1 **Dissolved Organic Carbon Chemostasis in Antarctic Polar Desert Streams**
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14 **Key Points:**

15 ● Although DOC concentrations in McMurdo Dry Valleys streams are very low, DOC-flow
16 relationships are chemostatic

17 ● Biogeochemical processes in microbial mats and the hyporheic zone support chemostasis
18 for DOC in Dry Valleys streams

19 ● Autochthonous organic matter pools in the hyporheic zone may also influence DOC
20 concentrations in temperate streams

21
22 **Index terms**
23 0414: Biogeochemical cycles, processes, and modeling; 0744: Rivers; 0428: Carbon cycling;
24 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 NO_3^-.

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,

55 which are saturated with streamwater. We used two different models to evaluate whether and

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

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

89   al., 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

119   biofilms (Maurice et al., 2002) and particulate organic matter (POM) (Heindel et al., 2021) that

120   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

127   tendency towards DOC-q chemostasis generally increases as stream order increases because each

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.

170

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

2.1 Dissolved Organic Carbon sources and sinks

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 heterotrophic organisms. Living phototrophs may release some of their fixed carbon to streams, and all organisms in the mat community are subject to decomposition and DOC release (Spencer et al., 2012). The mats also slough POM, which may degrade to DOC in the stream channel (Cullis et al., 2014) or be trapped within the substrate matrix at a location of hyporheic downwelling and degrade there (Heindel et al., 2021), eventually providing DOC to the hyporheic zone waters and the stream water. DOC sinks include biotic uptake by heterotrophic organisms in mats and in the hyporheic zone, and potential sorption on mineral surfaces in the hyporheic zone. Because DOC is biologically derived, its origin differs from weathering-derived solutes like Si; therefore, DOC-q dynamics may have different drivers.

187 **3 Methods**

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

189   The McMurdo Dry Valleys Long Term Ecological Research program (MCM LTER) has

190 maintained a network of stream gages and sampling sites throughout MDVs since 1993. Here we

191 analyze DOC-q relationships and compare them to Si-q relationships in seven Lake Fryxell basin

192 streams (Figure 1) using the long-term q, solute concentration, and microbial mat biomass data

193 sets from 1990-2019. These and other long-term data sets are hosted at mcmlter.org and at the

194 Environmental Data Initiative (environmentaldatainitiative.org/).

195   All seven study streams are gaged and have in-situ sensors that yield continuous records of

196 temperature, stage, and specific electrical conductance at 15-minute intervals during the flow

197 season. Seasonally-adjusted rating curves are used to convert stage to volumetric discharge (Q,

198 L sec^{-1}). Volumetric discharge was then converted to Darcy velocity (q, m day^{-1}) using the

199 following equation:

200

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

202

203 where A_x = the cross-sectional stream area (m^2), w_c = the stream channel width (m), w_{hz} = the

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.

213   Water chemistry samples are collected several times each season and analyzed for

214 various solutes, including weathering ions and DOC. These samples are kept chilled (4°C) and

215 are filtered within 24 hours of collection. DOC samples are collected in precombusted amber

216 glass bottles and filtered through a combusted glass microfiber filter

217   (WhatmanTM GF/CTM 47mm filter) into a second precombusted amber glass bottle. Next,

218   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*:

232   To answer our first question, whether the DOC-*q* relationship is chemostatic, flushing-

233   based or dilution-based, we used three established methods to quantitatively assess the shape of

234   the C-*q* relationship. First, we fit the DOC and *q* data to a power-law model:

235

236    $C = aq^b$ (2)

237

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* = -1

241   represents pure dilution, *b* = 0 represents perfect chemostasis (*C* is constant for all *q*), and *b* = 1

242   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.

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

251

252   where *C* is the concentration (ppm), C_{eq} is the solute equilibrium concentration (ppm), γ is a

253   dimensionless constant (= e^2), *Dw* is the Damköhler coefficient (m day^{-1}), and *q* is the Darcy

254   velocity (m day^{-1}). The model assumes an exponential distribution of fluid transit times along an

255   idealized flow path. It provides a process-based interpretation of the *C-q* relationship, where

256   model outputs are tied to physically-meaningful parameters.

257   We used this advection-reaction model to calculate the dimensionless Damköhler number

258   (*Da*) from the Damköhler coefficient (*Dw*). *Da* is also equal to the ratio of τ_f to τ_{gen} (or τ_{eq}, for

259   weathering solutes):

260

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

262

263   For our analyses, we used *Da$_{med}$*, the Damköhler number calculated using the median *q* for that

264   stream.

265   Fluid transit time (τ_f) represents the average time that water spends in surface and

266   subsurface flow paths, and is approximated as the ratio of channel length to seepage velocity ($\frac{q}{\phi}$):

267

268     $\tau_f = \frac{L\phi}{q}$ (5)

269

270   where *L* is the length of the stream (m) and ϕ is the porosity of hyporheic sediments (m^3 m^{-3}).

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

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

273   2018b).

274   The net DOC generation time scale (τ_{gen}) represents the characteristic time for DOC to

275   be generated and transported from the source to the streamwater. When used to simulate the

276   transport and reaction of weathering solutes, τ_{gen} is replaced with τ_{eq}, a reaction term that

277   incorporates the influence of kinetics of mineral weathering, temperature, sediment composition,

278   and erosion rate (Maher et al., 2010; Wlostowski et al., 2018b). The generation timescale τ_{gen} is

279   calculated by rearranging and simplifying Equations 4 and 5, to yield:

280

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

282

283   $Da < 1$ indicates that $\tau_{gen} > \tau_f$ and that the solute flux is generation-limited. $Da > 1$

284   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 $Da < 1$.

286   Third, we calculated the ratio of the coefficients of variation for the long-term records of

287   C and q (CV_c/CV_q) for each stream (Thompson et al., 2011). Because C-q chemostasis is defined

288   as a range of C that is relatively stable across a wide range of q, a $CV_c/CV_q \gg 1$ indicates the

289   concentration dataset is more variable than the discharge, meaning that the C-q relationship is

290   either flushing or diluting, while a $CV_c/CV_q \ll 1$ indicates that the relationship between C and q

291   is chemostatic (Thompson et al., 2011).

292

293   *3.2.2: Determining DOC-q controls*:

294   We hypothesize that both microbial mat biomass and τ_f will be strong indicators of the

295   DOC-q relationship. We expect that MDV streams with higher mat biomass will have both

296   higher DOC concentrations and less-diluting DOC-q relationships. We also hypothesize that τ_f,

297   not τ_{gen}, will control between-stream variation in the DOC-q relationship, because generation

298   rates per area of biomass would not vary much across streams while longer fluid transit times

299   would allow more contact with DOC source material.

300   To test the influence of mat biomass, we quantified annual microbial mat biomass (ash-

301   free dry mass, AFDM) based on the long-term MCM LTER data record. We focused this

302   analysis on the four modeled streams with a consistent long-term algal sampling record: Canada,

303   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_{gen} on between-stream differences in the DOC-q

315   relationship, we compared each of these timescale parameters to the three DOC-q shape

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_{gen} 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**

324   MDV DOC-q relationships are strongly chemostatic, showing little variation in DOC

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

336   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).
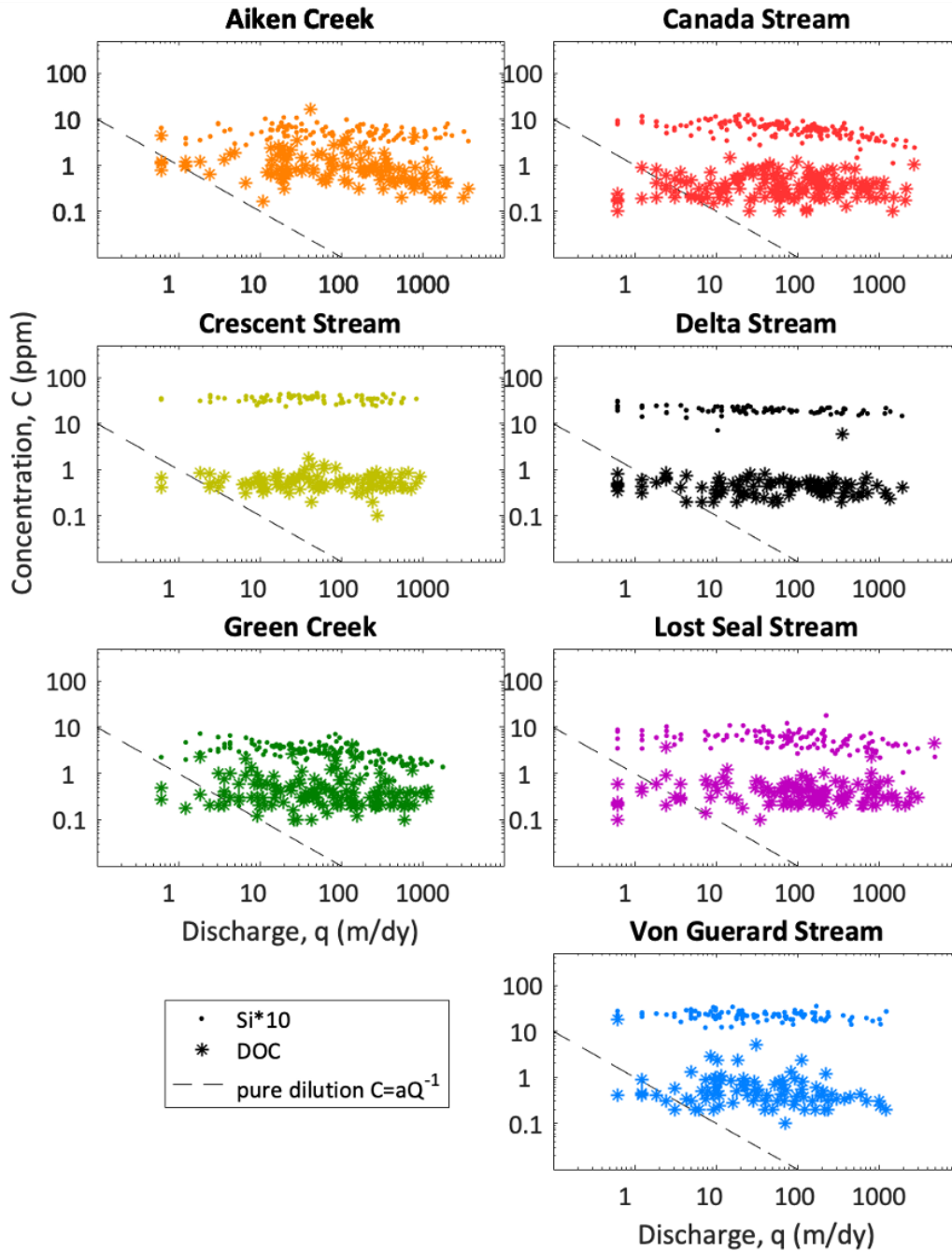
342

343

Figure 2: Visual inspection shows the chemostatic relationships of DOC and Si solute concentrations vs.
discharge (q) in seven MDV streams; Si concentrations are scaled for better visualization. Si represents a
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.
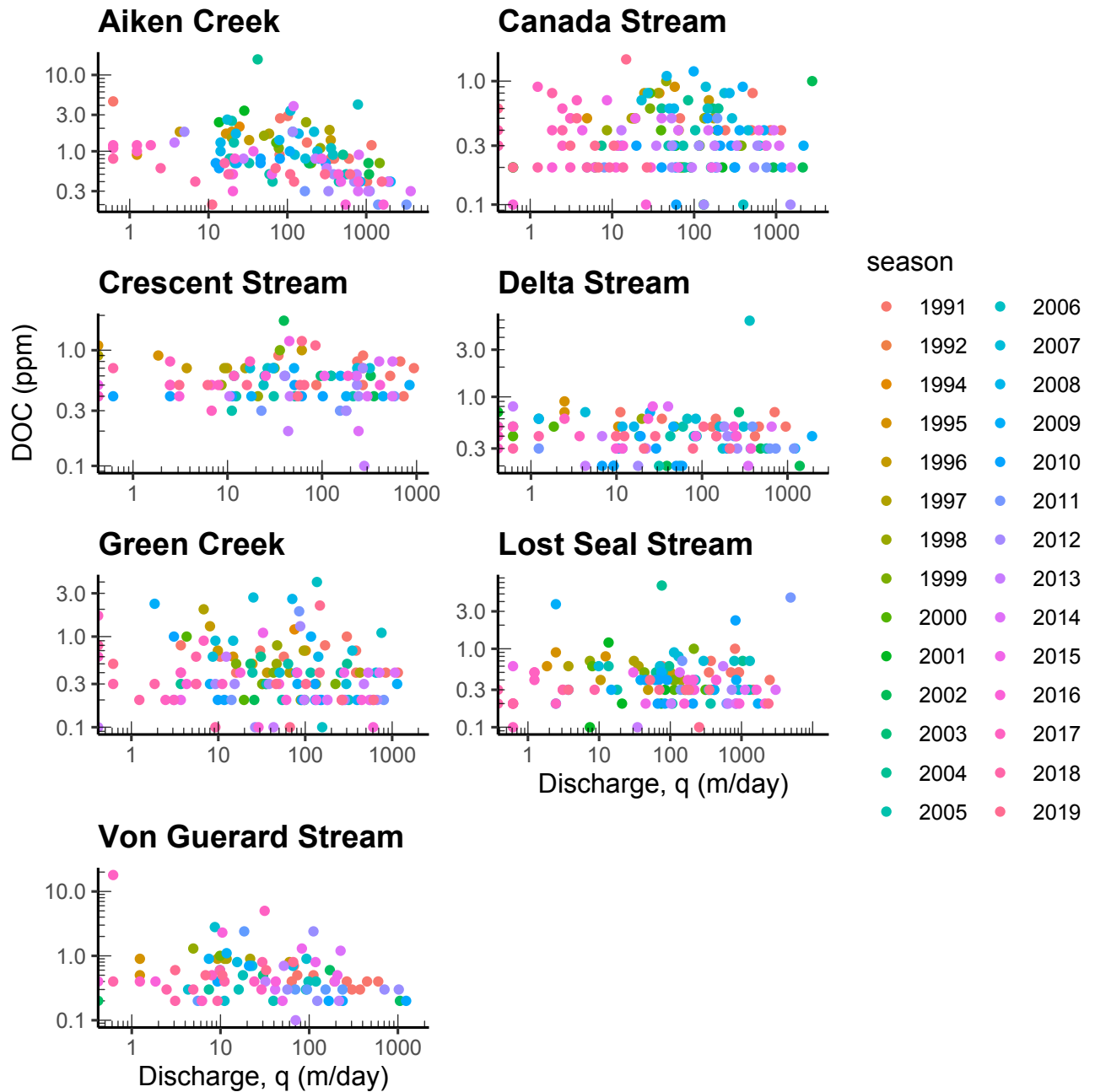
350

351

Figure 3: This shows the distribution of DOC-q relationships by study year in each stream.
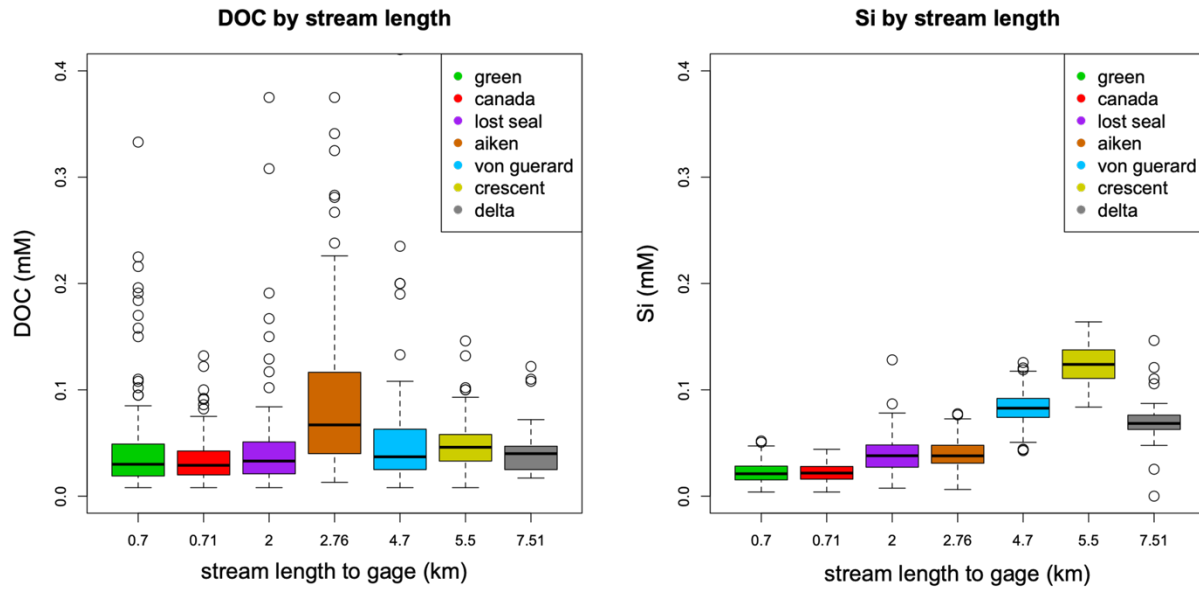
353

354

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

358

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
365 changing flow dynamics. The CV_c/CV_q analysis shows that all streams have CV_c/CV_q values less
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
368 four Fryxell Basin weathering solutes ranged from 0.07 to 0.76 with a mean value of 0.26, and
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 Da_{med}
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). Da_{med} 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

375   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} (m/dy)	$\tau_{f\,med}$ (dy)	C_{eq} (ppm)	b	CV_c/CV_q	Da_{med}
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

379

380   The regression analyses between the shape parameters and both τ_f and τ_{gen} show no

381   significant relationships (all $p > 0.05$, Figure 5). The one near-linear relationship for DOC is

382   between Da_{med} and τ_{gen} (Figure 5b, p = 0.064, R^2 = 0.53). As τ_{gen} increases, Da_{med} decreases,

383   indicating that τ_{gen} may be a stronger control on the stream's DOC-q transport-limitation than

384   τ_f: i.e. the values for τ_{gen}, not τ_f, are what impact the degree of DOC-q transport-limitation in

385   MDV streams.

386   As expected, Si-q relationships are quantitatively chemostatic across all streams. Values

387   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

388   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,

389   median of 25.93), indicating transport limitation. This supports the results of Wlostowski et al.

390   (2018b).

391   **5 Discussion**

392   5.1 DOC-q chemostasis in MDV streams

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

395   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

415   (p = 0.064), there does appear to be some gradient in the relationship of Da_{med} to τ_{gen}, indicating

416   that τ_{gen}, not τ_f, may have the stronger impact on the degree of DOC-q transport-limitation in

417   MDV streams, which does not support our expectations.

418

419   5.2 DOC generation - biological control

420   That DOC-q relationships are chemostatic across all streams is surprising, given the very

421   little amount of organic carbon in this landscape. Further, DOC generation is somehow supplied

422   across several orders of magnitude of q from autochthonous organic carbon alone. The

423   breakdown of POM primarily occurs in the stream channel and hyporheic zone. It is primarily a

424   biological process driven by the physical sloughing of in-channel mats and by decomposer

425   microorganisms in the mats and hyporheic sediments. Chemical equilibrium is not a factor here

426   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

431 (τ_{gen}) represents the average time required to reach this balance point of sources, sinks, storage

432 and exchange. It could be interpreted as the ratio of the "equilibrium" concentration to the net

433 DOC generation rate [NGR], or $\frac{C_{eq}}{NGR}$. Because C_{eq} is relatively steady across these streams (Table

434 1), variations in the net DOC generation rate control differences in τ_{gen}. Streams that have the

435 slowest generation rate would have the highest τ_{gen}, while streams that have more rapid DOC

436 generation rates would have a lower τ_{gen}. This interpretation is supported by the fact that

437 streams with the lowest τ_{gen} are more strongly chemostatic (Figure 5).
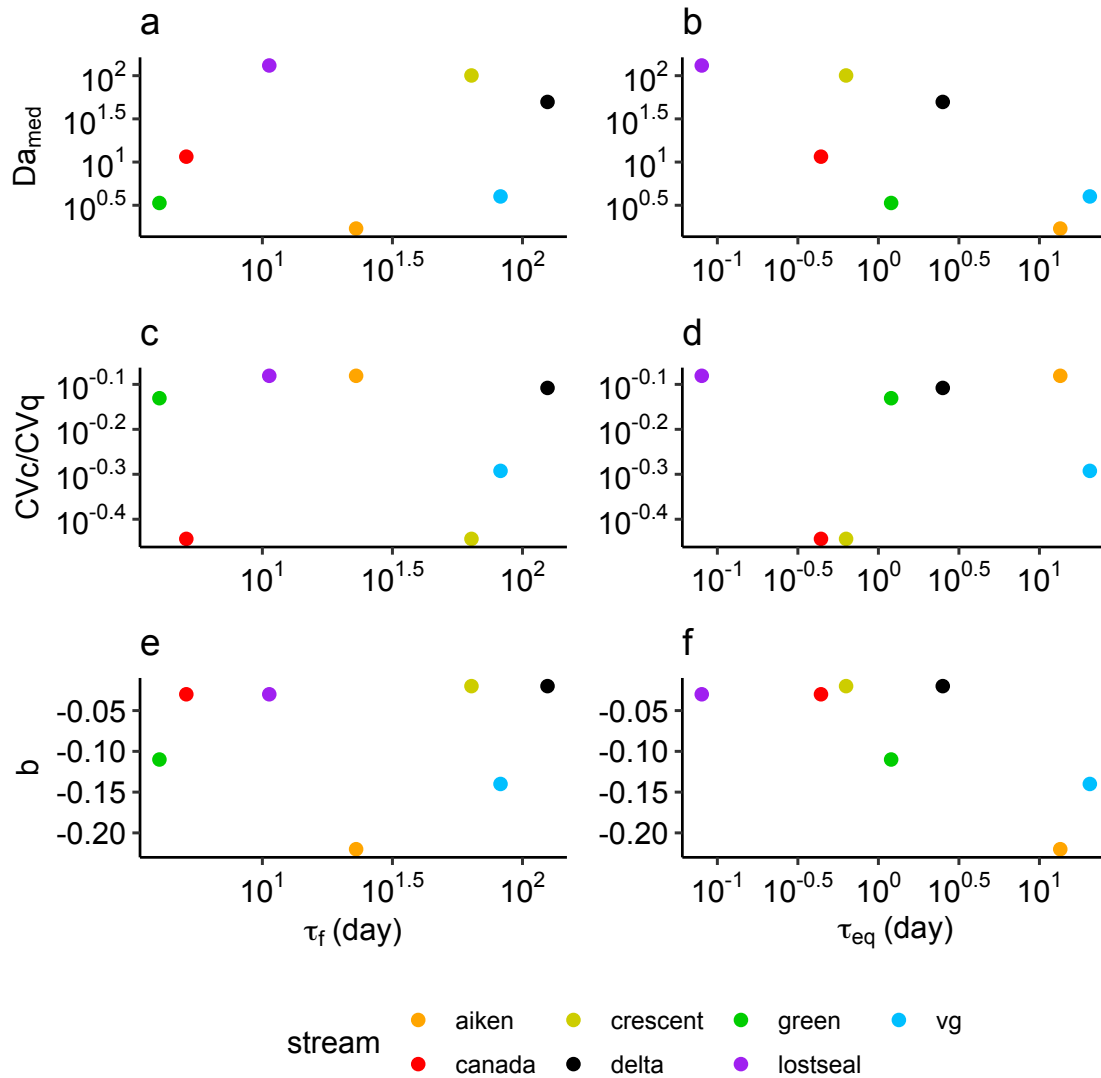
Figure 5: Relationship between the DOC-q shape parameters and (a, c, e) mean transit time at median q (τ_f) and (b, d, f) the equilibrium time scale (τ_{eq}). There are no significant relationships in any of these regressions (all p > 0.05). In contrast, Si relationships for the shape parameters and τ_f are all significant (Wlostowski et al., 2018b). This indicates that τ_f controls between-stream differences in the shape of the C-q curve for Si but neither τ_f nor τ_{eq} provide this control for DOC.

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445   5.3 Controls on DOC-*q* chemostasis

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.

458   We hypothesized that fluid transit time (τ_f) would be an important control on the DOC-q

459   shape and would explain between-stream differences in degree of chemostasis, because a longer

460   transit time (in longer streams, and/or in lower flow streams) would allow more opportunity for

461   DOC generation. This is not supported by the shape parameter analysis (Figure 5). If anything,

462   these results indicate that the differences in τ_{gen} may weakly influence differences in the degree

463   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 =

471   0.0004, R^2 = 0.92).

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>

487   The primary DOC source to streams is benthic microbial mats that grow on the bed and

488   wetted margins of streams (Barrett et al., 2007; Hawes & Howard-Williams, 1998; McKnight et

489   al., 1998). A secondary source is POM from these mats, which may be buried or lodged in

490   stream interstices. Unlike in temperate streams, there are no allochthonous DOC sources. DOC

491   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
520   sediments.

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524 *Figure 6: Stream cross-section illustrating the conceptual model for hyporheic DOC generation and*

525 *storage at low (a), median (b) and high flows (c). Orange, black, and striped boxes represent microbial*

526 *mats. Blue represents the stream water and the blue/ brown areas represent the saturated sediments of*

527 *the near and deep hyporheic zone. At each flow level, the hyporheic zone acts as a generation, storage*

528 *and release site for DOC, buffering the DOC-q relationship against the large changes in q this system*

529 *experiences. This parallels the role of the riparian zone in temperate stream DOC-q chemostasis. At very*

530 *high flows, mats also slough POM, some of which is buried in the hyporheic zone to seed future DOC*

531 *generation.*

532

533 At median flow, with a moderate water volume, many but not all of the mats would be

534 flooded and releasing DOC into the stream channel (Figure 6a). Hyporheic extent and exchange

535 would be moderate, and some areas would be well-connected with the channel, mobilizing DOC,

536 while others would not. The wetted areas that were not well-connected with the channel would

537 continue to break down organic matter into DOC, creating some storage pockets that would only

538 be accessed at relatively high flows.

539 At low flows, with a low water volume, the decrease in q would be compensated for by

540 the decrease in DOC generation and release (Figure 6b). Fewer mats would be submerged,

541 decreasing the amount of DOC released to the stream water. Hyporheic exchange would be

542 lower, and the hyporheic zone itself might contract if the flow is low enough. DOC generation

543 would continue in the wetted mats and hyporheic zone (where there is POM). Less of the DOC

544 generated and stored in the hyporheic zone would be released to the channel.

545 At high flows, the increase in q would be compensated for by a flushing of the stored

546 DOC that was generated at lower flow levels (Figure 6c). All of the mats would be submerged,

547 increasing the surface area of mat that would release DOC to the stream channel. At higher

548 flows, there is also more likely to be sloughing and entrainment of mat material that would

549 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

555 of a hyporheic OM source. This would inform both the conceptual model and improve the

556 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

558 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.

569 We propose a conceptual model where carbon C-q chemostasis is a product of the

570 interaction of the four bins: generation, uptake, storage (here, primarily hyporheic), and

571 exchange. The hyporheic storage and exchange locations have not previously been explored for

572 DOC. In the MDV, autochthonous hyporheic POM and wetted-margin microbial mats are the

573 carbon pool supporting DOC-q chemostasis, paralleling the allochthonous riparian/ hillslope

574 pools in temperate systems.

575 This is the first examination of the dynamics impacting DOC-q chemostasis in the MDV.

576 It is likely that the processes influencing DOC-q chemostasis were not fully captured by the

577 long-term data record we studied. Although this study does not provide a definitive solution to

578 the causes of DOC-q chemostasis in the MDV, it does provide clues to the processes involved

579 and can inform future investigations and models. It also provides insight into the ways

580 autochthonous carbon contributes to DOC-q relationships in systems where the autochthonous

581 influence is obscured by the dominance of allochthonous carbon inputs.

586 numerous collaborators and students who helped carry out lab and fieldwork associated with the
587 project, as well as the logistical and helicopter support contractors who have facilitated the MCM
588 LTER field research in Antarctica since 1993 through the US Antarctic Program: Antarctic
589 Support Associates, Raytheon Polar Services, Antarctic Support Contractors and Petroleum
590 Helicopters.

591 **Data availability**

592 The stream gage data (Gooseff & McKnight, 2019a-c; Gooseff & McKnight, 2021a-d); water

593 chemistry data (Lyons, 2016; Lyons & Welch, 2016); and microbial mat data (McKnight, 2019)

594 are available at the McMurdo Long Term Ecological Research website and the Environmental

595 Data Initiative.

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