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Modeling stream dissolved organic carbon concentrations during spring flood in the boreal forest: A simple empirical approach for regional predictions

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[1] Changes in dissolved organic carbon (DOC) concentration are clearly seen for streams in which chemistry is measured on a high-frequency/episode basis, but these high-frequency data are not available in long-term monitoring programs. Here we develop statistical models to predict DOC concentrations during spring flood from easily available geographic information system data and base flow chemistry. Two response variables were studied, the extreme DOC concentration and the concentration during peak flood. Ninety-seven streams in boreal Scandinavia in two different ecoregions with substantially different mean water chemistry and landscape characteristics (covering a large climatic gradient) were used to construct models where 56% of the extreme DOC concentration and 63% of the concentration during peak flood were explained by altitude. This highlights important regional drivers (gradients in altitude, runoff, precipitation, temperature) of material flux. Spring flood extreme DOC concentration could be predicted from only base flow chemistry ($r^2 = 0.71$) or from landscape data ($r^2 = 0.74$) but combining them increased the proportion of explained variance to 87%. The "best" model included base flow DOC (positive), mean annual runoff (negative), and wetland coverage (positive). The root mean square error was 1.18 mg L^{-1} for both response variables. The different ecoregions were successfully combined into the same regression models, yielding a single approach that works across much of boreal Scandinavia.

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1. Introduction

[2] Dissolved organic carbon (DOC) is an important constituent of freshwaters that influences many aspects of aquatic ecosystem function. DOC can lower pH due to its acidic properties, or buffer against minerogenic acidity [*Bishop et al.*, 2000]. It is also an important source of energy for heterotrophic bacteria and associated food webs of streams, wetlands, and lakes [*Hall and Meyer*, 1998; *Jansson et al.*, 2007]. DOC carries nutrients [*Kortelainen and Saukkonen*, 1998; *Stepanauskas et al.*, 2000] as well as metals [*Dillon and Molot*, 1997; *Ravichandran*, 2004; *Simonin et al.*, 1993] and organic contaminants [*Knulst*, 1992; *Patterson et al.*, 1996] and is therefore of great importance for the biota in streams and lakes.

[3] The major annual hydrologic event in boreal Scandinavia is snowmelt during spring which can account for half of the annual export of water. DOC concentrations often vary with discharge and typically increase during snowmelt [*Laudon et al.*, 2004a]. Dilution of acid-neutralizing capacity (ANC) and the increasing amount of organic acids during this period cause pH to drop which can lead to fish mortality [*Serrano et al.*, 2008]. Although the spring snowmelt is a short period, it is extreme regarding pH, and it has been found to be an ecologically critical period for acid-sensitive biota [*Lepori and Ormerod*, 2005]. Because of these biotic effects it is important to understand and predict episodic export of DOC from the terrestrial landscape. The often high DOC concentrations and vast amounts of water during spring flood often means that this is an important period when calculating loads. Studies have shown that this DOC load is important for the carbon balances both in freshwater and marine ecosystems [*Duarte and Prairie*, 2005].

[4] Although these changes in DOC concentration are clearly seen for streams in which chemistry is measured on a high-frequency/episode basis, direct measurements of peak flow chemistry are difficult to capture in long-term monitoring programs with less frequent measurements. Thus,

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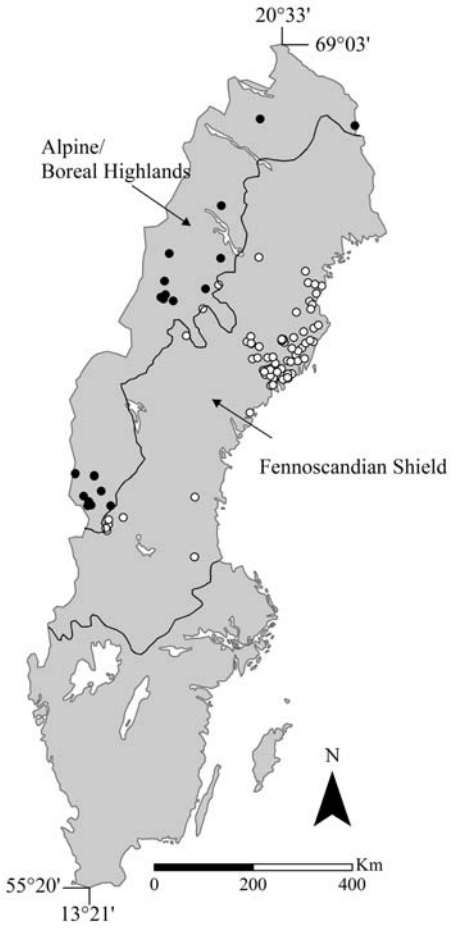

Figure 1. Location of stream sites in Sweden used for development of the model. White dots, sites in Fennoscandian Shield. Black dots, sites in Alpine/Boreal Highlands.

there is a need for statistical tools relating peak flow chemistry to other more widely available parameters.

[5] The principal objective of this study was to investigate the most important factors controlling spring flood DOC concentrations. This was achieved through the development of a statistical model which could predict spring flood DOC concentrations from widely available data on landscape structure and location as well as commonly measured hydrologic and base flow stream chemical parameters. We hypothesize that spring flood DOC concentrations can be predicted with fidelity from readily available data, and that landscape characteristics will be more highly correlated than base flow chemistry to spring flood DOC. Based on prior published studies of stream DOC [*Creed et al.*, 2003; *Gergel et al.*, 1999; *Mulholland*, 2003], we expected variation in wetland cover to explain the majority of the variation in spring flood DOC. We also expected a negative correlation with altitude [*Ivarsson and Jansson*, 1994; *Sobek et al.*, 2007]. Since long-term time series of DOC have showed a negative correlation with SO_4 deposition [cf. *Erlandsson et al.*, 2008; *Evans et al.*, 2006; *Monteith et al.*, 2007], we also investigated if DOC trends could be detected along the spatial SO_4 deposition gradient.

[6] The study was based on measurements of spring flood chemistry from a wide range of streams (n = 97) spanning 1–400 km^2 in size, in an elevation range of 1500 m, covering 8 degrees of latitude in boreal Sweden. Multiple linear regression was used to explore factors contributing to regional variability in stream DOC, and the statistical model was also tested for nonlinearities (a ubiquitous feature of natural systems) and over fitting.

[7] The basic approach builds upon an earlier study examining changes in DOC during spring flood in the Krycklan catchment in northern Sweden [*Buffam et al.*, 2007]. The use of base flow chemistry to predict episode chemistry has been used in a few studies before, both in the U.S. [*Davies et al.*, 1999; *Eshleman*, 1988; *Eshleman et al.*, 1995], and in Sweden [*Laudon and Bishop*, 2002b; *Laudon et al.*, 2004b] to model other biogeochemical parameters. To our knowledge this approach has not previously been tested for modeling DOC.

2. Materials and Methods

2.1. Study Area

[8] The episodes used in this study have been sampled in 97 streams in the northern part of Sweden (Figure 1), which comprises a large portion of boreal Scandinavia. Northern Sweden can be divided into two ecoregions, the Fennoscandian Shield and the Alpine/Boreal Highlands. The Fennoscandian Shield is characterized by boreal forest which covers on average 77% of the catchments in this study. Coniferous forest dominates in this region with spruce (*Picea abies*) and pine (*Pinus sylvestris, Pinus contorta*) being the dominant tree species. Deciduous species are also common in certain areas, and include: birch (*Betula pubescens, Betula pendula*), aspen (*Populus tremula)*, alder (*Alnus incana, Alnus glutinosa*) and mountain ash (*Sorbus aucuparia*). The Alpine/Boreal Highlands are characterized by thinner soils and more sparse tree cover dominated by mountain birch (*Betula czerepanovii*). In 14 of the 18 streams in the Alpine/Boreal Highland region portions of their catchments are located above the tree line which in the region is at approximately 700–800 m above sea level. Wetlands (bogs and fens with mainly *Sphagnum spp.*) are also common (1–43% in the selected catchments), especially in the Fennoscandian Shield area. The human impact in the catchments is generally low with a mean urban area of 0% (0–2.8%), agricultural land cover of 0.8% (0–12.1%) and open land cover of 1% (0–6.4%) (Table 1).

[9] The average duration of snow cover is 150–225 days depending on the location. The region is characterized by a climatic gradient from the southeast (mean annual temperature +4°C) to the northwest (mean annual temperature −2°C). The east-west gradient is due to the change in altitude from the sea level along the east coast of Sweden to the mountains along the western border (our catchments cover a range in altitude from 1 to 1475 m asl). Mean annual precipitation varies between 550 and 950 mm.

[10] Streams draining the Alpine/Boreal Highland region are generally clear-water mountain streams with low DOC concentrations (in our investigation, on average 3 mg L^{-1} during base flow and 7 mg L^{-1} during spring flood) while streams draining the predominately forested Fennoscandian Shield area are characterized by brown water and have high DOC content (in our investigation, on average 12 mg L^{-1} during base flow and 17 mg L^{-1} during spring flood). The

Table 1. Descriptive Statistics of the Variables Used in the Modeling[a]

Location	Units	N	Mean	Standard Deviation	Minimum	Maximum	Transformation
x coordinate (RAK)	10 m	97	709,119	14,838	673,809	753,460	*
y coordinate (RAK)	10 m	97	162,548	12,745	131,720	182,525	*
Ecoregion		97	1.2	0.4	1	2	*
Minimum altitude (site)	m	94	228	191	1	872	ln (x)
Median altitude (median of catchment)	m	95	325	236	37	940	ln (x)
Maximum altitude (maximum in catchment)	m	95	450	309	82	1475	ln (x)
Percent catchment above high coastline	%	95	53	45	0	100	na
Mean annual air temperature (region)	°C	96	2	1	−2	4	na
Mean annual runoff (region)	mm	94	395	100	250	750	na
Mean annual precipitation (region)	mm	95	724	78	550	950	na
			Catchment Characteristics				
Catchment area	km^2	96	38	62	1	392	ln (x)
Urban land cover in catchment	%	95	0.0	0.3	0	2.8	*
Lake cover in catchment	%	95	1.6	2.1	0	12.6	ln (x+1)
Forest cover in catchment	%	95	77	19	0	98	ln (100-x)
Open land cover in catchment	%	95	1.0	1.3	0	6.4	*
Agricultural land cover in catchment	%	95	0.8	1.8	0	12.1	*
Wetland cover in catchment	%	95	13	10	1	43	ln (x)
Subalpine land cover in catchment	%	95	7	20	0	96	*
Till	%	95	64.5	21.6	0	100	na
Sediments	%	97	8.6	12.0	0	55.7	ln (x+1)
			Winter Precipitation in Year of Sampling				
Winter precipitation	mm	97	147	38	52	210	na
Mean winter precipitation SO_4 concentration	$\mu eq\ L^{-1}$	97	20	5	8	35	ln (x)
Winter deposition of SO_4	$kg\ ha^{-1}$	97	0.98	0.38	0.28	1.76	ln (x)
			Chemistry				
DOC_B	$mg\ L^{-1}$	97	10.3	5.8	0.8	27.7	na, ln (x)**
DOC_E	$mg\ L^{-1}$	97	16.3	5.9	3.3	30.0	na, ln (x)**
DOC_F	$mg\ L^{-1}$	97	14.9	5.3	3.3	27.4	na, ln (x)**
pH_B	pH units	97	6.5	0.4	5.0	7.6	na
ANC_B	$\mu eq\ L^{-1}$	96	253	136	−10	790	ln (x)
Ca_B	$\mu eq\ L^{-1}$	97	200	106	24	503	ln (x)
Mg_B	$\mu eq\ L^{-1}$	97	87.7	49.1	6.0	313.7	na
Na_B	$\mu eq\ L^{-1}$	97	97	54	10	340	ln (x)
K_B	$\mu eq\ L^{-1}$	97	15.9	7.4	5.6	41.3	na
Cl_B	$\mu eq\ L^{-1}$	97	44	37	9	232	ln (x)
NO_{3B}	$\mu eq\ L^{-1}$	96	5.5	4.7	0	38.5	na
SO_{4B}	$\mu eq\ L^{-1}$	97	97	76	24	425	ln (x)
BC_B	$\mu eq\ L^{-1}$	97	399.8	173.3	49.6	862.7	na
SAA_B	$\mu eq\ L^{-1}$	97	147	101	47	530	na

[a]The column "transformation" describes how the variable was transformed prior to analysis, "na" means that no transformation was done, and "*" marks the variables excluded from the regression analyses. The ln (x) transformation of variable marked with "**" were conducted to be able to express a nonlinear relationship in a linear form. This is the only transformation that we state in the text. A subscript "B" stands for base flow variables, a subscript "E" stands for extreme concentration, and a subscript "F" stands for peak flood concentration.

carbon concentrations in this study were measured as total organic carbon, i.e., on unfiltered water. However, in this region the majority of the organic carbon is made up of the dissolved fraction, and the particulate form is usually below 5%, even during the highest flow situations [*Ågren et al.*, 2007; *Ingri*, 1996; *Ivarsson and Jansson*, 1995; *Laudon and Bishop*, 1999].

2.2. Data and Selection of Episodes

[11] The data in this study were collated from eight different episode-sampling programs in northern Sweden from 1995 to 2004. Together these provide nearly 300 spring flood episodes from 130 different catchments. Winter is an extended period of relatively stable base flow stream chemistry in the region [*Laudon and Bishop*, 2002a] and for this reason was chosen as the starting point for the modeling effort. We took the average of winter base flow chemistry using all available samples from January–April. At least two base flow samples were required for each stream site (Figure 2).

[12] For the response variable, the week of the most extreme DOC concentration (DOC_E) during the snowmelt (April–June) was chosen. DOC can either increase or decrease during spring flood, so this value can be either a maximum or a minimum value. The average of all samples during this period was calculated. At least two samples were required. Some episodes were sampled less frequently and in those cases (9 of the selected streams) 8–12 days were allowed instead of 7 days. The extreme DOC sometimes coincides with the week of the most extreme discharge. However, more often than not DOC peaked slightly before the discharge (Figure 2). Since discharge is very important for export calculations, we also tested if we could predict DOC concentration during the week of the highest discharge in spring flood (DOC_F). So, parallel to the analysis of DOC_E the same analysis was performed on DOC concentration

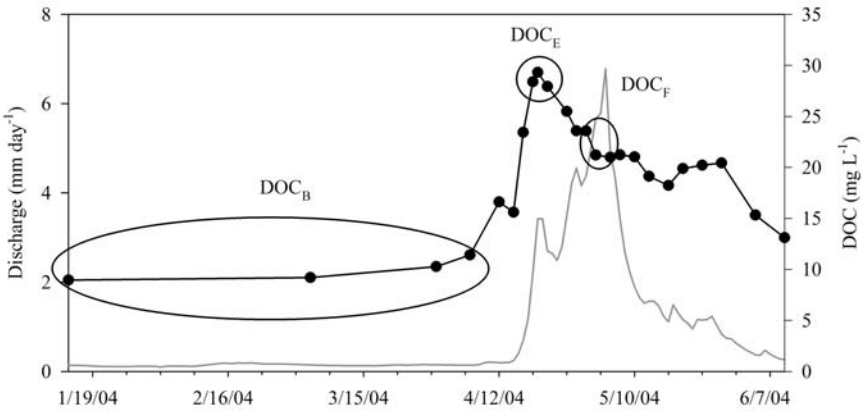

Figure 2. Stream discharge (gray solid line) and DOC concentration (black line with dots) for stream Fulbäcken during the late winter and spring flood of 2004. The selection of base flow DOC concentration (DOC_B), extreme DOC concentration (DOC_E), and DOC concentration during the highest discharge (DOC_F) are shown in the ovals.

during the week of the highest discharge in spring flood (DOC_F). We present the equations for both DOC_E and DOC_F in the results but focus on DOC_E.

[13] Of the original ~300 spring flood episodes, 166 fulfilled the aforementioned criteria to be included in the study, representing 107 independent sites. From those, additional criteria were used to select the final episodes for analysis: a limited number of episodes (N = 16 of 166) were removed from consideration because of variable base flow chemistry, typically coefficient of variation >20% for DOC_B and other major chemical constituents. At sites with multiple qualifying episodes, a single episode was selected for use in the model. Preference was given to years which had the highest number of samples. For sites with 3 or more years of data, atypical years (years with spring flood pH drop > 1 standard deviation different from the average pH drop at that site) were excluded from consideration. When many years were equally qualified, the most recent year was selected. Finally a size filter selecting only catchments between 1 and 500 km^2 was applied in order to exclude a handful of extremely small/large catchments which were outliers in terms of size, resulting in 97 episodes at 97 sites selected for this study (Figure 1).

2.3. GIS Data

[14] A digital elevation model (DEM) (Lantmäteriet, Gävle, Sweden) with 50 * 50 m grid cells was used to calculate minimum altitude (the sampling site), median catchment altitude and maximum altitude in the catchment. A map from the National atlas of Sweden was used to calculate the percentage of the catchment situated above the highest coastline. Catchments were delineated using a DEM, subcatchments from the Swedish Metrological and Hydrological Institute (Norrköping, Sweden) and manual methods. Mean annual temperature, mean annual runoff and mean annual precipitation were determined from national climatic maps from the Swedish Metrological and Hydrological Institute (SMHI, Norrköping, Sweden). The land cover (%) of forests, wetlands, lakes, urban land, open land, agricultural land, and subalpine land was determined from the digital Swedish road map (1:100,000 scale) (Lantmäteriet, Gävle, Sweden). The soil map 1:1,000,000 scale from the Geological Survey of Sweden, (SGU Uppsala, Sweden) was used to determine the proportion of till, peat, bedrock outcrops, sand, silt, glaciofluvial sediments and clay. Data regarding winter precipitation during the sampled year were provided by SMHI for deposition amounts (mm) and from the Swedish Environmental Research Institute, (IVL, Stockholm, Sweden) regarding mean winter precipitation SO_4 concentration (μeq L^{-1}) and winter deposition of SO_4 (kg ha^{-1}).

2.4. Statistical Calculations

[15] All the statistical analyses were conducted with SPSS 15.0, (SPSS Inc., Chicago, IL, USA). Prior to the statistical analysis the variables were transformed (Table 1) to fulfill the criteria of normality (according to one-sample Kolmogorov-Smirnov test with a normal test distribution) of the data required for regression analysis. Since ecoregion is a categorical variable it was excluded from the regression analysis. Many of the GIS land cover and soil variables occur very infrequently in the catchments, meaning that only a few observations exist for each variable; therefore, the following variables could not be appropriately transformed and were excluded from the statistical analysis: urban land, open land, agricultural land, subalpine land, and rock outcrops. Sand, silt, glaciofluvial sediments and clay were lumped into the variable "Sediments" to increase the number of observations so that they could be included in the model. Tests were carried out to see that the regression assumptions, for example issues regarding collinearity and heteroskedasticity, were not violated.

2.5. Extreme DOC Concentration Versus Base Flow Chemistry

[16] We first determined whether base flow chemistry (variables marked with a subscript "B" in Table 1) could be used to predict extreme DOC concentration. To do this, a stepwise multiple linear regression analysis was conducted with base flow chemistry as independent variables. A stepwise criteria of probability of F to enter < = 0.05 and probability of F to remove > = 0.10 was used for all step-

Table 2. Adjusted r^2 and AIC for the Different Models Created by the Stepwise Multiple Linear Regression Analysis With Both Base Flow Chemistry and Landscape Variables Included[a]

	Equation (5)				Equation (6)			
Model	$lnDOC_E$ Constant	Adj r^2 Change (From SPSS)	AIC (From R)	Uncertainty (%)	$lnDOC_F$ Constant	Adj r^2 Change (From SPSS)	AIC (From R)	Uncertainty (%)
1	$lnDOC_b$	0.707	18.1	14	$lnDOC_b$	0.763	−2.5	14
2	runoff	0.120	−33.9	19	runoff	0.078	−46.3	21
3	wetland (%)	0.037	−57.8	34	wetland (%)	0.019	−59.9	31
4	forest (%)	0.022	−65.0	53	forest (%)	0.025	−72.1	47
5	Na_b	0.008	−66.2	80	SAA_b	0.015	−78.9	57
6	winter precipitation	0.007	−75.8	89	lakes (%)	0.004	−67.7	

[a]The uncertainties were calculated with Monte Carlo simulations and are expressed as standard deviation/average (%).

wise multiple linear regression analysis. In order to explore the possibility of a nonlinear relationship between the extreme DOC concentration and the explanatory variables the SPSS curve estimation procedure was used, which compared 11 different models. The model with the highest adjusted r^2 was chosen (with exception of the cubic function), if significant ($\alpha = 0.05$). Since all 97 episodes were used to construct the regression model a Bootstrapping resampling technique was employed [*Leger et al.*, 1992]. In this procedure a random number of streams were deleted from the data set. From the remaining data set some streams were included twice or more, until the data set is again composed of 97 streams. The criteria for the CNLR algorithm was set to: maximum number of major iterations = 999, step limit = 2, infinite step size = 1E+20. Slopes and constants were calculated for this new data set. Then the randomization process was repeated 1000 times and new constants and slopes were calculated for the new data set. Standard deviation was calculated for the slopes and constants from the repeated runs (SPSS v. 15.0). The same procedures were performed for all the following analyses as well.

2.6. Extreme DOC Concentration Versus Landscape Characteristics

[17] The second step was to test if information from the landscape/regional variables could be used to predict the extreme DOC during snowmelt. The variables on location of the catchment, catchment characteristics and winter precipitation (Table 1) were used as independent variables in stepwise multiple linear regressions with extreme DOC concentration.

2.7. Extreme DOC Concentration Versus Base Flow Chemistry and Landscape Characteristics

[18] The third step was to test if information from both the base flow chemistry and the landscape/region could be combined to improve the model. Since the curve estimation showed that the best model was nonlinear, a nonlinear model was also applied in this next step. Using the assumption that a nonlinear model can be expressed in linear model form by logarithmic transformation of the y variable, extreme concentration and base flow DOC were ln transformed (since the power function can be expressed as both ($y = \beta_0 \times {}^{\beta 1}$) and ($\ln(y) = \ln(\beta_0) + \beta_1 \ln(x)$)). Then stepwise multiple linear regression analysis was conducted with $lnDOC_E$ as the dependent variable and $lnDOC_B$, base flow chemistry, location, catchment characteristic, winter precipitation data in year of sampling (Table 1) as independent variables. For these equations, which we foresee having a practical use as a predictive instrument, we put a lot of effort into selecting the "best" model. We calculated Akaike Information Criterion (AIC) [*Akaike*, 1974] (using R v. 2.9.0), which is a model selection criteria, for the different models (Table 2). We also calculated the uncertainty of the different models suggested by the stepwise multiple linear regression analysis (MLR) (Table 2). First, the estimates (constant and slopes) were calculated using MRL Enter method (SPSS) then the uncertainties in the estimates were calculated using Bootstrapping (as described earlier). Finally, the combined uncertainty of the estimates from the equations were calculated using Monte Carlo simulations, where we propagated the uncertainty in the estimates using 10,000 realizations with random parameters generated from the distributions above. The uncertainties were expressed as %, calculated as standard deviation/average.

2.8. Principal Component Regression

[19] To further test the appropriateness of our linear regression models in the face of covariation between some of the independent variables, a Principal Component Analysis (PCA) was performed on the potential predictor variables including both base flow chemistry and landscape/regional variables described for each site. A PCA is used to compress information of many, often covariate variables into a few, uncorrelated principal components that can be used as independent variables in further analyses. A multiple linear regression analysis was then performed with the principal components scores as potential predictors and DOC_E as the response variable. The results of this analysis were compared to the results with the original multiple linear regression models.

2.9. Different Ecoregions

[20] The two different ecoregions (Alpine/Boreal Highlands and Fennoscandian shield) have substantially different mean water chemistry and landscape characteristics. To investigate if the same explanatory variables are similarly important in both regions, the stepwise multiple linear regressions were conducted on each region separately (the Alpine/Boreal Highlands and the Fennoscandian Shield), in addition to the main analysis with all sites lumped together.

3. Results

[21] Eighty-five of the 97 episodes showed a distinct increase between base flow concentrations and spring flood, and the average increase during those episodes was 7 mg L^{-1} (1.7–18.6 mg L^{-1}). Three sites showed a decrease, but less

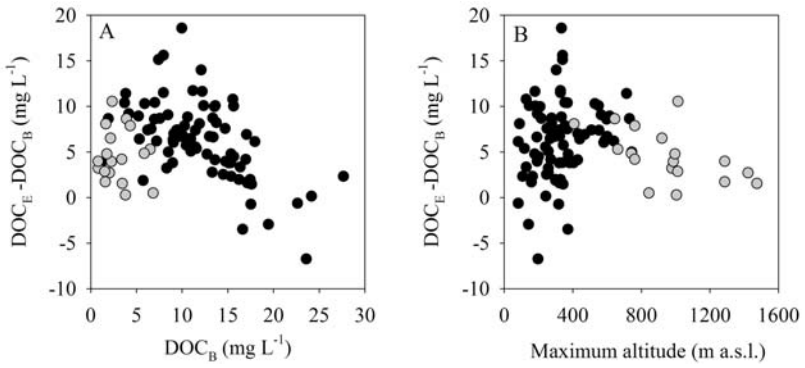

Figure 3. The difference between DOC_E and DOC_B versus (a) DOC_B (mg L^{-1}) and (b) maximum altitude (m asl). Streams from the Fennoscandian Shield region are marked with black dots, and streams from the Alpine/Boreal Highland region are marked with gray dots.

pronounced, with an average decrease of 4 mg L^{-1} (2.9–6.7 mg L^{-1}). Nine of the sites showed constant DOC concentrations (<1.6 mg L^{-1} change) between winter base flow and spring flood. The episodic change in DOC from base flow to the snowmelt extreme concentration ($DOC_E - DOC_B$) varied much more in the Fennoscandian Shield region (average difference 6.3 mg L^{-1} (−6.7–18.6 mg L^{-1})) compared to the Alpine/Boreal Highland region (average difference 4.5 mg L^{-1} (0.3–10.6 mg L^{-1})) (Figure 3). It was the streams with the highest winter base flow concentration that showed a decrease in concentration during snowmelt.

3.1. Extreme DOC Concentration Versus Base Flow Chemistry

[22] The models for DOC_E and DOC_F were similar with respect to included variables and explanatory power; however, the predicted levels differ as DOC_F concentrations are lower than DOC_E (Figure 4). A nonlinear relationship with only base flow DOC resulted in a better model (higher Adj. r^2 values) (equation (1)) than a linear model with additional base flow chemistry predictor variables. According to the curve estimation procedure the relationship between snowmelt DOC concentrations and base flow DOC was best described by a power function (Figure 4). The bootstrap estimates of SD are given in parentheses after the constants.

$$DOC_E = 4.97(\pm 0.52) DOC_B^{0.52(\pm 0.04)} \left(\text{Adj. } r^2 = 0.71, p < 0.001\right) \quad (1)$$

$$DOC_F = 4.55(\pm 0.39) DOC_B^{0.52(\pm 0.03)} \left(\text{Adj.} r^2 = 0.75, p < 0.001\right) \quad (2)$$

3.2. Extreme DOC Concentration Versus Landscape/Regional Characteristics

[23] Maximum altitude proved to be the major explanatory variable, explaining 56% of the extreme DOC con-

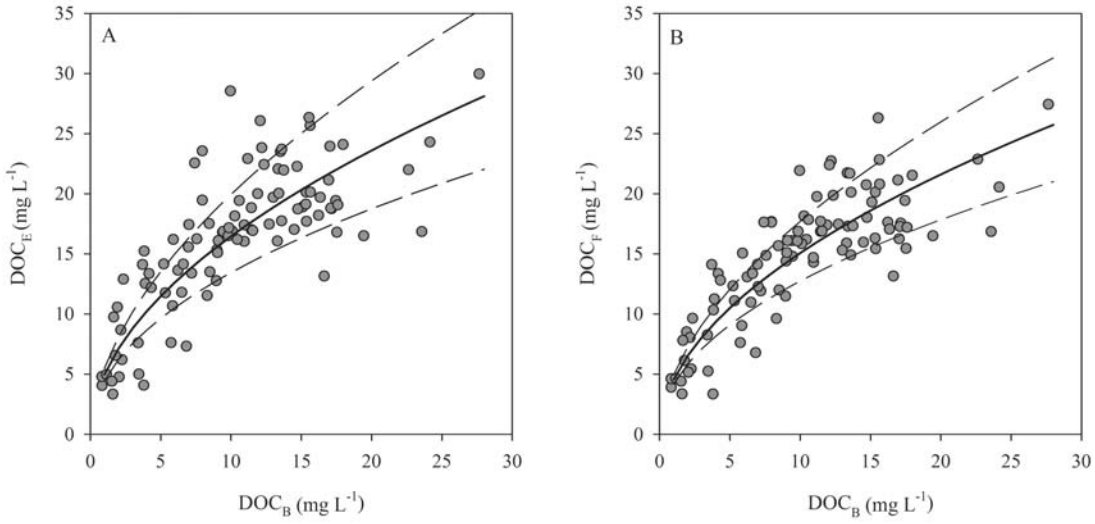

Figure 4. The black solid lines indicate the power relationship between spring DOC concentration and base flow DOC concentration, for (a) extreme DOC and for (b) DOC during maximum discharge. The dashed lines indicate the maximum and minimum predictions generated using bootstrapped parameter estimates that are one standard deviation above or below the mean.

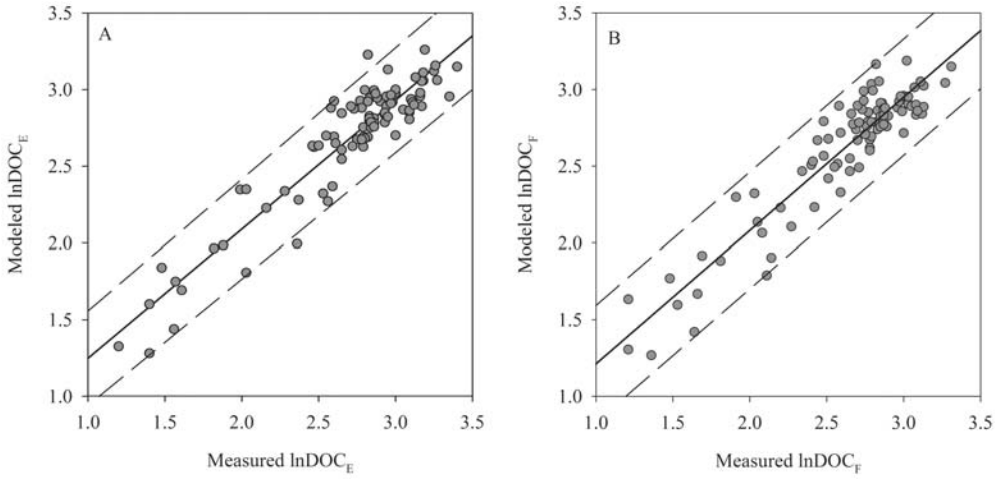

Figure 5. Measured values versus modeled values from the stepwise multiple linear regression analysis for (a) extreme DOC (equation (5)) and (b) DOC during maximum discharge (equation (6)). Dashed lines as in Figure 4.

centration (equation (3)) and 63% of the concentration during peak flood (equation (4)). We again focused on the strongest predictor variable (maximum altitude), and explored nonlinear relationships with this variable as well as linear relationships with other additional variables. This time nonlinear relationships did not improve the coefficient of determination. The bootstrap estimates of SD are given in parentheses after the constants.

$$DOC_E = 49.3(\pm 4.5) - 4.8(\pm 0.9)Max\ altitude - 0.02(\pm 0.006)Runoff + 1.3(\pm 0.5)Wetland \quad \left(\text{Adj. } r^2 = 0.74, p < 0.001\right) \tag{3}$$

$$DOC_F = 47.8(\pm 4.2) - 5.0(\pm 0.8)Max\ altitude - 0.01(\pm 0.005)Runoff + 0.9(\pm 0.4)Wetland \quad \left(\text{Adj. } r^2 = 0.72, p = 0.007\right) \tag{4}$$

3.3. Extreme DOC Concentration Versus Base Flow Chemistry and Landscape/Regional Characteristics

[24] In the third step we tested if information on both the base flow chemistry and the watersheds could be combined to an improved model. The stepwise procedure with DOC_E and DOC_F as the dependent variables produced similar results. Based on the uncertainty of the model, which increase when more variables are included (Table 2), we selected a model with three independent variables ($lnDOC_B$, Runoff and Wetlands). We believe an uncertainty in the model of about 30% is acceptable; inclusion of yet another variable would increase the uncertainty by another 20% and we would only gain another 2% of explained variance in $lnDOC_E$ and $lnDOC_F$. We therefore decided not to use AIC as the criterion for model selection. This gave the final models for extreme DOC and DOC during the week of the maximum discharge (Figure 5 and equations (5) and (6)). Note that the explanatory variables were transformed according to Table 1 to fit normality. The bootstrap estimates of SD are given in parentheses after the constants.

$$lnDOC_E = 2.654(\pm 0.14) + 0.343(\pm 0.032)lnDOC_B - 0.002(\pm 0.0002)Runoff + 0.105(\pm 0.0207)Wetlands \quad \left(\text{Adj. } r^2 = 0.87, p < 0.001\right) \tag{5}$$

$$lnDOC_F = 2.434(\pm 0.15) + 0.375(\pm 0.028)lnDOC_B - 0.002(\pm 0.0003)Runoff + 0.069(\pm 0.0210)Wetlands \quad \left(\text{Adj. } r^2 = 0.87, p < 0.000\right) \tag{6}$$

Mean average error (MAE) was 1.14 mg L^{-1} and root mean squared error (RMSE) was 1.18 mg L^{-1} for both DOC_E and DOC_F. The final regression (equation (5)) was tested for "collinearity diagnostics" during the SPSS regression procedure. The collinearity condition index showed that no significant collinearity existed among the explanatory variables selected for the best model.

3.4. Principal Component Regression

[25] Principal Component Analysis (PCA) resulted in 8 principal components that together explained 86% of the variance between catchments. In order to best separate the influence of the different variables on the principal components we separated them using Varimax rotation with Kaiser normalization (using 19 iterations). The MLR using principal components axis scores as independent variables showed that 82% of the variance in DOC_E could be explained by inclusion of four principal components (equation (7)). PC1 explained most of the variation in extreme concentrations. PC1 was most highly correlated with altitude (max altitude −0.92, median altitude −0.91) and base flow DOC ($lnDOC_B$ 0.89). PC7 correlated best with lake cover (0.71)

and forest cover (0.68) and PC5 best with precipitation (0.94) and runoff (0.65). PC3 was most highly correlated with wetland cover (0.86).

$$DOC_E = 2.7 + 0.3PC1 - 0.12PC5 - 0.10PC7 + 0.08PC3\left(\text{Adj. } r^2 = 0.82, p = 0.001\right) \quad (7)$$

$$DOC_F = 2.6 + 0.3PC1 - 0.09PC7 - 0.09PC5 + 0.05PC3\left(\text{Adj. } r^2 = 0.81, p = 0.023\right) \quad (8)$$

The variables that were important for the MLR, i.e., $lnDOC_B$, altitude, runoff, wetland cover, (see equation (5) but also equation (3)) are similarly important variables in the Principal Component Regression (PCR) as well. In both approaches most of the variation was explained by $lnDOC_B$ and altitude. The similarity between the PCR and MLR suggests that covariance between independent variables did not give rise to misleading results for the MLR analysis.

3.5. Different Ecoregions

[26] Division of the data set did not improve the MLR models (with respect to r^2) but indicated that different processes regulate DOC variation within the two different ecoregions. In the Alpine/Boreal Highlands region DOC_E was best explained by landscape/regional characteristics (equation (9)) while base flow DOC concentration was the major explanatory variable for DOC_E in the Fennoscandian Shield region (equation (10)).

[27] Alpine/Boreal Highlands (18 streams):

$$lnDOC_E = 6.321 - 0.417\ max\ altitude + 0.245\ annual\ temperature - 0.002\ annual\ precipitation \left(\text{Adj. } r^2 = 0.76, p = 0.033\right) \quad (9)$$

[28] Fennoscandian Shield (79 streams):

$$lnDOC_E = 3.527 + 0.239\ lnDOC_B - 0.001\ annual\ precipitation + 0.051\ wetlands - 0.031\ lakes \left(\text{Adj. } r^2 = 0.58, p = 0.035\right) \quad (10)$$

4. Discussion

4.1. Altitude

[29] Stream DOC concentrations during snowmelt could be predicted rather successfully from simple landscape/regional characteristics (equations (3) and (4)). The highest snowmelt DOC concentrations were found along the east coast and decreased toward the mountains in the west. Maximum altitude was the major explanatory variable for extreme DOC concentration across the entire region (equations (3) and (4)). This result is similar to the trend observed by *Ivarsson and Jansson* [1994] of decreasing DOC concentrations in tributary streams on a transect from mountains to coast in northern Sweden. In smaller-scale studies, altitude has been found to be positively and negatively correlated with DOC [*Ågren et al.*, 2007; *Helliwell et al.*, 2007; *Temnerud and Bishop*, 2005]. A large-scale investigation by *Sobek et al.* [2007] predicting DOC concentration among 7500 lakes (primarily in North America and Europe but including some lakes in New Zealand and Asia) showed that at a global scale highland waters generally have lower DOC concentrations. In our study, the combination of high runoff and shallow organic soils (small pool of DOC in the soil) results in the low DOC concentrations in the Alpine/Boreal Highlands compared to the higher concentrations in the Fennoscandian Shield area with thick organic layers near the stream in forested areas. In addition, temperature-driven increases in biological activity, from mountains to the coast, may promote the leaching of DOC, and as such contribute to our ability to predict stream concentrations on the basis of altitude. It should be noted that altitude was not included for the predictive model when we only studied the more low relief Fennoscandian Shield area (equation (10)). It has been hypothesized that the location of wetlands in a catchment affects DOC exports. Wetlands near the streams would have a higher connectivity to the streams and the riparian zone has been found to have a first-order control on stream chemistry [*Bishop et al.*, 1995, 2004; *Smart et al.*, 2001]. Riparian wetlands are more common in the coastal region and are probably a more important source of DOC than the extensive blanket mires in the inland [*Ivarsson and Jansson*, 1994]. Topography may also affect the distributions of wetlands and thus DOC concentration. DOC concentrations have been found to correlate negatively to slope [*Andersson and Nyberg*, 2008]. One explanation is that flat topography give rise to wetlands some of which are not included on maps, so-called "cryptic wetlands" [*Creed et al.*, 2003]. Low relief areas, toward the east coast of northern Sweden in our case will give rise to higher DOC concentrations. The negative relationship between extreme DOC concentration and altitude is explained by many processes. Hence, altitude can be seen as a master variable that incorporates effects of changes in soils, climate, topography and biological activity.

4.2. Importance of Wetlands

[30] We expected wetlands to be the dominant explanatory variable of stream DOC among the landscape/regional characteristics, as has been found in many similar studies studying the spatial variability in DOC concentrations and exports [*Ågren et al.*, 2007; *Creed et al.*, 2003, 2008; *Dillon and Molot*, 1997; *Kortelainen and Saukkonen*, 1998; *Laudon et al.*, 2004a; *Mattsson et al.*, 2005]. But, we were met with mixed results. Wetlands did appear as a significant explanatory variable in many of our equations ((equations (3)–(6) and (10)), but it explained relatively little of the variance in DOC, ranging from 2% (equation (6)) to 5% (equation (3)). At the regional scale of this study which traverses large gradients in altitude (1–1475 m asl), annual average temperature (from −2 to +4 C) and precipitation (550–950 mm) regional drivers were more important than wetlands. The most probable explanation for the marked difference is that

our study focuses on the spring flood period, during which the influence of wetlands on boreal stream DOC is decreased. During spring flood the high DOC in water draining wetlands is diluted by low DOC snow meltwater. But at the same time the forest is becoming a stronger source, so that these two landscape elements are more similar [*Ågren et al.*, 2007; *Buffam et al.*, 2007; *Laudon et al.*, 2004a]. This documented "evening" of DOC outputs between wetland and forest is likely the explanation of the low importance of wetlands in our study.

4.3. Base Flow Chemistry

[31] Stream DOC concentrations during snowmelt could, equally successfully, be predicted from base flow DOC alone (equations (1) and (2)). The increase in DOC concentration during spring flood has been found in many previous investigations on boreal forest catchments [*Ågren et al.*, 2007; *Mattsson et al.*, 2005] and is explained by the rising of the water table during snowmelt into shallower carbon-rich soil horizons [*Bishop et al.*, 1995; *Hinton et al.*, 1998]. However, several streams decreased in concentration from base flow to spring flood. These were the streams with high DOC during base flow, thereby explaining why a nonlinear power function (with higher slope on the low DOC end and less slope on the high DOC end) provides the best model. The finding that the catchments with high DOC during base flow experience a decrease in DOC during spring flood, is in line with previous process based studies. Wetlands are a large source of DOC in stream water especially during winter base flow [*Ågren et al.*, 2007; *Buffam et al.*, 2007]. During spring flood the DOC rich water in wetlands is diluted due to overland flow by low DOC snow meltwater [*Buffam et al.*, 2007; *Laudon and Buffam*, 2008]. Surprisingly, in our study the streams which decreased in DOC from base flow to spring flood did not have a significantly higher proportion of wetlands in the catchment based on land cover maps. This again raises the question regarding effective wetland influence on the stream, and the potential importance of wetland connectivity and location which may be more important than the total wetland proportion within a catchment.

4.4. Combining Base Flow Chemistry and Landscape/Regional Characteristics

[32] By combining both base flow DOC concentration and landscape/regional characteristics the models explained as much as 87% of the variance in spring DOC concentrations (equations (5) and (6)). In addition to base flow DOC, which explained most of the variation, catchments with high annual runoff tended to have less of a relative increase in DOC during spring flood (equations (5) and (6)). This could be explained either by dilution of high flow DOC caused by overland flow in catchments with high runoff, or by higher base flow DOC in high runoff catchments, if water tables remain high even during winter base flow. The precise mechanism cannot be determined from the current data set, but as stream DOC is known to be sensitive to runoff [*Mulholland*, 2003; *Sedell and Dahm*, 1990], effects on both high flow DOC and base flow DOC are plausible. An interesting result in this study was the lack of correlation between DOC and winter deposition of SO_4.

4.5. Different Ecoregions

[33] In the Alpine/Boreal Highlands region the spring flood concentrations were strongly related to landscape/regional characteristics (equation (9)). Given the limited number of observations (n = 18) the model for this region may be subject to considerable uncertainty; however, there was a conceptual justification for the results. For the Alpine/Boreal Highlands region the dominant explanatory variable was altitude, as in the previous equation (3) and (4), followed by a positive relationship with temperature. This positive relationship with temperature has also been found in previous studies, both in experiments [*Andersson et al.*, 2000; *Christ and David*, 1996; *Godde et al.*, 1996] and in catchment studies [*Dawson et al.*, 2008; *Worrall et al.*, 2003] suggesting that the leachable organic carbon is positively related to temperature. The negative correlation between annual precipitation and DOC_E concentrations among the mountain streams is probably also related to the altitude of these catchments. Runoff in the Alpine/Boreal Highlands region was positively correlated to maximum altitude (Pearson $r = 0.60$, $p < 0.001$). The principal behind this is that the highest areas are affected by orographic lift resulting in high precipitation over these areas which also, due to the cold climate on these exposed areas, have very shallow organic soils. The combination of high runoff and shallow organic soils results in the low DOC concentrations.

[34] In the Fennoscandian Shield area, DOC_B explained most of the variance in the extreme DOC concentrations (equation (10)), followed by annual precipitation, wetlands and lakes. All explanatory variables have been discussed previously except lakes. That high lake area has a negative impact on the DOC concentrations in catchments has been shown long ago [*Eriksson*, 1929]. In large lakes the water residence time will increase and the DOC may be decomposed by photooxidation or microbial processes [*Algesten et al.*, 2004; *Bertilsson and Tranvik*, 2000; *Pers et al.*, 2001]. Another effect of lakes is that because of the longer residence time of water, lakes smooth hydrological and chemical temporal variation relative to streams, and thus would reduce the difference between DOC_E and DOC_B.

[35] Although the two ecoregions considered here (Alpine/Boreal Highlands and Fennoscandian Shield) had substantially different mean water chemistry and landscape characteristics, analyzing the two regions separately did not improve the models with respect to r^2. Instead, they were successfully combined into the same regression models (equations (5) and (6)), yielding a single approach that works for the whole northern part of boreal Sweden.

4.6. Limitations and Uncertainties of the Modeling Approach

[36] This statistical modeling approach should best be seen as a single tool within a program of multipronged research [*Pace and Groffman*, 1998] to understanding the relationship between landscape characteristics and stream chemistry in the boreal zone. A statistical modeling approach has the advantage of producing a simply constructed model which often fits the data at hand well, but will not provide the detailed information on response to environmental perturbation as would a process-based model [*Aitkenhead et al.*, 2007]. Commonly however, statistical

models are more adept at prediction than more complex process-based models [*Carpenter et al.*, 2005]. In this study the statistical models serves two purposes: first, they provide a potentially useful management tool for predicting spring flood DOC within the range of the data set, i.e., all of the streams in boreal/alpine regions of Sweden with catchments ranging from 1 to 500 km^2. In addition, the results from statistical modeling efforts are used to inform future research projects, including the development of process based models of DOC export from boreal streams [e.g., *Futter et al.*, 2008; *Yurova et al.*, 2008]. Because statistical modeling is based on correlation, a cautious approach is justified in interpreting the results. However, the results of this study do lend themselves to interpretation based on the consistency of the results for the MLR and PCR models, and the fact that variables significant in the MLR models could be sensibly explained based on what is known about DOC cycling in boreal landscapes [*Ågren et al.*, 2007; *Ivarsson and Jansson*, 1994; *Sobek et al.*, 2007].

[37] When calculating statistical models we are often faced with selecting the "best" model from a set of potential models. The criteria for selecting the "best" model depend on the purpose of the investigation. If regressions are to be used as a predictive tool, it is important not to overparameterize the model and make it too complicated. If the purpose is to explore potential predictors in search of underlying processes one might allow more variables to be included, but the result should be interpreted with caution. When selecting the "best" model, it is often compelling to choose the model with the highest r^2. But, this is not always a good selection method, given that r^2 always increases with an increasing number of included variables, and the largest model is not necessarily the "best." Adjusted r^2 is a slightly better measure for this, since it penalizes increasing numbers of included variables. A commonly used selection method is the Akaike Information Criterion [*Akaike*, 1974]. AIC also use a penalty term that increase with the number of parameters, in order to prevent the overparameterized models. In our study we used even more stringent selection criteria. Based on the uncertainty estimates for the slopes and constant derived using the bootstrapping procedure we propagated the model uncertainty. Using this approach we observed that the models suggested by Adj. r^2 and AIC had a model uncertainty that was unacceptable (Table 2). Instead we allowed a total model uncertainty of about 30%, and used that as a selection criterion for selecting the best model.

4.7. Practical Applications for Stream Assessment

[38] Based on the success of the models, which can explain 87% of the variance in DOC concentrations during spring flood, they can form a useful tool for assessing the critical condition for the biota during spring flood (equation (5)) as well as creating better flux estimates (equation (6)) (Figure 5). Our method offers the opportunity to use a single base flow sample to characterize stream chemistry during the spring flood. This provides a simple, cost effective complement to long-term monitoring programs. The DOC model developed here may also be a component of predictive spring flood pH models. In this region DOC controls much of the variation in pH, which in turn is an important controlling variable for biota in the streams during this short but critical spring period [*Petrin et al.*, 2007; *Serrano et al.*, 2008].

[39] The terrestrial export of DOC to downstream freshwaters and marine ecosystems is important for the carbon balances in these ecosystems [*Duarte and Prairie*, 2005]. Periods with high flow are very important in export calculations, and the approach used in this study was successful in predicting the DOC concentrations during the week of highest discharge (DOC_F). Because many metals and persistent organic pollutants are strongly correlated to DOC [*Björkvald et al.*, 2006; *Cory et al.*, 2006; *Frankki et al.*, 2007; *Persson*, 2007] this model can also be used to get better estimates of the flux and peak concentrations of these contaminants.

5. Conclusions

[40] Our hypothesis that snowmelt DOC concentrations in streams can be predicted with a simple empirical model using widely available data on landscape structure as well as commonly measured base flow stream chemical parameters proved correct. However, our expectations for the primary explanatory variables met with mixed results. Contrary to expectations wetlands were not a useful predictor, but variation in altitude was well correlated with spring flood DOC. This is likely attributable to the relatively large spatial scale of our study. Also of interest, is that sulfate concentrations at base flow and winter sulfate deposition were not strongly correlated with spring flood DOC, indicating that variation in spring flood DOC concentration in this region is not primarily controlled by acid deposition processes. However, base flow DOC concentration could be used to predict spring flood DOC with high fidelity, both the extreme value and the value during peak flood. Thus a single measure of base flow chemistry may contain enough information to predict chemistry behavior during peak flood. This is a relationship of great practical value in stream monitoring and assessment.

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