitat preference, with black, Nostoc-dominated mats 154 preferring the wetted margins of streams and orange (*Phormidium* sp. dominated) and green 155 (Praziolla sp. dominated) mats preferring the channel (Alger et al., 1997; Kohler et al., 2015; 156 Niyogi et al., 1997; Vincent et al., 1993). Each mat type responds differently to changes in 157 discharge and substrate (Kohler et al., 2015), but in general, streams with high algal mat 158 coverage tend to have common characteristics, including relatively low flows, moderate 159 gradients, and a stable 'desert pavement' substrate rather than shifting sand (Cullis et al., 2014; 160 Kohler et al., 2015). With only sparse grazers, primarily nematodes and tardigrades, mat extent is 161 kept in check largely by hydrology; and changes in mat abundance are more closely aligned with 162 seasonal peak flow scouring than daily scouring (Kohler et al., 2015; Gooseff et al., 2017). 163 For this study, we selected seven streams in the Lake Fryxell basin of the MDVs (Figure 164 1). These streams all have a long-term record of discharge and water chemistry, and many have 165 established transects for sampling microbial mats. The streams were selected to represent a wide 166 range of microbial mat coverage, from Lost Seal Stream with no visible mats to Green Creek 167 with thick and widespread mats. Aiken Creek's microbial mat coverage exists primarily in Many 168 Glaciers Pond, a large pond that hosts abundant microbial mats and is situated between the

169 source glacier and the stream gage/water sampling site.



171

172 Figure 1: Image of Fryxell Basin with study streams and stream gage locations highlighted.

174 <u>2.1 Dissolved Organic Carbon sources and sinks</u>

175 The primary DOC source is benthic microbial mats (Barrett et al., 2007; Hawes & Howard-Williams, 1998; McKnight et al., 1998), which contain both phototrophic and 176 177 heterotrophic organisms. Living phototrophs may release some of their fixed carbon to streams, 178 and all organisms in the mat community are subject to decomposition and DOC release (Spencer 179 et al., 2012). The mats also slough POM, which may degrade to DOC in the stream channel 180 (Cullis et al., 2014) or be trapped within the substrate matrix at a location of hyporheic 181 downwelling and degrade there (Heindel et al., 2021), eventually providing DOC to the 182 hyporheic zone waters and the stream water. DOC sinks include biotic uptake by heterotrophic 183 organisms in mats and in the hyporheic zone, and potential sorption on mineral surfaces in the 184 hyporheic zone. Because DOC is biologically derived, its origin differs from weathering-derived 185 solutes like Si; therefore, DOC-q dynamics may have different drivers. 186

187 3 Methods

188 <u>3.1 Data sets:</u>

The McMurdo Dry Valleys Long Term Ecological Research program (MCM LTER) has maintained a network of stream gages and sampling sites throughout MDVs since 1993. Here we analyze DOC-q relationships and compare them to Si-q relationships in seven Lake Fryxell basin streams (Figure 1) using the long-term q, solute concentration, and microbial mat biomass data sets from 1990-2019. These and other long-term data sets are hosted at mcmlter.org and at the Environmental Data Initiative (environmentaldatainitiative.org/).

All seven study streams are gaged and have in-situ sensors that yield continuous records of temperature, stage, and specific electrical conductance at 15-minute intervals during the flow season. Seasonally-adjusted rating curves are used to convert stage to volumetric discharge (Q, L sec⁻¹). Volumetric discharge was then converted to Darcy velocity (q, m day⁻¹) using the following equation:

200

201
$$q = \frac{Q}{A_x} = \frac{Q}{[(w_c + 2w_{hz})z_{thaw}]}$$
 (1)

202

where A_x = the cross-sectional stream area (m²), w_c = the stream channel width (m), w_{hz} = the 203 204 width of the hyporheic zone (m), and z_{thaw} = the thawed active layer depth (m) (Wlostowski et 205 al., 2018b). We assume that $w_c = 4m$, $w_{hz} = 5m$, and $z_{thaw} = 1m$ based on prior observations of 206 channel and hyporheic extent (Northcott et al., 2009) and maximum annual thaw depth below 207 streams (Conovitz et al., 1996). We chose to use Darcy velocity for these analyses because it 208 explicitly incorporates hyporheic flowpaths and flow velocities, which are important both to 209 calculate total fluid transit time and as sites of organic and inorganic carbon storage and 210 transformation (Mulholland et al., 1997; Welch et al., 2010). It is also consistent with 211 Wlostowski et al.'s (2018b) work on weathering solute C-q relationships in MDV streams, 212 facilitating comparison.

Water chemistry samples are collected several times each season and analyzed for various solutes, including weathering ions and DOC. These samples are kept chilled (4°C) and are filtered within 24 hours of collection. DOC samples are collected in precombusted amber glass bottles and filtered through a combusted glass microfiber filter 217 (WhatmanTM GF/CTM 47mm filter) into a second precombusted amber glass bottle. Next,

samples are acidified to a pH of 2 to 3 with a 50% solution of hydrochloric acid to drive off

219 inorganic carbon, then analyzed for DOC using a non-purgeable organic carbon method.

220 Method detection limit is typically 0.1 mg L^{-1} of DOC.

221 Microbial mat samples have been collected along established transects in various MDV 222 streams since 1994, and their ash-free dry mass [AFDM] is used to measure long-term variations 223 of instream biomass within and across the sample streams. Mat sampling has been annual since 224 2002; prior to 2002, these samples were collected approximately every three years. Each 225 sampling visit collects 2-4 plugs of each type of microbial mat near each transect, using a 1.7 cm 226 diameter brass cork borer. These samples are analyzed for AFDM by drying at 100°C for 24 227 hours, weighing, ashing at 450°C for 4 hours, then re-weighing to determine the mass lost to 228 combustion (Kohler et al., 2015).

229

230 <u>3.2 Data analysis:</u>

231 *3.2.1: Determining the DOC-q relationship:*

To answer our first question, whether the DOC-q relationship is chemostatic, flushingbased or dilution-based, we used three established methods to quantitatively assess the shape of the C-q relationship. First, we fit the DOC and q data to a power-law model:

235

(2))
	(2

238 where C is the concentration (ppm), q is the Darcy velocity (m day⁻¹), a is a constant, and b is a 239 scaling parameter, and assessed the slope (exponent, b) of the modeled C-q relationship (Godsey 240 et al., 2009). The best-fitting b value indicates a log-log slope of the relationship: b = -1241 represents pure dilution, b = 0 represents perfect chemostasis (C is constant for all q), and b = 1242 represents pure flushing. The *b* values for DOC-*q* will indicate whether the relationship is 243 flushing, diluting or chemostatic: per Godsey et al. (2009), b values between -0.20 and 0.20 244 indicate a chemostatic relationship, while values below -0.20 indicate a diluting relationship and 245 values greater than 0.20 would indicate flushing.

²³⁷

246 Second, we fit the data to an advection-reaction model to determine the Damköhler

247 number (Da), which describes whether the C-q relationship is transport- or reaction-limited

248 (Maher et al., 2011; Maher & Chamberlain, 2014; Wlostowski et al., 2018b):

249

250
$$C = C_{eq} \frac{\frac{\gamma D w}{q}}{1 + \frac{\gamma D w}{q}}$$
(3)

251

where *C* is the concentration (ppm), C_{eq} is the solute equilibrium concentration (ppm), γ is a dimensionless constant (= e²), *Dw* is the Damköhler coefficient (m day⁻¹), and *q* is the Darcy velocity (m day⁻¹). The model assumes an exponential distribution of fluid transit times along an idealized flow path. It provides a process-based interpretation of the *C-q* relationship, where model outputs are tied to physically-meaningful parameters.

We used this advection-reaction model to calculate the dimensionless Damköhler number (*Da*) from the Damköhler coefficient (*Dw*). *Da* is also equal to the ratio of τ_f to τ_{gen} (or τ_{eq} , for weathering solutes):

260

261
$$Da = \frac{Dw}{q} = \frac{\tau_f}{\tau_{gen}} = \frac{\tau_f}{\tau_{eq}}$$
(4)

262

For our analyses, we used Da_{med} , the Damköhler number calculated using the median q for that stream.

Fluid transit time (τ_f) represents the average time that water spends in surface and subsurface flow paths, and is approximated as the ratio of channel length to seepage velocity $(\frac{q}{\phi})$:

269

270 where *L* is the length of the stream (m) and ϕ is the porosity of hyporheic sediments (m³ m⁻³).

271 This simple approximation is appropriate given the simplicity of the MDV stream hydrologic

system, which can be compared to a natural flume (Gooseff et al., 2004; Wlostowski et al.,

273 2018b).

The net DOC generation time scale (τ_{gen}) represents the characteristic time for DOC to be generated and transported from the source to the streamwater. When used to simulate the transport and reaction of weathering solutes, τ_{gen} is replaced with τ_{eq} , a reaction term that incorporates the influence of kinetics of mineral weathering, temperature, sediment composition, and erosion rate (Maher et al., 2010; Wlostowski et al., 2018b). The generation timescale τ_{gen} is calculated by rearranging and simplifying Equations 4 and 5, to yield:

280

281
$$au_{gen} = \frac{\tau_f}{Da} = \frac{L\phi}{qDa} = \frac{L\phi}{Dw}$$
 (6)

282

283 Da < 1 indicates that $\tau_{gen} > \tau_f$ and that the solute flux is generation-limited. Da > 1284 indicates that $\tau_{gen} < \tau_f$ and that the solute flux is transport-limited (Maher & Chamberlain, 285 2014; Wlostowski et al., 2018b). We expect DOC to be generation-limited, with a Da < 1.

Third, we calculated the ratio of the coefficients of variation for the long-term records of C and q (CV_c/CV_q) for each stream (Thompson et al., 2011). Because C-q chemostasis is defined as a range of C that is relatively stable across a wide range of q, a $CV_c/CV_q >> 1$ indicates the concentration dataset is more variable than the discharge, meaning that the C-q relationship is either flushing or diluting, while a $CV_c/CV_q << 1$ indicates that the relationship between C and qis chemostatic (Thompson et al., 2011).

292

3.2.2: Determining DOC-q controls:

We hypothesize that both microbial mat biomass and τ_f will be strong indicators of the DOC-*q* relationship. We expect that MDV streams with higher mat biomass will have both higher DOC concentrations and less-diluting DOC-*q* relationships. We also hypothesize that τ_f , not τ_{gen} , will control between-stream variation in the DOC-*q* relationship, because generation rates per area of biomass would not vary much across streams while longer fluid transit times would allow more contact with DOC source material.

To test the influence of mat biomass, we quantified annual microbial mat biomass (ashfree dry mass, AFDM) based on the long-term MCM LTER data record. We focused this analysis on the four modeled streams with a consistent long-term algal sampling record: Canada, Delta, Green, and Von Guerard. If a stream had multiple mat sampling transects, we chose the 304 one closest to the stream gage, which is where the DOC samples are collected. We used a 305 regression analysis to test relationships between both the average DOC concentration vs. the 306 average biomass for each season, and also the average DOC concentration vs. the high biomass 307 for each season, since the high-biomass mats would be expected to generate a larger DOC 308 source. We tested for significant relationships by stream, by mat type and by within-stream 309 location (i.e. margins vs. channel). We also tested for significant relationships between DOC 310 concentration and stream length, as longer streams may allow longer contact time with DOC 311 sources in the stream and hyporheic zone. Our hypothesis that biomass controls the DOC-q 312 relationship is supported if DOC concentrations have a positive relationship with stream biomass 313 or stream length.

314 To test the influence of τ_f and τ_{qen} on between-stream differences in the DOC-q relationship, we compared each of these timescale parameters to the three DOC-q shape 315 316 parameters (Da, b, and CV_c/CV_q) that indicate the degree of dilution or chemostasis for each 317 stream. Significant correlations (positive or negative) between either τ_f or τ_{aen} and these shape 318 parameters would indicate that timescale parameter controls between-stream differences in 319 DOC-q. If the three shape parameters become more chemostatic as τ_f increases, this would 320 support our hypothesis that τ_f controls between-stream variation in DOC-q dynamics. 321 We ran the same series of analyses on Si, to provide a comparison to a true weathering 322 solute. This updates the Wlostowski et al. (2018b) analysis with more recent data.

323 4 Results

MDV DOC-q relationships are strongly chemostatic, showing little variation in DOC 324 325 concentration over four orders of magnitude of q (Figure 2). DOC does have more variance than 326 the weathering solute Si in most streams, with DOC variance ranging from 0.06 to 3.35 while Si 327 variance ranges from 0.05 to 0.26 (Figure 2). This variance is greater than the analytical 328 uncertainty and is consistent across decades of high-quality DOC data. DOC concentrations are 329 consistent through time, with only 2004 showing any significant differences (Figure 3); this may 330 be driven by the relatively high number of high-end outliers in the 2004 DOC data. 331 DOC concentration is also consistent across the study streams regardless of stream length

332 (Figure 4a) or mat biomass (Figure S1). Regressions between DOC vs. biomass and DOC vs.

333 stream length showed no significant relationships (p > 0.05 for all comparisons), which is not

- 334 surprising as there are no apparent spatial or temporal trends in DOC concentration (Figure 3).
- 335 Of the seven study streams, only Aiken Creek shows a significant difference in mean DOC
- concentrations, with a higher mean DOC concentration than any other stream (p < 0.05 for all
- 337 comparisons). This difference is likely driven by Many Glaciers Pond, which supports relatively
- 338 high biomass and increases the fluid transit time, equating to increased water contact with a DOC
- 339 source. In contrast, the weathering solutes (e.g., Si), while chemostatic, do have concentrations
- 340 that increase with stream length (Figure 4b), due to the greater amount of substrate supplying
- 341 weathering solutes in longer streams (Gooseff et al., 2002).



Figure 2: Visual inspection shows the chemostatic relationships of DOC and Si solute concentrations vs.

345 discharge (q) in seven MDV streams; Si concentrations are scaled for better visualization. Si represents a

346 weathering solute signal and DOC represents a biological solute signal. The dotted line indicates where

a pure dilution relationship would fall on the graph. Variances of Si and DOC are shown to illustrate the

difference in spread between the two solutes. The script used for these visualizations is based on code

developed by Wlostowski et al. (2018b), to facilitate comparisons between our findings.



Figure 3: This shows the distribution of DOC-q relationships by study year in each stream.



354

Figure 4: These boxplots indicate DOC and Si concentrations by length in the 7 study streams. Si, a
weathering solute, shows an influence of channel length on concentration. In contrast, concentrations of
DOC, a biologically derived solute, do not vary with stream length.

359 All three shape parameters quantitatively characterize MDV DOC-q relationships as 360 chemostatic rather than diluting or flushing behavior (Table 1). Using b, the slope of the best-fit 361 power-law relationship, all streams except Aiken meet Godsey et al.'s (2009) definition for 362 chemostasis: b values range from -0.22 to -0.02, with a mean value of -0.08. Aiken Creek (b = -363 (0.22) is likely an outlier because of Many Glaciers Pond, which contains a high amount of 364 organic matter; the pond would impact both DOC concentration and DOC variability due to changing flow dynamics. The CV_c/CV_q analysis shows that all streams have CV_c/CV_q values less 365 366 than one, indicating chemostasis (Thompson et al., 2011): values range from 0.36 to 0.83, with a 367 mean value of 0.63. For comparison, Wlostowski et al. (2018b) found that CV_c/CV_q values for four Fryxell Basin weathering solutes ranged from 0.07 to 0.76 with a mean value of 0.26, and 368 369 Thompson et al. (2011) found that typical CV_c/CV_q values for both weathering and biologically-370 derived solutes in temperate streams ranged from 0.15 to 3.5 with a mean of 0.68. Using a Damed 371 (Da calculated at median q for each stream) derived from the best-fit advection-reaction model, 372 MDV streams have a $Da_{med} > 1$, indicating they are transport-limited (Maher et al., 2011; Maher 373 & Chamberlain, 2014; Wlostowski et al., 2018b). Damed values range from 1.70 to 131.23, with a 374 median value of 43.15. Streams with smaller magnitude b values (i.e. values closer to 0) also

- have higher *Da_{med}* values, showing agreement between the power law and advection-reaction
- 376 models.
- 377
- 378 Table 1. Stream and Stream DOC Model Parameters and Shape Factors

Stream	Length	q_{med}	$\tau_{f\mathrm{med}}$	C_{eq}	b	CV _c /CV	Dame
		(m/dy)	(dy)	(ppm)		q	Damed
Aiken	2760	48.14	22.93	1.40	-0.22	0.83	1.70
Canada	700	54.93	5.10	0.38	-0.03	0.36	11.55
Crescent	5500	34.56	63.66	0.52	-0.02	0.36	100.56
Delta	7510	24.07	124.81	0.42	-0.02	0.78	49.66
Green	700	69.74	4.02	0.46	-0.11	0.74	3.36
Lost Seal	2000	75.29	10.63	0.43	-0.03	0.83	131.23
VG	4700	22.83	82.33	0.57	-0.14	0.51	4.00

The regression analyses between the shape parameters and both τ_f and τ_{gen} show no significant relationships (all p > 0.05, Figure 5). The one near-linear relationship for DOC is between Da_{med} and τ_{gen} (Figure 5b, p = 0.064, R² = 0.53). As τ_{gen} increases, Da_{med} decreases, indicating that τ_{gen} may be a stronger control on the stream's DOC-q transport-limitation than τ_f : i.e. the values for τ_{gen} , not τ_f , are what impact the degree of DOC-q transport-limitation in MDV streams.

As expected, Si-*q* relationships are quantitatively chemostatic across all streams. Values for *b* range from -0.13 to -0.01, with a mean of -0.06; CV_c/CV_q values are all less than one and range from 0.09-0.27, with a mean of 0.17; and Da_{med} values are all greater than 1 (1.62-41.11, median of 25.93), indicating transport limitation. This supports the results of Wlostowski et al. (2018b).

391 **5 Discussion**

392 <u>5.1 DOC-q chemostasis in MDV streams</u>

393 Analysis shows that DOC-*q* relationships are strongly chemostatic in MDV streams

394 (Figure 2), with DOC concentrations showing little variation across orders of magnitude of

discharge. There is also little net variation across years (Figure 3) or streams (Figure 4); apart

396 from Aiken Creek, there is no significant difference in the mean DOC concentrations of the

397 study streams. Therefore, it is not surprising that there was no relationship between DOC

398 concentration and either stream length or mat biomass, both of which are more variable,

399 relatively, than mean DOC concentrations.

400 DOC variance is greater than Si variance in almost all streams (Figure 2). This is 401 consistent with differences in the source materials of the two solutes. Silicate materials that make 402 up the soils and streambeds of the MDVs are relatively uniform throughout the Fryxell basin 403 (Gooseff et al., 2002), while DOC sources are inherently patchy. Benthic biomass in streams is 404 largely dictated by substrate and hydrologic regime (Kohler et al., 2015). The perennial mats 405 thrive on rocky, stable desert pavement and are sparse or nonexistent on sandy, mobile reaches, 406 which do not accommodate much establishment and growth (McKnight et al., 1998). Thus 407 hyporheic POM, as a source for hyporheic and ultimately stream DOM, is also expected to be 408 spatially dispersed (Heindel et al., 2021).

409 For all streams, the slope of the DOC-q power-law relationship (b) is close to zero, there 410 is little variation in C over a wide variation in q, and the steady-state advection-reaction model 411 shows these streams to be predominantly transport-limited (Table 1). Together, these findings 412 support a chemostatic DOC-q relationship across all of the study streams. There is between-413 stream variation in the degree of DOC-q chemostasis (Table 1), but no significant correlations to 414 indicate whether this variation is controlled by transport or generation. While it is not significant (p = 0.064), there does appear to be some gradient in the relationship of Da_{med} to τ_{gen} , indicating 415 that τ_{aen} , not τ_f , may have the stronger impact on the degree of DOC-q transport-limitation in 416 417 MDV streams, which does not support our expectations.

418

419

5.2 DOC generation - biological control

That DOC-*q* relationships are chemostatic across all streams is surprising, given the very little amount of organic carbon in this landscape. Further, DOC generation is somehow supplied across several orders of magnitude of *q* from autochthonous organic carbon alone. The breakdown of POM primarily occurs in the stream channel and hyporheic zone. It is primarily a biological process driven by the physical sloughing of in-channel mats and by decomposer microorganisms in the mats and hyporheic sediments. Chemical equilibrium is not a factor here in the same way it is for weathering solute chemostasis, and MDV DOC concentrations do not 427 increase with stream length (Figure 4). Instead, the DOC "equilibrium" concentration (C_{eq}) 428 would integrate the DOC source and sink processes upstream of that sampling point and 429 represent the balance of DOC net generation and exchange specific to that sampling location; it 430 is more of a 'net balance' than a chemical equilibrium. Thus the DOC net generation timescale (τ_{gen}) represents the average time required to reach this balance point of sources, sinks, storage 431 432 and exchange. It could be interpreted as the ratio of the "equilibrium" concentration to the net DOC generation rate [NGR], or $\frac{C_{eq}}{NGR}$. Because C_{eq} is relatively steady across these streams (Table 433 434 1), variations in the net DOC generation rate control differences in τ_{gen} . Streams that have the slowest generation rate would have the highest τ_{gen} , while streams that have more rapid DOC 435 generation rates would have a lower τ_{aen} . This interpretation is supported by the fact that 436 streams with the lowest τ_{gen} are more strongly chemostatic (Figure 5). 437



439 *Figure 5: Relationship between the DOC-q shape parameters and (a, c, e) mean transit time at median q*

440 (τ_f) and (b, d, f) the equilibrium time scale (τ_{eq}) . There are no significant relationships in any of these

441 regressions (all p > 0.05). In contrast, Si relationships for the shape parameters and τ_f are all significant

442 (Wlostowski et al., 2018b). This indicates that τ_f controls between-stream differences in the shape of the

443 *C-q curve for Si but neither* τ_f *nor* τ_{eq} *provide this control for DOC.*

444

445 <u>5.3 Controls on DOC-q chemostasis</u>

446 We initially expected that the amount of source material, or algal mat biomass, would be

447 one key factor influencing DOC-q chemostasis. However, we find no apparent relationship

448 between DOC concentration and algal mat biomass (Figure S1). In fact, with the exception of

449 Aiken Creek, there is little variation in mean DOC concentration across most our study streams 450 (Figure 4), which agrees with the findings of Aiken et al. (1996). Aiken Creek has both a 451 significantly higher mean DOC concentration and a wider range of concentrations compared to 452 other study streams. This can likely be attributed to the influence of mat-rich Many Glaciers 453 Pond on the Aiken stream channel. The higher DOC mean can be explained by the high mat 454 density and longer water residence time in the pond. The wider DOC range can be explained by 455 the natural variation in stream discharge. When the system experiences relatively high diel flood 456 pulses, water would move through the pond quickly and spill into lower Aiken Creek without 457 much time for solute generation.

We hypothesized that fluid transit time (τ_f) would be an important control on the DOC-qshape and would explain between-stream differences in degree of chemostasis, because a longer transit time (in longer streams, and/or in lower flow streams) would allow more opportunity for DOC generation. This is not supported by the shape parameter analysis (Figure 5). If anything, these results indicate that the differences in τ_{gen} may weakly influence differences in the degree of chemostasis observed between the study streams.

464 We propose that the relationships between τ_f , τ_{gen} , and other transport metrics (Figure 5) 465 also indicate the hyporheic influence on DOC-q chemostasis. While τ_f is not correlated with 466 transport limitation, it is clearly a factor (Equation 4). Fluid transit time varies with flow path 467 length, and hyporheic flow paths are both longer and have a lower velocity than in-stream flow 468 paths. In the MDV, where sediment porosity is relatively uniform across streams, total hyporheic 469 area and potential flow path length increases with stream length. At median discharge, longer 470 streams have longer mean fluid transit times due to these longer hyporheic flow paths (p = $0.0004, R^2 = 0.92).$ 471

472 Controls on DOC-*q* chemostasis in the MDV must differ from temperate stream controls. 473 In temperate streams, the chemostatic DOC-q balance is maintained by an allochthonous DOC 474 source that is accessed at higher flows (Hale & Godsey, 2019; Mulholland & Hill, 1997). There 475 are no large allochthonous carbon sources in the MDV. In spite of this, the MDV DOC-q balance 476 is remarkably consistent across time (decades), range of discharge (multiple orders of 477 magnitude), and channel length (Figures 2, 3, 4). We propose that in the MDV, intermittently-478 connected areas in the hyporheic zone and wetted margins may serve as carbon storage sites, 479 analogous to riparian and hillslope carbon storage in temperate streams. To help explain this

480 process, we propose the following 4-bin conceptual model, consisting of generation (source),

481 loss (sink), storage, and hyporheic-surface water exchange "bins". The source and sink bins have

482 not changed from our earlier description, so we provide a concise review here. In contrast, this

483 study has changed our conception of the contributions of hyporheic storage and exchange,

484 especially for DOC chemostasis. These bins are described in detail, below.

485

486 <u>5.4 Conceptual model for dissolved carbon chemostasis:</u>

The primary DOC source to streams is benthic microbial mats that grow on the bed and wetted margins of streams (Barrett et al., 2007; Hawes & Howard-Williams, 1998; McKnight et al., 1998). A secondary source is POM from these mats, which may be buried or lodged in stream interstices. Unlike in temperate streams, there are no allochthonous DOC sources. DOC sinks include biotic uptake by heterotrophic organisms in mats and in the hyporheic zone.

492 Because of the large diel and seasonal variations in streamflow, the stream channel 493 expands and contracts on a daily and seasonal scale. The hyporheic zone also expands over the 494 course of the flow season due to active layer thaw, and it may contract during low or no-flow 495 periods. These changes impact both hyporheic storage and the exchange of water and solutes 496 with the stream channel. High flows access and flush stored hyporheic solutes into the stream, 497 while lower flows "strand" (isolate) damp sediments, allowing them to accumulate solutes 498 (Figure 6). At lower flows, hyporheic organic matter is temporarily isolated, either by diminished 499 exchange or reduced preferential flow paths (Figure 6a); but it continues to produce DOC, 500 creating a pool that can be mobilized to maintain chemostasis at higher flows (Figure 6b, c). The 501 expansion and contraction of streamflow also impacts the benthic DOC source, as the margin 502 and some in-channel mats are alternately wetted and dried, i.e., connected and disconnected from 503 releasing DOC into the channel. The wetted margins of streams may also act as a DOC storage 504 site at lower flows, as subsurface POM and surface mats continue to release DOC into the wetted 505 margins but have little to no DOC exchange with the stream channel. In effect, the isolated sites 506 in both the margins and hyporheic zone are parallel to riparian storage zones in temperate 507 streams; they function as storage pools of organic carbon, buffering DOC-q chemostasis when 508 they are tapped at higher flows.

509 The long-term datasets used in these analyses do not distinguish between in-channel and 510 hyporheic DOC sources. However, a hyporheic DOC source is plausible based on other research. 511 We know that the hyporheic zone contains POM that is sloughed from microbial mats (Cullis et 512 al., 2014; Heindel et al., 2021; Singley et al., 2021), and that this organic matter contributes 513 dissolved nitrogen and likely other solutes to the stream channel (Singley et al., 2021). 514 Another line of evidence supporting the importance of a hyporheic OM source is the 515 DOC levels in Lost Seal. Surprisingly, Lost Seal has a DOC level similar to that of other streams, 516 even though it does not have apparent benthic mats. Lost Seal is a medium-length stream with an 517 extensive area for hyporheic storage and exchange. In the absence of a visible instream source, it 518 could be that the DOC source here may not be mats but instead both thin biofilm and particulate 519 organic matter carried from lake algal mats by aeolian transport, in the benthic and hyporheic







Figure 6: Stream cross-section illustrating the conceptual model for hyporheic DOC generation and storage at low (a), median (b) and high flows (c). Orange, black, and striped boxes represent microbial mats. Blue represents the stream water and the blue/ brown areas represent the saturated sediments of the near and deep hyporheic zone. At each flow level, the hyporheic zone acts as a generation, storage and release site for DOC, buffering the DOC-q relationship against the large changes in q this system experiences. This parallels the role of the riparian zone in temperate stream DOC-q chemostasis. At very high flows, mats also slough POM, some of which is buried in the hyporheic zone to seed future DOC

- 531 generation.
- 532

At median flow, with a moderate water volume, many but not all of the mats would be flooded and releasing DOC into the stream channel (Figure 6a). Hyporheic extent and exchange would be moderate, and some areas would be well-connected with the channel, mobilizing DOC, while others would not. The wetted areas that were not well-connected with the channel would continue to break down organic matter into DOC, creating some storage pockets that would only be accessed at relatively high flows.

At low flows, with a low water volume, the decrease in *q* would be compensated for by the decrease in DOC generation and release (Figure 6b). Fewer mats would be submerged, decreasing the amount of DOC released to the stream water. Hyporheic exchange would be lower, and the hyporheic zone itself might contract if the flow is low enough. DOC generation would continue in the wetted mats and hyporheic zone (where there is POM). Less of the DOC generated and stored in the hyporheic zone would be released to the channel.

At high flows, the increase in *q* would be compensated for by a flushing of the stored DOC that was generated at lower flow levels (Figure 6c). All of the mats would be submerged, increasing the surface area of mat that would release DOC to the stream channel. At higher flows, there is also more likely to be sloughing and entrainment of mat material that would subsequently generate (stored then flushed) DOC.

550 There are several ways to test this new conceptualization of hyporheic storage and 551 exchange impacting instream DOC. One method would be to use probes or repeated sampling to 552 monitor hyporheic DOC at various flows and distances from the stream, to test whether there 553 actually is a pool of organic carbon waiting to be mobilized at higher flows. More accurate 554 measurements of hyporheic biomass would also be useful, to support and quantify the existence of a hyporheic OM source. This would inform both the conceptual model and improve the

accuracy of tested relationships between DOC and biomass. In addition to fieldwork, this

557 conceptual model could be tested by developing a DOC-specific mathematical model to describe

the instream flows. It would include terms for the storage and exchange components described

559 here, in addition to terms for the more widely-accepted sources and sinks.

560 6 Conclusions

561 In streams, DOC is generated by the breakdown of particulate organic matter. In spite of 562 the sparse POM storage in the MDV streams, concentrations of DOC are chemostatic across 563 several orders of magnitude in q. In temperate streams, organic matter is largely allochthonous 564 and DOC chemostasis is understood to be influenced by legacy pools of this allochthonous 565 carbon in the riparian zone. As there is no 'riparian zone' nor pools of allochthonous carbon in 566 the MDV, we must seek a different explanation for the chemostatic DOC-q behavior. This 567 explanation must involve the primary MDV DOC source: microbial mat material, either in the 568 channel or buried in the hyporheic zone.

We propose a conceptual model where carbon C-*q* chemostasis is a product of the interaction of the four bins: generation, uptake, storage (here, primarily hyporheic), and exchange. The hyporheic storage and exchange locations have not previously been explored for DOC. In the MDV, autochthonous hyporheic POM and wetted-margin microbial mats are the carbon pool supporting DOC-*q* chemostasis, paralleling the allochthonous riparian/ hillslope pools in temperate systems.

This is the first examination of the dynamics impacting DOC-q chemostasis in the MDV. It is likely that the processes influencing DOC-q chemostasis were not fully captured by the long-term data record we studied. Although this study does not provide a definitive solution to the causes of DOC-q chemostasis in the MDV, it does provide clues to the processes involved and can inform future investigations and models. It also provides insight into the ways autochthonous carbon contributes to DOC-q relationships in systems where the autochthonous influence is obscured by the dominance of allochthonous carbon inputs.

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591 Data availability

- 592 The stream gage data (Gooseff & McKnight, 2019a-c; Gooseff & McKnight, 2021a-d); water
- chemistry data (Lyons, 2016; Lyons & Welch, 2016); and microbial mat data (McKnight, 2019)
- are available at the McMurdo Long Term Ecological Research website and the Environmental
- 595 Data Initiative.

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Supporting Information for

Dissolved Organic Carbon Chemostasis in Antarctic Polar Desert Streams

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Contents of this file

Figure S1

Introduction

Figure S1 is a graph of dissolved organic carbon [DOC] vs. microbial mat ash-free dry mass [AFDM] for the four study streams that have a long-term record of microbial mat sampling. None of these relationships were significant (all p > 0.05). These results were reported in the main manuscript, but not depicted due to the lack of statistical significance. This figure supports that information.



Figure S1. Relationship between mean annual dissolved organic carbon (DOC) and mean annual ash-free dry mass (AFDM) from streambed samples (all p > 0.05) in the four study streams. The plot margins show boxplots of the distributions for AFDM (top margin) and DOC (right margin) for each stream.