



# Supplement of

# A global hotspot for dissolved organic carbon in hypermaritime watersheds of coastal British Columbia

Allison A. Oliver et al.

Correspondence to: Allison A. Oliver (aaoliver@ualberta.ca)

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#### **1** Supplemental Material

#### 2 S1. Watershed and soil attributes

#### 3 S1.1 Extent of wetlands and lakes

4 Estimates of lake and wetland cover were extracted from the Province of British 5 Columbia Terrestrial Ecosystem Mapping (TEM) (Green, 2014; Gonzalez Arriola et al., 2015). 6 The estimate of wetland cover is derived by combining the cover of nine ecosystem classes 7 typically considered to have wet (hygric to subhydric) to very wet (hydric) soils, including 8 blanket bogs, bog woodlands, basin bogs, fens and swamps (Banner et al., 1993, MacKenzie and 9 Moran, 2004). This metric omits the widespread bog forests of Calvert and Hecate Islands, 10 which have very moist (subhygric) to wet soil moisture regimes (Banner et al., 1993) and are 11 transitional between upland and wetland ecosystems. The TEM dataset has polygons containing 12 up to three ecosystem classes, with no information on the location of classes within polygons. 13 Where TEM a polygon was intersected by watershed boundaries, we assumed a homogenous 14 distribution of ecosystem classes within the polygon. After summing the cover of wetlands in 15 each watershed we calculated the percentage of land (watershed area less lakes) covered by wetlands. 16

#### 17 S1.2 Soil sampling and depth predictions

Soil data were collected at a total of 353 field sites. Of these sites, 322 were located at fixed distances along transects established using a conditioned latin hypercube sampling design (Minasny and McBratney, 2006). The transect method was adopted because access on this remote island is restricted, and it was not possible to visit all of the points identified in the original hypercube procedure. The effect was to have small clusters of points that were well distributed and representative of the study area. At all sites, the thickness of organic horizons,

24 thickness of mineral horizons, and total soil depth to bedrock were recorded, along with 25 observations needed for categorization according to the Canadian System of Soil Classification 26 (Soil Classification Working Group, 1998) and the British Columbia terrain classification 27 (Howes and Kenk, 1997), where mineral soil horizons have  $\leq 17\%$  organic C, while organic soil 28 horizons have >17% organic C, as per the Canadian System of Soil Classification (Soil 29 Classification Working Group, 1998). Boundaries between surface organic horizons and the 30 underlying mineral soil were usually obvious, based on colour, consistence, and presence/absence of mineral grains, but for occasional ambiguous cases, grab samples were 31 32 collected for laboratory determination of C content by a ThermoFischer Scientific Flash 2000 CHNS analyser at the Ministry of Environment laboratory in Victoria, B.C. For some sites, total 33 34 depth exceeded the reach of sampling tools, so recorded thicknesses were likely conservative. 35 Data were also collected at an additional 31 sites that were located in previously established 36 ecosystem inventory plots with the same soil attributes (Giesbrecht et al., 2015). In addition to 37 field-sampled points, 40 sites with exposed bedrock (0cm soil depth) were located using aerial 38 photography.

Total organic horizon thickness, total mineral horizon thickness, and total soil depth were combined with a suite of topographic, vegetation, and remote sensing data for each sampling point, and the resulting dataset was used to train a random forest model (randomForest package in R; Liaw and Wiener, 2002) which predicted soil depth values and soil/terrain types for all points on the landscape. Depth predictions represent a modification of the procedure used by Scarpone et al. (2016) for depth predictions in interior British Columbia.

45 S2. Hydrology- Rating curve calculations of stream discharge and error analysis

46 S2.1 Stage Measurements

47 Stations were installed in the spring and early fall of 2014 as part of a telemetry network allowing for near real time download of data. At each station, an OTT PLS – L (OTT 2016) 48 49 pressure transducer (0 - 4 m range SDI-12) was installed. Each sensor was connected to a 50 CR1000 (Campbell Scientific, 2015) data logger. Stage measurements were recorded every five 51 minutes with a five second sampling interval and mean, max, min and standard deviation of 52 stream stage recorded over each five minute period. Each watershed also had stand-alone 53 Odyssey Capacitance Water Level recorder (Data Flow Systems PTY Ltd 2016) installed in 54 proximity to the pressure transducer to act as a back-up in case of sensor or data logger 55 malfunction.

56 S2.2 Discharge Measurements

57 Stream discharge was measured using multiple methods. Low and moderate flows, generally below 0.5 m<sup>3</sup> s<sup>-1</sup>, were measured using the velocity area method midsection discharge 58 59 equation (ISO, 1992; ISO, 1997). The flow velocities were measured with the Swoffer 2100 60 propeller type mechanical current meter (Swoffer Instruments Inc., Seattle, USA) or the Sontek Flowtracker acoustic doppler velocimeter (SonTek, San Diego, USA). Flow velocities were 61 62 averaged by the Swoffer over a five second measurement interval and by the Flowtracker over a 63 30 second measurement interval for each location. A suitable river cross-section site was defined 64 by: a) general flow direction perpendicular to the cross-section line, b) uniform stream bed 65 conditions, and c) constrained flow conditions with no back eddies and low turbulence. 66 At some watersheds, multiple velocity-area sites were used depending on conditions at time of 67 measurement.

At flows greater than 0.5 m<sup>3</sup> s<sup>-1</sup>, salt dilution was the primary method to measure
discharge, specifically salt in solution ("salt solution") as described by Moore (2005). Discharge
was calculated using the following formula:

 $Q = \frac{V}{\sum RC_t \cdot t_{int}}$ (4)

where V represents the volume of salt solution ( $m^3$ ), RC<sub>t</sub> the relative concentration of salt solution (mL mL<sup>-1</sup>) and t<sub>int</sub> is the time interval of measurement. RC<sub>t</sub> is obtained using a relative concentration, related to electrical conductivity (EC):

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$$RC_t = (EC_t - EC_0) \cdot CF$$
(5)

where EC<sub>t</sub> is the temperature corrected EC measured at time t ( $\mu$ S cm<sup>-1</sup>), EC<sub>0</sub> is the baseline conductivity of the stream ( $\mu$ S cm<sup>-1</sup>) defined as the five minute average prior to the salt wave, and CF is the calibration factor. The end of the salt wave was defined as the point in which the five minute EC average equaled EC<sub>0</sub>. In some instances the post-five minute average would not return to EC<sub>0</sub> due to changes in background chemistry not associated with the salt dump. When this occurred, EC<sub>0</sub> was determined by linear interpolation for baseline EC, pre and post measurement.

The CF is defined as the relationship between additions of primary solution (made up of salt solution and stream water) to a known volume of secondary solution (stream water only), with the resulting slope of the line corresponding to the CF value. The primary solution was typically made up of 10 mL salt solution (used in discharge measurement) added to 1000 mL of stream water. Then, 2 or 5 mL increments of the primary solution was pipetted into 3000 mL of the secondary solution, and corresponding changes in EC were recorded. Linear regression was performed to determine slope of the line. Due to difficulties associated with being on location to measure high discharge, a "salt dilution system" was designed using the salt solution method described above. The system was entirely automated and located within an extensive telemetry network enabling remote activation off-site or through pre-programmed stream stages where discharge measurements had not been previously measured.

95 A volume of salt solution, stored in two, 200 L barrels on site, allowed for up to thirty 96 measurements between refills. Recharging of the salt solution reservoir was done manually and 97 the CF completed following the refill and prior to the next refill (the reservoir was designed to 98 ensure that at least 5 L of solution remained after the final discharge measurement), for a 99 minimum of two CF's between refills. When the water level reached a predefined stage, a signal 100 was sent to release a pre-determined volume of salt solution from a reservoir connected to the 101 salt solution storage barrels. To increase the accuracy of this volume, the salt solution was first 102 pumped into a stainless steel cylinder with a pressure transducer at the bottom to measure water depth, and in turn volume. The solution was then transferred to a dumping mechanism located 103 104 above the stream designed for near instantaneous release. Upon initiation of the salt solution 105 dump sequence, a second command was sent to a downstream data logger to activate two Global 106 Water-WQ Cond sensors (Global Water instrumentation, Inc., College Station, USA) to measure 107  $EC_t$  at one second intervals, and therefore capture the passing salt wave. Once the dump 108 sequence was completed, the ECt data were transmitted via the telemetry network to a server 109 accessed via the internet. The volume of salt depended on estimated discharge measurements, 110 with maximum EC measurements targeted to be no more than 40 uS above background, well below the most sensitive toxicity threshold of 400 mg  $L^{-1}$  (Moore 2004a, 2004b). 111

112 S2.3 Error and uncertainty analysis

#### S2.3.1 Discharge measurement error analysis

Errors associated with manual direct discharge measurements were estimated using statistical techniques and on-site observations. For the velocity-area method, discharge uncertainty was calculated using the Interpolated Variance Estimator (IVE) (Cohn et al., 2013). For the salt dilution method, a statistical and site specific uncertainty estimation method was developed.

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#### S2.3.2 Uncertainty analysis for the velocity-area measurements

121 As described in Cohn et al. (2013), the IVE was used to estimate uncertainty in velocity 122 area discharge measurements. It is based on the assumption that depth and velocity vary 123 gradually across a channel cross-section and that depth and velocity vary linearly between 124 adjacent stations. The difference between the assumed and the measured value is used to 125 calculate measurement uncertainty. In addition, uncertainties associated with calibration and 126 systemic errors in the width, depth, and velocity were assumed to be 1% for the Sontek 127 Flowtracker (the accuracy of the device calibration; Sontek/YSI, 2007) and 5% for the Swoffer 128 current meter, due to increased potential uncertainty from the shorter time interval used to 129 determine average velocity. Total uncertainty was estimated based on the above uncertainties 130 and the number of measurement stations (see Cohn et al. 2013).

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#### S2.3.3 Salt dilution discharge uncertainty

The discharge uncertainty for salt dilution measurements was estimated using the
sensor resolution, calibration errors, salt volume errors, and salt mixing errors. Uncertainty (u<sub>Q</sub>),
associated with discharge calculated from a conductivity sensor is based on the following:

- 136  $u_{Q} = u_{v} + \frac{\sum_{i=1}^{m} ((u_{EC,i} + u_{CF})C_{i})}{\sum_{i=1}^{m} C_{i}}$ (6)
- 137

Where  $u_v$  is the relative uncertainty due to salt volume error (%),  $u_{EC,i}$  is the relative uncertainty in EC measurement i due to the resolution of the sensor (%),  $u_{CF}$  is the relative uncertainty in CF (%),  $C_i$  is the calculated salt concentration at measurement i (g m<sup>-3</sup>), and m is the total number of EC measurements.

Error associated with determining the volume of salt  $(u_v)$  was estimated by:

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 $u_v = \frac{\Delta v}{v} \cdot 100 \tag{7}$ 

where V is the volume of salt solution released to the stream (L), and  $\Delta V$  is the estimated error in salt solution volume (L). The error in solution volume was estimated based on the resolution (1 mm) of the pressure transducer inside the stainless steel cylinder salt dump reservoir. With an uncertainty of 0.5 mm in solution height inside the cylinder and a cylinder diameter of 304 mm, the uncertainty in solution volume for each release was 36.3 mL. Because the cylinder was never completely emptied, two level measurements were made to calculate water, thus total maximum error in solution volume ( $\Delta V$ ) was 72.6 mL.

153 Electrical conductivity measurement uncertainty (u<sub>EC</sub>), dependent on the resolution of
 154 the conductivity sensor (Res) is described below:

155 156  $u_{EC} = \frac{0.5 \cdot \text{Res}}{\text{EC}} \cdot 100 \tag{8}$ 

Uncertainty related to  $u_{CF}$  was a function of the errors associated with the measurement of salt concentration of the primary and secondary solution, a combination of volumetric error of the primary solution (±0.3 mm, volumetric flask precision), the secondary solution (±3.0 mm volumetric flask precision plus rain splash and field conditions) and each primary solution dose (0.006 mL, based on precision of the pipette) added in 2 or 5 mL increments. Uncertainty of the CF was derived from the maximum variation in slope, a product of the salt concentration error ranges. The calibration regression curve was plotted using three data points for each conductivity measurement: the assumed salt concentration, the assumed salt concentration plus maximum error, and the assumed salt concentration minus maximum error (Figure S2.1). Next, the maximum variation of slope was calculated using the standard deviation of slope ( $\sigma_s$ ):

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$$\sigma_{s} = \sqrt{\frac{(\frac{1}{n-2})\sum_{i=1}^{n}(y_{i}-\hat{y}_{i})^{2}}{\sum_{i=1}^{n}(x_{i}-\bar{x})^{2}}}$$
(9)

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where n is the number of data points,  $y_i$  is the assumed salt concentration (± error) of measurement i (mL mL<sup>-1</sup>),  $\hat{y}_i$  is the modelled salt concentration (mL mL<sup>-1</sup>),  $x_i$  is the measured electrical conductivity of measurement i ( $\mu$ S cm<sup>-1</sup>), and  $\bar{x}$  is the mean average electrical conductivity ( $\mu$ S cm<sup>-1</sup>). Finally, the CF relative uncertainty ( $u_{CF}$ ) was defined as two times the standard deviation of slope divided by the CF:

174  $u_{CF} = (2 \cdot \sigma_s)/CF \qquad (10)$ 

176 If the EC sensors showed different EC readings and confirmed the salt was not 177 completely mixed at the measurement site, additional uncertainty was added to the discharge 178 measurement. To measure the degree of salt mixing at the measurement site, discharges 179 calculated from both conductivity sensor measurements were compared, while taking their 180 uncertainties into account:

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$$M = \frac{(Q2 - \varepsilon_{Q2}) - (Q1 + \varepsilon_{Q1})}{(Q1 + \varepsilon_{Q1})} \cdot 100$$
(11)

183 where M is the relative uncertainty due to improper mixing (%), Q1 is the lower discharge value 184  $(m^3 s^{-1})$ , Q2 is the higher discharge value  $(m^3 s^{-1})$ ,  $\epsilon_{Q1}$  is the absolute uncertainty of the lower 185 discharge value, derived from  $u_Q$  (Equation 6) and  $\epsilon_{Q2}$  is the absolute uncertainty of the higher 186 discharge value. If  $M \le 0$ , the salt was assumed to be properly mixed. Any positive outcome of 187 M implies incomplete mixing and is added to the total uncertainty of the discharge measurement.

#### 188 S2.4 Rating curve development and uncertainty

Discharge is related to stage through the formula:

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$$Q = a(h - h_0)^b$$
 (12)

where O is discharge  $(m^3 s^{-1})$ , h is stage level (m), h<sub>0</sub> is the water level at zero flow (m) and a and 192 193 b are coefficients specific to the gauging station of a river. The values for  $h_0$ , a, and b are 194 obtained by the curve fitting results of simultaneous stage and discharge measurements. For this 195 work, stage-discharge curves were created using a non-linear least-squares fitting Python model 196 (lmfit; LMFit Development Team, 2015). This model approximates the variables (a, b, and  $h_0$ ) 197 by minimizing the residuals scaled by data uncertainties:  $[Q_i^{\text{meas}} - Q_i^{\text{model}}(v)]/\varepsilon_i$ 198 (13)where  $Q_i^{\text{meas}}$  is the measured discharge (m<sup>3</sup> s<sup>-1</sup>),  $Q_i^{\text{model}}$  is the fitted discharge (m<sup>3</sup> s<sup>-1</sup>), v the set 199 200 of variables in the model (a, b and  $h_0$ ) to be optimized, and  $\varepsilon_i$  the uncertainty in the discharge 201 measurement. This was a two step process where the curve was first fit taking into account 202 uncertainties related to Q and then fit again taking into account uncertainties in h. 203 As described above, uncertainty for individual discharge measurements were accounted 204 for in the curve fitting process, with measurements of greater uncertainty having less influence 205 on position of the curve. To account for uncertainty in the stage discharge relation, 95% 206 confidence intervals were created per Herschy (1994) and applied to the final discharge times-207 series as an estimate of discharge.

#### 208 S2.5 Results of stream discharge measurement and calculations

A total of 168 total measurements, including 92 measures made using the automated system, were used to develop rating curves for each watershed (Figure S2.1; Floyd et al., 2016). Watershed 703 had the highest total discharge over the study period, which was more than the

212	combined total from watersheds 626, 819, 844 and 1015. Total discharge calculated from the
213	95% confidence intervals from the rating curves were $\pm 6.5\%$ of the mean of all watersheds, with
214	a range between $\pm 2.93\%$ (708) and $\pm 9.98\%$ (819) (Table S2.3). In general, discharge data from
215	watershed 708 had the lowest uncertainty, due to it having the most discharge measurements and
216	the best developed rating curve. Watershed 819 had the highest uncertainty largely due to the
217	limited number of high flow discharge measurements on the rating curve (max measured was 4.5
218	$m^{3}s^{-1}$ ) and variation in stage during the discharge measurements at high flow. Four of the seven
219	watersheds had total discharge measurements less than $\pm 5.0\%$ of the estimated measurements
220	from the rating curve, and none were $> 10\%$ for the entire project study period, however for
221	water year 2015/2016, 819 had a total discharge uncertainty of $\pm 13.0\%$ .
222	<b>Figure S2.1.</b> Stage discharge rating curves for seven focal watersheds. Confidence intervals

Figure S2.1. Stage discharge rating curves for seven focal watersheds. Confidence intervals
 (95%) are calculated based on Herschy (1994). Error bars represent uncertainty from individual
 measurements.



Table S2.1. Uncertainty (%) in total discharge, by water year and over the entire study period, based on rating curve confidence intervals (95%). Values are plus or minus the modelled output. 

Watershed	2014-15	2015-16	2014-2016
626	5.57	5.54	5.55
693	3.35	2.97	3.19
703	10.14	9.37	9.83

708	2.93	2.93	2.93
819	7.49	13.01	9.98
844	4.98	4.47	4.78
1015	9.01	8.58	8.84

233 Figure S2.2: Response times of watersheds with and without extensive lake area. Discharge and

total precipitation are shown for a series of rain events in four of our seven focal watersheds.

Panels "a" and "b" represent watersheds without extensive lake area, and panels "c" and "d"

represent watersheds with a large lake area. Specific information on lake area can be found in the manuscript, Table 1. Rapid response to rain events can be observed in each watershed, while the

falling limb of the hydrograph is delayed in systems with extensive lake area compared to those

without.



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#### 242 S3. Generating model estimates of DOC flux using rloadest

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**Table S3.1:** The number of samples and specific regression model used by rloadest for

calculating stream loads. Estimated bias of each model shows relatively low overall bias foreach model, with 844 clearly showing the highest bias.

Watershed	n	Model #	Regression model	Estimated % bias
626	23	7	$a_0 + a_1 \ln Q + a_2 \sin(2\pi dtime) + a_3 \cos(2\pi dtime) + a_4 dtime$	2.026
1015	24	7	$a_0 + a_1 \ln Q + a_2 \sin(2\pi dtime) + a_3 \cos(2\pi dtime) + a_4 dtime$	-2.502
819	23	7	$a_0 + a_1 \ln Q + a_2 \sin(2\pi dtime) + a_3 \cos(2\pi dtime) + a_4 dtime$	2.011
844	20	3	$a_0 + a_1 \ln Q + a_2 dtime$	-11.49
708	24	6	$a_0 + a_1 \ln Q + a_2 \ln Q^2 + a_3 \sin(2\pi dtime) + a_4 \cos(2\pi dtime)$	-0.206
693	23	6	$a_0 + a_1 \ln Q + a_2 \ln Q^2 + a_3 \sin(2\pi dtime) + a_4 \cos(2\pi dtime)$	0.092

#### **S4. PARAFAC Modeling of DOM composition**

Figure S4.2: Fingerprint map showing the six fluorescence components determined by 

PARAFAC analysis. 



- 256 Figure S4.3: Split half validation plots for the six fluorescence components determined by
- PARAFAC analysis.





**Figure S4.4:** Box plots showing the percent contribution to total fluorescence from each of the

six components determined by PARAFAC analysis for each of the seven watersheds used in this

study. Means and standard deviations for each component summed across all watersheds isincluded at the top of each panel.



Table S4.1: Locations of maximum fluorescence values and the corresponding excitation and 

emission wavelengths for each of the six peaks (components) determined with PARAFAC

modelling.

Component	Excitation	Excitation	Emission	Emission
	(nm)	F <sub>max</sub>	(nm)	F <sub>max</sub>
1	315	0.2502	436	0.1688
2	270	0.2607	484	0.1422
	380	0.2539		
3	270	0.4125	478	0.1212
4	305	0.2648	522	0.1504
	435	0.1512		
5	325	0.1408	442	0.1321
6	285	0.3108	338	0.2350

- **Table S4.2:** Pearson correlation coefficients for PARAFAC components represented as percent contribution to total fluorescence. Symbols "\*\*", "\*", represent p-values <0.001 and 0.001, respectively.

	C1	C2	C3	C4	C5	C6
C1	1	0.55 **	-0.45 **	0.38 *	-0.66 **	-0.47 **
C2	-	1	-0.78 **	0.95 **	-0.90 **	-0.46 **
C3	-	-	1	-0.81 **	0.93 **	-0.13
C4	-	-	-	1	-0.87 **	-0.34 *
C5	-	-	-	-	1	0.16
C6	-	-	-	-	-	1

S5. Redundancy analysis: Relationships between watershed characteristics and DOC

exports

Figure S5.1: Partial-RDA Axis 1 versus Axis 3. RDA was performed under type 2 scaling. 



**Figure S5.2:** Partial-RDA Axis 2 versus Axis 3. RDA was performed under type 2 scaling.



**Table S5.3:** Relative eigenvalues and the statistical significance of each axes in the partial-RDA.

Axis	Eigen -value	F marginal	F forward	P- marginal	P- forward	% total variance in Y	% total variance explained by all
		. 0		0			axis
1	1.420	18.717	11.047	0.0001	0.0001	15.78	47.3
2	0.902	11.887	9.158	0.0001	0.0001	10.02	30.1
3	0.654	8.622	8.531	0.0002	0.0002	7.27	21.8
4	0.013	0.175	0.175	1.0000	1.0000	0.15	0.4
5	0.011	0.143	0.143	0.9965	0.9965	0.12	0.4

- 291 Table S5.4: Results of permutation test on the marginal effects of terms given under the reduced
- RDA model.

	df	Variance	F	Pr (>F)
Lakes	1	1.093	6.4789	0.001
Slope	1	0.5722	3.392	0.005
Wetlands	1	0.1207	0.7153	0.651
MinSoil	1	0.8403	4.9807	0.001
OrgSoil	1	0.6937	4.1118	0.001
Residual	34	5.7359		

	Axis1	Axis2	Axis3	Axis4	Axis5
Lakes	0.8471	0.1028	0.4853	-0.1871	0.0349
Slope	0.2658	0.0275	-0.8769	-0.0410	0.3825
Wetlands	-0.3789	-0.0527	0.4940	0.4033	-0.6664
MinSoil	0.4540	-0.2311	-0.3205	0.1128	0.7905
OrgSoil	0.1503	0.2569	0.5178	0.3138	0.7341

Table S5.5: Biplot scores for partial-RDA axes using type 2 scaling.

Table S5.6: Standardized coefficients for variables included in the partial-RDA using type 2
 scaling. Coefficients represent the length of the vector in relation to the given axis and its relative
 contribution to that axis.

	Axis1	Axis2	Axis3	Axis4	Axis5
DOC	0.10308	0.78375	0.79112	0.79174	0.79204
DO13C	0.02198	0.05953	0.26876	0.27104	0.27141
Sr	0.25971	0.25971	0.39575	0.39901	0.39921
FI	0.37008	0.44613	0.47187	0.47188	0.47616
SUVA	0.04024	0.06987	0.07513	0.07548	0.07560
FRESH	0.37330	0.40960	0.48886	0.48886	0.49153
C1	0.00422	0.04047	0.10175	0.10612	0.10622
C4	0.21552	0.22043	0.32432	0.32674	0.32701
C6	0.03199	0.03257	0.05873	0.05873	0.06128

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# S6. Evaluating relationships in DOC concentration and DOM character with stream discharge and temperature

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**Figure S6.1:** Linear regressions of discharge versus DOC concentration for all watersheds (n=

306 158) combined and for each individual watershed (n=21 for watersheds 703, 708, 819; n=23 for

307 watersheds 626, 693, 844, 1015) included in our study for each watershed).



Table S6.1: Results of linear mixed effects models used to evaluate the relationship between DOC concentration or proxies of DOM

character with stream discharge and stream temperature. Random effects are displayed using the format "Random (random slope | random intercept)", where "~" indicates no random slope was included in the model. P-values significant at the 95% confidence level 

are presented in bold. 

						Fixed Effects			
Variable	Model	df	RMSE	Intercept	log Q	Temp	logQ * Temp	Conditional R <sup>2</sup>	Marginal R <sup>2</sup>
DOC	$b_1(\log Q) + b_2(Temp) +$ Random(logQ Watershed)	136	3.51	8.27 SE= 1.33	$b_1 = 0.613$ SE= 0.131 t= 4.68 p< 0.001	b <sub>2</sub> = 0.162 SE= 0.063 t= 2.59 p= 0.0107		0.574	0.087
$\delta^{13}$ C-DOC	$b_1(\log Q) + b_2(\text{Temp}) + \text{Random}(\log Q \text{Watershed})$	133	0.324	-26.31 SE= 0.104	b <sub>1</sub> = -0.049 SE= 0.131 t= -2.49 <b>p= 0.014</b>	b <sub>2</sub> = -0.024 SE= 0.007 t= -3.50 <b>p&lt; 0.001</b>	72	0.353	0.096
$S_{\rm R}$	$b_1(\log Q) + b_2(Temp) + b_3(\log Q * Temp) + (Random(Temp Watershed))$	121	0.030	0.808 SE= 0.014	<i>b</i> <sub>1</sub> = -0.026 SE= 0.004 t= -6.92 <b>p&lt; 0.001</b>	$b_2$ = -0.0013 SE= 0.0009 t= -1.32 p= 0.186	$b_3 = 0.0015$ SE= 0.0003 t= 5.29 p < 0.001	0.621	0.288
SUVA234	$b_1(\log Q) + b_2(Temp) + Random(\sim  Watershed)$	111	0.513	4.50 SE= 0.129	$b_1 = 0.033$ SE= 0.026 t= 1.27 p= 0.206	b <sub>2</sub> =-0.011 SE= 0.012 t= -0.919 p= 0.3603	8	0.072	0.041
Fluorescence Index	$b_1(\log Q) + b_2(Temp) + Random(\sim  Watershed)$	25	0.030	1.37 SE= 0.017	$b_1 = -0.009$ SE= 0.005 t= -1.76 p= 0.090	$b_2 = 0.0002$ SE= 0.002 t= 0.106 p= 0.916		0.702	0.083
Freshness Index	$b_1(\log Q) + b_2(Temp) + Random(\sim  Watershed)$	25	0.018	0.470 SE= 0.010	b <sub>1</sub> = 0.004 SE= 0.003 t= 1.25 p= 0.223	$b_2$ = -0.003 SE= 0.001 t= -2.91 p= 0.008		0.589	0.234

315 **Table S6.2:** Results of linear mixed effects models used to evaluate the relationship of PARAFAC components C1- C6 with stream

316 discharge and stream temperature. Random effects are displayed using the format "Random (random slope | random intercept)",

317 where "~" indicates no random slope was included in the model. P-values significant at the 95% confidence level are presented in

- 318 bold.
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					Fixed Effects		Conditional	Marginal R <sup>2</sup>
Model	df	RMSE	Intercept	log Q	Temp	logQ * Temp	Conditional R <sup>2</sup>	
$O) + h_2(Temp) +$			0 344	b <sub>1</sub> = -0.002 SE= 0.002	$b_2 = 0.001$ SE= 0.001			
m(~  Watershed)	25	0.0109	SE= 0.005	t= -1.03 p= 0.315	t= 1.99 p= 0.050	22	0.276	0.275
				b1=-0.005	b <sub>2</sub> = 0.0003			
$Q) + b_2(Temp) + m(\sim  Watershed)$	25	0.0110	0.209 SE= 0.006	t= -2.44 p= 0.022	t= 0.42125 p= 0.677	52	0.414	0.204
				bi= 0.006	b2= -0.003			
$Q) + b_2(\text{Temp}) + m(\sim  \text{Watershed})$	25	0.0112	0.183 SE= 0.006	SE= 0.002 t= 3.278	SE= 0.001 t= -3.26		0.529	0.420
				p= 0.003	p= 0.003			
Q) + b <sub>2</sub> (Temp) + m(~  Watershed)	25	0.0132	0.143 SE= 0.007	b <sub>1</sub> = -0.008 SE= 0.002 t= -3.39 <b>p= 0.002</b>	B <sub>2</sub> = 0.003 SE= 0.001 t= 4.26 p< 0.001	÷	0.690	0.457
Q) + b <sub>2</sub> (Temp) + m(~ [Watershed)	25	0.0213	0.103 SE= 0.011	b <sub>1</sub> = 0.011 SE= 0.003 t= 3.07 p= 0.005	b <sub>2</sub> = -0.003 SE= 0.001 t= -2.36 p= 0.027		0.453	0.331
Q) + b <sub>2</sub> (Temp) + m(~  Watershed)	25	0.0234	0.006 SE= 0.012	b <sub>1</sub> = -0.002 SE= 0.003 t= -0.55	b <sub>2</sub> = 0.005 SE= 0.002 t= 3.12		0.380	0.379
Q m Q m	$+ b_2(\text{Temp}) + (- \text{Watershed})$ $+ b_2(\text{Temp}) + (- \text{Watershed})$	$(-  Watershed) + b_2(Temp) + 25$ $(+ b_2(Temp) + (-  Watershed) + 25$	(- Watershed) 25 0.0213 $(+b_2(Temp) + (- Watershed)$ 25 0.0234	$\begin{array}{cccc} & 0.103 \\ (-  Watershed) \end{array} & 25 & 0.0213 & SE=0.011 \\ & 0.103 \\ SE=0.011 \\ & 0.006 \\ (-  Watershed) \end{array} & 25 & 0.0234 & \frac{0.006}{SE=0.012} \end{array}$	$\begin{array}{ccccccc} & 0.103 &$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

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