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Research Article

Landscape predictors of stream dissolved organic matter concentration and physicochemistry in a Lake Superior river watershed

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Abstract. We examined landscape predictors of dissolved organic matter (DOM) concentration, molecular weight (M_w), and molar absorptivity at 280 nm (ε_{280}) in 60 streams from the Ontonagon River watershed in northern Michigan. During our sampling period (September 19–22, 2002), DOM concentration ranged from 4 to 35 mg C L^{-1} across streams. DOM M_w and ε_{280} also showed considerable variation among streams. Multiple factor regression showed that stream DOM concentrations were related to watershed area, mean watershed slope, and the percentage of watershed area in certain types of land cover (lake, total wetlands, emergent wetlands, and lowland conifer forests). Streams with higher DOM concentration also had higher DOM M_w and molar absorptivity. Moreover, DOM M_w and ε_{280} were negatively related to the % lake and positively related to the % total wetlands in the watershed. In general, landscape variables explained more among stream variation in DOM concentration than in DOM M_w or ε_{280} in this watershed. It thus appears that the many biogeochemical processes controlling DOM input, transportation, and degradation weaken relationships between stream DOM composition and terrestrial organic matter dynamics in this relatively large watershed. Our results indicate that the total proportion of wetlands alone may be inadequate to predict DOM concentration or physicochemistry in streams flowing from large watersheds of variable morphology and land cover composition.

Key words. Dissolved organic matter; streams; wetlands; AIC; landscape; lakes.

Introduction

Dissolved organic matter (DOM) affects many physicochemical characteristics and biological processes in freshwaters (Williamson et al., 1999; Xenopoulos and Schindler, 2001). For example, DOM can alter nutrient supply by binding free forms of some biologically important elements (e.g., iron and phosphorus; Maranger and Pullin, 2003). DOM is also an important energy and nutrient source for microbes and thereby affects whole-ecosystem metabolism (Tranvik, 1998; Hanson et al., 2003). Consequently, factors that control the concentration and physicochemistry of DOM can strongly affect the physical and chemical template upon which the aquatic ecosystem operates (Xenopoulos and Schindler, 2001; Sinsabaugh and Findlay, 2003).

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The flux of DOM into streams and rivers appears to be controlled by a number of interacting hydrological (Hagedorn et al., 2000), geological (Nelson et al., 1993), and biological factors (Brooks et al., 1999). In riparian zones, soil water moving along shallow flow paths can transport large quantities of DOM into adjacent surface waters (Hinton et al., 1998). Deeper flow paths result in less contact with organic rich soil profiles, greater DOM adsorption in subsurface soil horizons, and, consequently, lower DOM concentrations in receiving streams (Hinton et al., 1998). Catchment slope (Rasmussen et al., 1989; Mulholland, 1997; Xenopoulos et al., 2003) also affects the concentration of DOM in receiving surface waters. Steeper slope and porous geological materials allow faster movement of water through the land, which limits the amount of DOM reaching adjacent streams. The hydrogeological controls of stream DOM can be modified by hydrological conditions in the watershed. Different relationships between stream DOM concentrations and the landscape have been been found in the same set of watersheds during periods of high versus low flow (Mulholland, 2003). DOM concentrations in streams often decrease during low flow conditions when groundwaters with low DOC concentrations dominate sources of water to the stream (Eckhardt and Moore, 1990; Dalva and Moore, 1991; Maurice et al., 2002). Other studies, in areas of lesser groundwater input, have found an opposite pattern with greater DOM concentrations under low flow conditions (Schindler et al., 1997; Schiff et al., 1998).

The landscape controls of DOM concentration and physicochemistry in streams at broader spatial scales are also of considerable interest (Gergel et al., 1999; Mulholland, 2003). The landscape (e.g., watershed morphology and landcover) likely influences DOM concentrations in streams by affecting, in part, the hydrological connections between landscape units and receiving waters (Mulholland, 1997; 2003). In addition, in-stream processing and retention of DOM may be affected by the size, shape, and composition of the landscape. For example, opportunities for carbon removal by bacteria, abiotic adsorption, and photo-degradation in the stream channel likely increase with increasing stream length (McKnight et al., 2002). Wetlands are a well-known source of DOM (Thurman, 1985; Dillon and Molot, 1997) that contribute significant amounts of DOM to rivers and streams (Koprivnjak and Moore, 1992; Mulholland, 2003). The DOM concentration in lakes and rivers has been found repeatedly to be positively related to the percentage of wetlands in the watershed in many contrasting ecoregions (Mulholland, 2003; Xenopoulos et al., 2003). In contrast, the importance of other landscape features (e.g., % area of watershed in lake, agriculture, or upland forest) in controlling the amount and physicochemistry of DOM in streams flowing in relatively large watersheds remains largely unknown (Canham et al., 2004).

The type of wetland found in the landscape is another landcover characteristic that may affect DOM concentrations in aquatic ecosystems (Xenopoulos et al., 2003). DOM concentrations in lakes from northern Michigan were positively correlated to coniferous forested wetlands and negatively correlated to open water wetlands (Xenopoulos et al., 2003). These differences in the relationships between lake DOM concentrations and different wetlands types are likely a result of the contrasting hydrology, vegetation, and soils found among wetlands types (e.g., Mitsch and Gosselink, 2000). However, the relationships between DOM in streams and the prevalence of different wetland types have yet to be examined.

DOM physicochemical properties, such as molar absorptivity at 280 nm (ε_{280}) and weight average molecular weight (M_w), are important indicators of bioavailability and of the extent of previous DOM transformations (Cabaniss et al., 2000). Relationships between landscape characteristics and DOM physicochemical properties in streams and rivers remain largely undescribed. For example, how does DOM photo-absorptivity or M_w in streams relate to differences in wetland or lake area? DOM M_w should be related to landscape factors that add or remove terrestrially-derived organic matter in streams. For example, greater lake area in watersheds should increase the residence time of the DOM in the stream drainage network. This would potentially increase the extent of its microbial and/or photo-processing and reduce DOM M_w. Lakes might also increase the relative contribution of algal-derived DOM to the combined DOM pool. Algal-derived organic matter is known to have different optical and chemical properties than DOM derived from terrestrial sources (McKnight et al., 1994). Other factors, such as stream length or wetland type, could also alter the amount of entering terrestrial DOM or the residence time of DOM in the river system and, thereby, affect DOM M_w and its molar absorptivity.

In this study, we examine stream DOM concentration and physicochemical properties in a large heterogeneous watershed that has contrasting landscape characteristics in its subwatersheds. Our primary objective was to relate DOM concentration, M_w, and ε_{280} in the Ontonagon River watershed (Michigan, USA) to watershed morphology, land cover, and the prevalence of different wetland types. Our study shows the effects that multiple landscape characteristics may have on DOM concentration and physicochemistry in a relatively large and heterogeneous river watershed.

Methods

Site description

We sampled streams at 60 locations in the Ontonagon River watershed (3,460 km^2, U.S. Geological Survey Hy-

Figure 1. Map of Ontonagon River watershed in northern Michigan, USA. Smaller order streams (<3) are not shown but were included in the current study.

drologic Unit 04020102), which drains portions of northern Wisconsin and the upper peninsula of Michigan, USA (Fig. 1). Streams were chosen primarily for wide geographical coverage of the watershed and secondarily based on accessibility. Sampled streams ranged from 1st-order, headwater streams to the 6th order, main stem of the Ontonagon River. The watershed is predominantly forested and remains largely undeveloped. Quaternary geologic deposits include glaciolacustrine and glacial outwash sediments, fine- to coarse-textured glacial till, coarse-textured end moraines, and peat deposits (Farrand, 1982). Underlying Precambrian bedrock formations include Jacobsville sandstone (middle Proterozoic), the Michigamme formation (early Proterozoic), and granite and gneissic bedrock (late Archean) in headwater areas (Wilson, 1987). The central and eastern portions of the watershed contain an extensive surficial aquifer in thick glacial deposits (Olcott, 1992). In the Middle Branch and East Branch of the Ontonagon River flowing through this area, more than 75 % of river discharge is derived from deep ground water (Holtschlag and Nicholas, 1998). In contrast, there are relatively few aquifers in the western portion of the watershed and the Precambrian bedrock is exposed or is covered by only a few feet of glacial drift (Doonan and Hendrickson, 1968).

Sampling and water analysis

All streams were sampled once between September 19–22, 2002. During this period, streams were near baseflow conditions and did not receive any significant precipitation. Water sampled from each location was transported back to the laboratory in the dark and filtered within 6 hr of collection. Water was sequentially filtered through a pre-ashed, Whatman GF/F filter and a 0.2-μm polycarbonate filter. Polycarbonate filters were rinsed with >50 ml of distilled water to remove potential organic contaminants (Yoro et al., 1999). Filtered stream water used for DOM analysis was stored in glass amber bottles at 4 ºC until analysis. Samples for base cation analysis were placed into plastic bottles, acidified with HNO_3, and refrigerated. All samples of DOM and base cations were analyzed within ten days of sampling.

We determined the concentration of dissolved organic carbon (DOC) with a Shimadzu TOC 5000 analyzer (Columbia, MD) after acidification and purging of CO_2 (Sharp et al., 1993). UV absorption at 280 nm (Abs_{280}) was measured with a Varian UV-VIS scanning spectrophotometer (Walnut Creek, CA). DOM molar absorptivity at 280 nm (ε_{280}) was calculated as the ratio of Abs_{280} to the DOC concentration expressed in moles of C (Maurice et al., 2002). DOM weight average molecular weight (M_w) was assessed with high-pressure size-exclusion chromatography (HP-SEC) using UV detection at 254 nm. We used a modified HPSEC method as described by Zhou et al. (2000), with a Waters Protein-Pak 123 silica column on Waters HPSEC instrumentation (Milford, MA). See Cabaniss et al. (2000) for additional information on the estimation of DOM M_w using HPSEC. In addition, when we refer to M_w of DOM this should be considered to be the weight average molecular weight of DOM components that absorb light at 254 nm (Her et al., 2002). In addition, the concentrations of base cations (Na, Ca, Si, K, Mg) were determined with a Perkin-Elmer inductively coupled plasma atomic emission spectrometer. The molar concentrations of all measured base cations were pooled for use in subsequent statistical analyses and provided an approximate surrogate for the degree of groundwater inputs.

Landscape analysis

Watershed characteristics were determined with the use of an ESRI ArcView® Geographic Information System (GIS), Version 3.3. Several geospatial datasets covering the Ontonagon watershed were downloaded from the U.S. Geological Survey: the National Elevation Dataset Digital Elevation Model (DEM, http://ned.usgs.gov/), the National Hydrography Dataset (NHD, http://nhd.usgs.gov) and the National Land Cover Dataset (NLCD, http://www.mrlc.gov). National Wetlands Inventory (NWI) data were downloaded from Michigan Geographic Data Library (http://www.mcgi.state.mi.us/mgdl/) for Ontonagon, Gogebic, Iron, and Houghton Counties, and merged into a single data layer. Wisconsin Wetland Inventory (WWI) data were also obtained for the portion of the watershed in Wisconsin. River Reach File 3 (RF3) stream data, modified to classify Strahler (1957) stream orders, were obtained from the U.S. Environmental Protection Agency (personal communication, Tony Olsen, EPA National Health and Environmental Effects Research Laboratory, Western Ecology Division, Corvallis, Oregon).

The Basin1.avx ArcView Basin Extension (Petras, 2000) was used with field sample locations determined with the global positioning system and the DEM data to delineate individual catchments for each sample point and to calculate watershed areas. Catchment boundaries were used to clip the NHD drainage networks to calculate total stream length and drainage density (stream length divided by catchment area). The catchment boundaries were also used to clip the DEM data to calculate mean percent slope and the NLCD data to calculate land cover categories for each catchment: % of agriculture, lake, and upland conifer forest. Michigan NWI data were clipped with the catchment boundaries and areas of all palustrine wetlands within the sub-watershed were summed. The total area of palustrine wetlands was divided by watershed area to calculate % total wetland. One difference between the NWI and the WWI is that lakes were not mapped by the WWI, so lakes were added to the WWI by extracting them from the NHD dataset and performing a GIS union with the Wisconsin WWI data. The combined lake and WWI data layer was then clipped with the catchment boundaries, and WWI codes in data were transformed to NWI codes according to the method from Johnston and Meysembourg (2002). Wetland types were generalized to eight categories to reduce the 229 original NWI codes and 146 original WWI codes to a more manageable number. The final categories retained wetland system and class information, but not water regimes. Subclasses for palustrine forested and shrub/scrub wetland were used to distinguish bog shrubs (e.g., leatherleaf, *Chamaedaphne calyculata*) from other shrub/scrub types and lowland conifer forest (e.g., black spruce, *Picea mariana*) from other wetland forest types. Three of the eight categories, PFO5, POW and PFO/SS, were dropped from the analysis due to their low prevalence in the watershed and to limit the number of possible regression models compared (see below). The catchments were found to have a wide range of watershed morphology and land cover characteristics (Table 1).

Data analysis. To meet conditions of normality, all data were transformed prior to analysis. Stream water chemistry and watershed morphological data were natural-log transformed. Land cover and wetland type variables, as proportions, were arc sine square root transformed (Zar, 1999). To assess the relatedness of stream water chemistry variables, we computed simple linear correlations (Pearson's r) among DOC concentration, DOM chemical characteristics, and base cations.

We described relationships between stream water DOC concentration and individual landscape variables alone (all data post-transformation) using simple linear regression. These regressions were repeated after removing data from 3rd-order streams and larger to examine the effects of grouping streams of increasing order from the same watershed. The relationship between DOC concentration, DOM physicochemical properties, and base cations (each individually) and landscape factors were as-

Table 1. Summary of landscape characteristics (watershed morphology, landcover and wetland type) of the sub-watersheds of streams sampled in the Ontonagon River watershed. C.V. = coefficient of variation, Min. = minimum, Max. = maximum.

Landscape factor	Abbreviation	Units	Mean	C.V.	Min.	Max.
stream length	strm len	km	79.9	353	1.42	2083
watershed area	shed area	km^2	145	324	2.5	3460
drainage density	dr den	km^{-1}	0.52	47.4	0.14	1.46
mean % slope	slope		3.96	33.4	0.91	8.07
% lake	%lake		4.06	129	0	22.6
% upland conifer	%up con		12.0	82.8	0.03	40.3
% agriculture	%ag		4.93	210	0.05	62.8
% total wetland	%tot wet		21.6	46.1	0.52	52.9
% emergent wetland	PEM		1.00	83.1	0	3.58
% forested wetland	PF		2.36	73.3	0	8.42
% lowland conifer	PFNL		8.04	98.3	0	34.6
% scrub/shrub wetland	PSS		4.41	83.1	0	16.6
% bog scrub/shrub wetland	PBOG		0.87	172	0	5.10

sessed with multiple factor regressions using SAS (SAS Institute, 2001). We considered all possible models between each response variable and three groups of predictor variables, watershed morphology (4 variables), land cover (4 variables), and wetland type (5 variables). As a result, we compared for each response variable a total of 15 models in the morphology and land cover analysis and 31 models for wetland type analysis. We used Akaike Information Criterion (AIC) to select the best model fit. In general, larger ΔAIC indicate a smaller probability of that model being the best in the set of models being considered. We also calculated Akaike weights (w_i), which approximate the probability that a particular model is the best fit among all alternatives (see Westphal et al. (2003) for additional information on these metrics and this regression approach). We also tested for collinearity among predictor variables using the variance inflation factor (VIF) and the condition index (CI; Belsley et al., 1980). In the three groups of predictor variables, we detected no collinear variables (VIF < 10 and CI < 30) and, as such, did not remove any variables from these multiple regressions. Following this preliminary analysis, predictor variables from the top models in each category (morphology, landcover, and wetland type) were combined into one multiple factor regression. This final model analysis used 10 predictor variables (3 morphology, 3 land cover and 4 wetland type variables each) and compared the fit of a total of 1023 models. We also used ordination to detect structure among all stream water chemistry and landscape variables. We extracted two factors in a principal component analysis (PCA) using SAS to identify the direction and magnitude of relationships among DOM concentration and physicochemistry, base cation concentrations, and landscape characteristics.

Results

DOC concentration ranged widely (<4 to >35 mg C L^{-1}) among the study streams of the Ontonagon River watershed with about one-half of streams containing >12 mg C L^{-1} (Fig. 2). DOM physicochemical properties were also variable with DOM Abs_{280}, ε_{280}, and M_w all displaying a wide range of values (Fig. 2). The range of base cation concentrations among streams was also substantial (Fig. 2), which together with the variation in DOM illustrates the extent to which stream water chemistry varies within the Ontonagon River watershed even during a

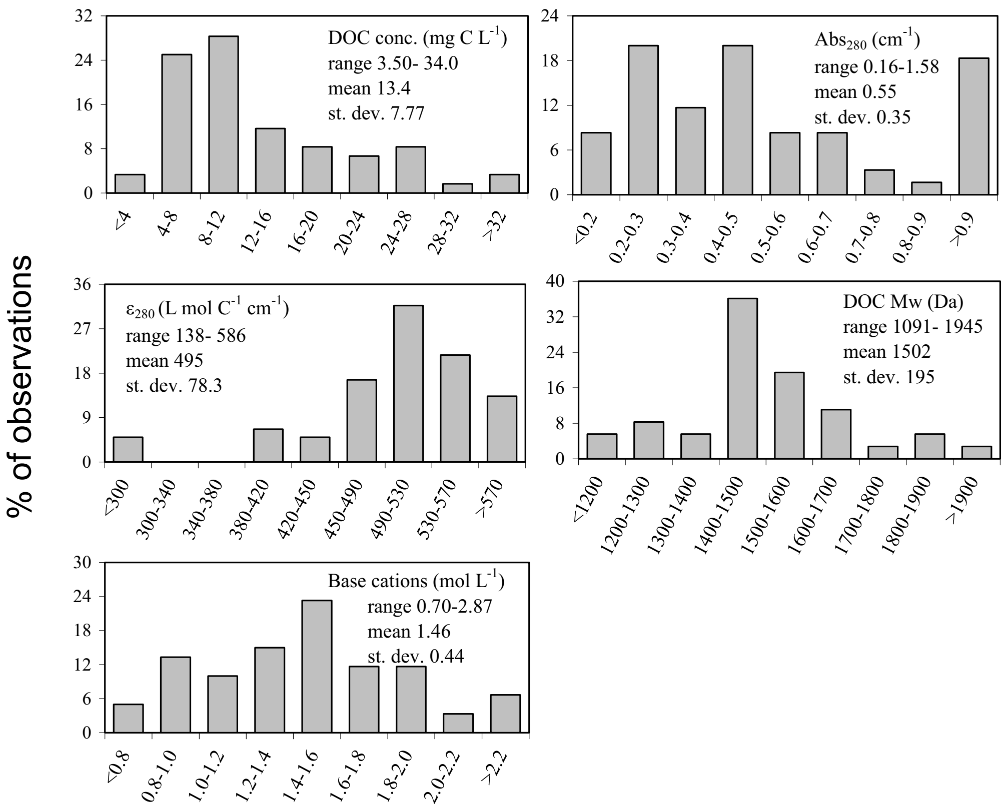

Figure 2. Frequency diagrams of DOC concentration, DOM physicochemistry, and related stream water chemistry from 60 streams studied in the Ontonagon River watershed (Michigan, USA).

Table 2. Pearson correlations among stream water chemistry variables. All variables were natural log-transformed prior to analysis. See Table 1 for abbreviations. Significant (p<0.05) correlations are shown in bold.

	Abs_{280}	ε_{280}	DOC M_w	Cations
DOC	**0.97**	0.16	**0.69**	**-0.47**
Abs_{280}		**0.39**	**0.82**	**-0.42**
ε_{280}			**0.72**	–0.08
DOC M_w				–0.28

short period with no significant rainfall events. Stream water chemistry variables were strongly correlated among themselves. In particular, DOC concentration was strongly and positively correlated with DOM Abs_{280} and M_w (Table 2). DOM ε_{280} was highly correlated with DOM M_w but not correlated with DOC concentration (Table 2). Stream DOC concentration was also negatively correlated with pooled base cation concentrations in our dataset (Table 2).

We found several landscape variables were significantly correlated with stream DOC concentration (Fig. 3). Although significantly related, these landscape variables individually explained relatively small amounts of among-stream variation in DOC concentration (<30 %, Fig. 3). Of significant predictor variables, mean slope, stream length, watershed area, % of area in upland conifer forest, % lake, and % emergent wetlands were negatively correlated with DOC concentration (Fig. 3). DOC concentration was positively correlated to the % of wa-

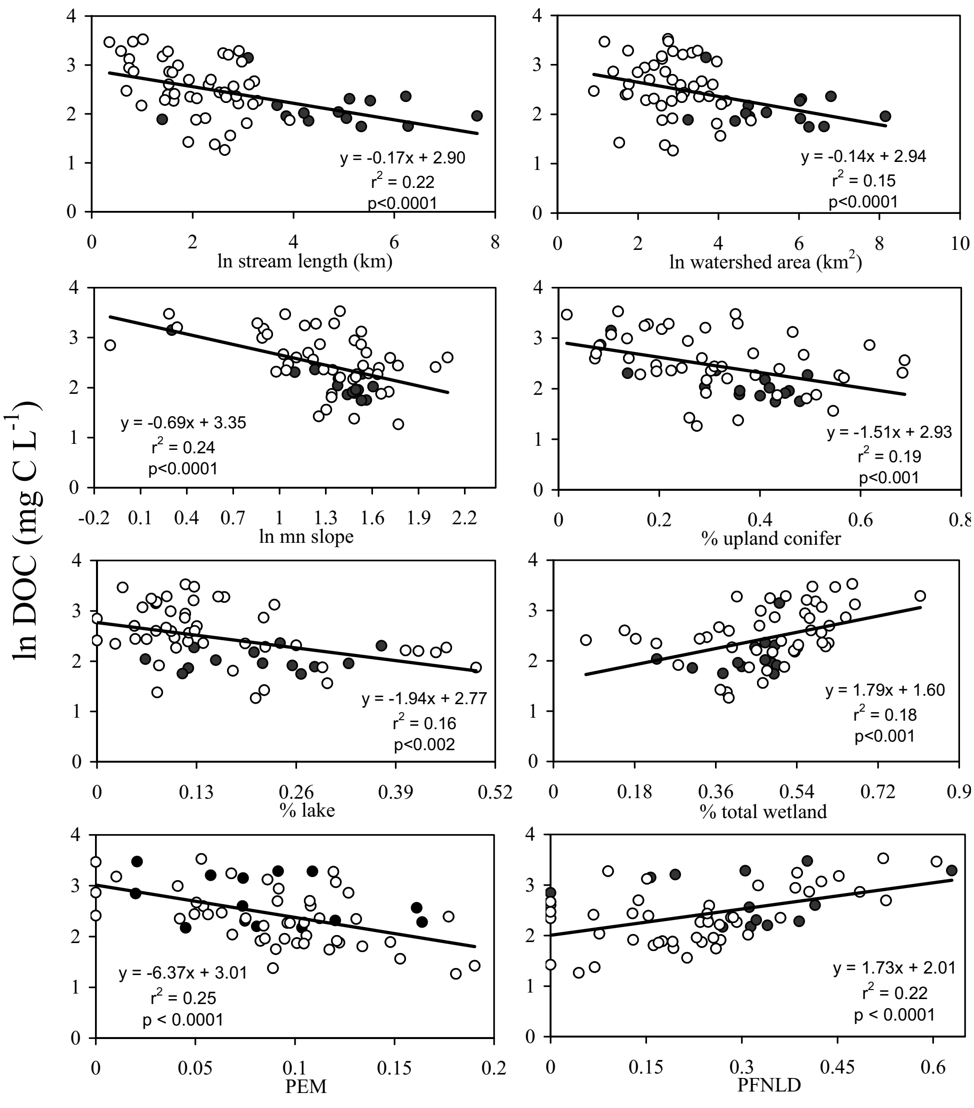

Figure 3. Linear regressions between DOC concentration and landscape variables. See Table 1 for explanation of abbreviations. Dark circles denote data from rivers of greater than 3rd order. All land cover variables were arc-sin square root transformed.

Table 3. Results of multiple regressions for in-stream variables against landscape characteristics. All stream water chemistry variables were natural-log transformed prior to running the regression analysis. Landscape variables also were transformed (see Methods). Each model represents a best fit based on the highest r^2, smallest ΔAIC, and highest w_i. The best two models are listed. See Table 1 for abbreviations.

response variable	predictor variables	candidate model	ΔAIC	w_i	r^2
DOC	morphology	–shed area –dr den –slope	0	0.29	0.44
		–dr den –slope –strm len	0	0.29	0.44
	landcover	–%lake –%up con +%tot wet	0	0.70	0.51
		–%lake –%up con –%ag +%tot wet	1.99	0.26	0.51
	wetland type	–PEM +PFNL +PSS –PBOG	0	0.66	0.54
		–PEM –PF +PFNL +PSS –PBOG	1.65	0.29	0.54
Abs_{280}	morphology	–slope –strm len	0	0.32	0.34
		–shed area –dr den –slope	0.97	0.20	0.35
	landcover	–%lake –%up con +%tot wet	0	0.59	0.52
		–%lake –%up con –%ag +%tot wet	1.31	0.31	0.52
	wetland type	–PEM +PFNL +PSS –PBOG	0	0.51	0.47
		–PEM –PF +PFNL +PSS –PBOG	1.22	0.28	0.47
ε_{280}	morphology	+dr den	0	0.22	0.05
		+dr den +strm len	1.58	0.10	0.05
	landcover	–%lake	0	0.23	0.09
		–%lake –%ag	0.31	0.20	0.11
	wetland type	+PEM +PFNL –PBOG	0	0.16	0.15
		+PEM +PFNL –PSS –PBOG	0.07	0.16	0.18
DOC M_w	morphology	–strm len	0	0.14	0.10
		–slope –strm len	0.30	0.13	0.14
	landcover	–%lake –%up con +%tot wet	0	0.44	0.55
		–%lake +%tot wet	1.07	0.26	0.50
	wetland type	–PF +PFNL +PSS –PBOG	0	0.18	0.49
		+PFNL –PBOG	0.05	0.17	0.43
Cations	morphology	+slope +strm len	0	0.19	0.20
		+dr den +slope	0.34	0.16	0.20
	landcover	+%up con +%ag –%tot wet	0	0.39	0.35
		+%up con –%tot wet	1.10	0.22	0.32
	wetland type	+PEM –PFNL –PSS	0	0.21	0.29
		+PEM –PF –PFNL –PSS	0.45	0.18	0.31

tershed area in total wetlands and in lowland conifer wetlands (Fig. 3). Removing streams of 3rd-order or greater did not alter the strength or nature of any of these relationships between DOC concentration and landscape variables (Fig. 3).

Multiple factor regression analysis also showed many strong relationships among stream water DOC concentration and landscape characteristics. All watershed morphology variables (watershed area, drainage density, mean slope and stream length) were negatively related to stream water DOC concentration (Table 3). Two regression models, each having three of the above watershed morphology variables, were equally likely to be the best fit and both explained 44 % of among stream variation in DOC concentration. Of land cover variables, % lake, % upland conifer forest, and % total wetlands were included in the best model (i. e., highest w_i) and together explained 51 % of the variation in stream DOC concentrations (Table 3). In this model, % lake and % upland conifer forest were negatively related to DOC concentrations whereas % total wetlands was positively related to DOC concentrations. The best fit model of wetland type variables included % emergent, % lowland conifer, % scrub/shrub, and % bog scrub/shrub and explained more variation in stream DOC (~54 %) than the other two landscape categories (i. e., morphology and land cover). Two of these wetland types (% emergent and % bog scrub/shrub) were negatively related to DOC concentrations while the two other categories (% lowland conifer and % scrub/shrub) were positively related to DOC concentrations (Table 3).

DOM Abs_{280} was correlated with a set of watershed morphology (slope, stream length), land cover (% lake, % total wetlands), and wetland type (% emergent wetlands, % lowland conifer, and % bog scrub/shrub) variables similar to those that predicted DOC concentration (Table 3). ε_{280} was not strongly correlated to any of the

Table 4. Results of multiple regression analysis for stream DOC concentration against selected landscape characteristics. See Methods for information on predictor variable selection and transformation. Given are the top ten best fit models based on the smallest ΔAIC and the highest w_i. See Table 1 for abbreviations.

response variable	candidate model	ΔAIC	w_i	r^2
DOC	–slope –dr den –shed area –%lake –PEM +PFNL	0	0.12	0.70
	–slope –dr den –shed area –%lake –PEM +PFNL +PSS	1.06	0.07	0.71
	–slope –dr den –shed area –%lake +%tot wet –PEM +PFNL	1.51	0.06	0.71
	–slope –dr den –shed area –%lake –%up con –PEM +PFNL	1.85	0.05	0.70
	–slope –dr den –shed area –%lake –PBOG	2.00	0.04	0.70
	–slope –dr den –shed area –%lake +%tot wet –PEM	2.78	0.03	0.69
	–slope –dr den –shed area –%lake –PFNL	3.36	0.02	0.68
	–slope –dr den –shed area –%lake –%up con –PEM +PFNL +PSS	2.50	0.03	0.71
	–dr den –shed area –%lake +%tot wet –PEM	3.47	0.02	0.67
	–slope –dr den –shed area –%lake +%tot wet –PEM +PFNL +PSS	3.02	0.03	0.70

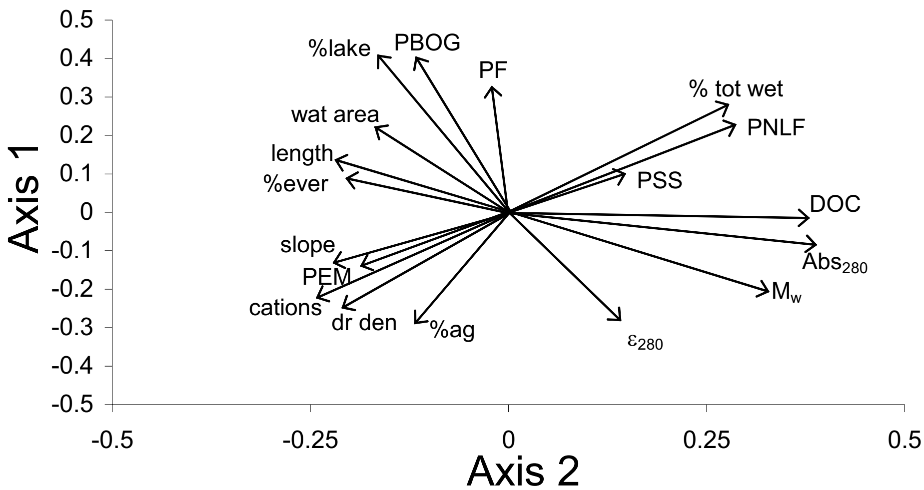

Figure 4. PCA analysis of DOC, stream morphology, and land cover. Axis 1 explains 32 % of the variance in our dataset and axis 2 explains an additional 21 %. See Table 1 for explanation of abbreviations.

landscape predictor variables, indicated by the low r^2 and small AIC w_i of the two best fit models in each of the landscape categories (Table 3). DOM M_w was not strongly correlated with watershed morphology, but was strongly correlated to a similar set of landcover (% lake and % total wetlands) and wetland type (% lowland conifer, % scrub/shrub, and % bog scrub/shrub) variables as DOC concentration (Table 3). Base cations were also correlated (although in opposite directions) with similar variables as DOC concentrations. In particular, stream length, mean slope, % lake, % upland conifer, % total wetlands, % emergent wetlands, and % lowland conifer were all found to significantly correlate with stream base cation concentrations (Table 3).

The top ten models (based on w_i) from the multiple regression analysis of all significant predictors from the three landscape categories each accounted for about 70 % of among stream DOC variation (Table 4). The highest w_i of these models was 0.12 and the summed w_i for the ten models together was 0.49. The six predictor variables (slope, drainage density, watershed area, % lake, % emergent wetlands, and % lowland conifer wetlands) in the top model were each present in seven or more of the top ten models. Three other variables (% upland conifer, % scrub shrub, and % bog scrub shrub) were found in three or fewer of the top ten models (Table 4).

PCA analysis captured the strong relationships among stream DOC concentration, physicochemical properties, and landscape characteristics. Stream water DOC concentrations were negatively associated with stream length, mean slope, watershed area, % emergent wetlands, and % upland conifer but positively associated with % total wetlands (Fig. 4). ε_{280} was positively associated with DOC M_w and both variables were negatively associated with %

lake, % bog scrub/shrub, and watershed area (Fig. 4). Base cation concentrations were positively associated with slope, drainage density, and % emergent wetlands and negatively associated with % total wetlands.

Discussion

Stream water DOM was strongly related to several landscape-level predictors in our study, which likely reflect the landscape's influence on the loading, transportation, removal, and dilution of DOM in streams of the Ontonagon watershed. Understanding the influence of the landscape on stream water DOM during baseflow is particularly important given that baseflow conditions persist for most of the growing season, which constitutes approximately 25 % of the annual season. While many previous studies have examined the landscape predictors of DOM flux, we focused on the controls of DOM concentration and chemistry, which are also of considerable importance. The concentration of DOM plays a central role in determining the stream solar radiation regime, alters the availability of important nutrients, and is an important source of energy for microbial communities (Xenopoulos and Schindler, 2001; Sinsabaugh and Findlay, 2003).

Of the watershed morphological variables, DOM concentration was negatively correlated to watershed area, mean slope, and drainage density. The negative relationship of DOM concentrations to watershed area may reflect the higher residence time of water in larger watersheds. Greater residence times in large watersheds should result in greater removal of DOM due to photo- and/or microbial degradation. DOM concentrations were also negatively related to mean watershed slope. This relationship is likely a result of shallower organic-rich soil horizons and faster movement of water in steeper sloped watersheds (Rasmussen et al., 1989). Greater slope in the watershed may also be associated with an increased contribution of deep groundwater to stream flow. Deep groundwater is known to have low DOM concentrations (Leenheer et al., 1974) and often has high base cation concentrations, particularly in this region (Gorham et al., 1983). Consistent with this possibility, we found a positive association between the concentration of base cations and mean slope (Fig. 4). Future research should explicitly examine these proposed explanations for the relationships described here by directly quantifying the water residence times and the rate of DOM degradation in streams of Ontonagon watershed. In addition, it would be informative to determine the contributions of deep groundwater to streams having watersheds with differing slope in this region.

We also found DOM concentration to significantly correlate with several aspects of watershed land cover. In particular, the percentage of watershed area found in lakes was a significant predictor of DOM concentration in all of the regression models. Lakes can serve as strong sinks and transformers of terrestrially derived DOM (e. g., Hanson et al., 2003), which should reduce DOM concentrations in streams flowing from lake-rich watersheds. The percentage of watershed as upland conifer forests (% upland conifer) was also negatively correlated to DOM concentrations, which is difficult to explain as there are no readily available mechanisms that directly link stream DOM to this land cover type. This result perhaps reflects the positive association between watershed area and % upland conifer in the landscape (Fig. 4). We also found a positive relationship between DOM concentration and the proportion of watershed area in total wetlands. This result is consistent with previous work showing that wetlands contribute significant quantities of DOM into lakes and streams, although we found % total wetlands alone to be less important than in other studies (i. e., Mulholland, 2003, Xenopoulos et al., 2003). It is unclear whether the relationships between DOM concentrations, which varies temporally, and landscape characteristics, which do not change at short-time scales, would change as the hydrological connectivity between the stream network and the landscape change seasonally. Nevertheless, the relationships of DOM with watershed land cover described here appear to reflect broad-scale processes that dictate the contribution and removal of DOM in the watershed.

The relatively small amount of variability (~18 %) in DOM concentrations explained by % total wetlands in this study is likely a consequence, in part, of the relatively large (3460 km^2) and varied nature of Ontonagon watershed (Aitkenhead et al., 1999). We found a considerable range in values for many of our non-wetland landscape variables (e. g., % lake) across the subwatersheds of the Ontonagon (Table 1). Given these differences in landcover, the subwatersheds of the Ontonagon watershed probably have contrasting soil composition, subsurface hydrology, and even local climatic conditions (e. g., precipitation). This variation in non-wetland landcover and other hydrogeological factors could affect in-stream and terrestrial processing of DOM between sub-watersheds. For example, given the mixture of peatlands, wetlands, and mixed forests in the Ontonagon River watershed, the mineral content of soil and its C:N ratio are likely to vary substantially among the subwatersheds in this study. In areas of mineral-rich soils, DOM may be immobilized in the upland and riparian zones before reaching the stream (McDowell, 1998; Guggenberger and Kaiser, 2003). Consequently, it is perhaps not surprising that one landscape characteristic (% total wetlands) failed to explain a large proportion of among stream variability of DOM concentration in this study.

DOM concentration and physicochemical properties were also correlated to the prevalence of different wetland types in the Ontonagon watershed. Stream DOM concentration was positively correlated with the % of watershed area found in lowland conifer and scrub shrub wetlands. Other wetlands (e.g., % emergent wetlands and % bog scrub/shrub) were negatively correlated with DOM concentration in streams. The positive correlation between DOM and % lowland conifer wetlands is probably because of their greater capacity to contribute DOM to aquatic ecosystems (Xenopoulos et al., 2003). The negative correlations of stream DOM with the area of bogs and emergent wetlands is probably a result of their correlation with other land types given their low prevalence in the watershed and their strong correlations with other landscape factors. For example, bog scrub/shrub is positively associated with % lake area (Fig. 4), a potentially strong carbon sink in this watershed (see above). The % emergent wetlands was positively associated with watershed slope and stream length (Fig. 4), both of which are strongly negatively correlated with stream water DOM. Alternatively, the emergent vegetation may be meadows associated with beaver ponds, which have been shown to reduce streamwater fluxes of total organic carbon (Correll et al., 2000). These relationships between wetland type and DOM concentration may also result from simple over-fitting of the data (Burnham and Anderson, 2000). Such over-fitting is a distinct possibility especially if no plausible mechanisms appear to link the landscape characteristic to spatial variability in DOM concentration. Future work should focus on examining the mechanisms (source/sink dynamics and processing) that link the specific types of wetlands in the watershed to DOM concentrations in streams.

Landscape characteristics were also significant predictors of physicochemical properties of DOM. In general, landcover and wetland type variables were better predictors compared to watershed morphology of DOM M_w and ε_{280}. Of landcover variables, % lake and % total wetlands were both significant predictors of DOM M_w and ε_{280}. This suggests that processes adding and removing DOM from streams can affect important physicochemical attributes of this organic matter. For example, the relatively low M_w and UV-absorptivity of the DOM in streams flowing from watersheds relatively rich in lakes is probably a result of greater processing by heterotrophic bacteria and photoreactions in these systems. It is known that microbial processing decreases DOM M_w (Amon and Benner, 1996) and solar radiation increases DOM transparency to ultraviolet radiation (Osburn et al., 2001). On the other hand, less photo-processing of DOM probably occurs in many of the headwater streams of this region because they receive little direct UV radiation exposure due to extensive forest canopy (Frost et al., 2005). Another possible explanation (not necessarily exclusive) for the negative correlation between the physicochemical properties of DOM (M_w and ε_{280}) and lake area is that autochthonous carbon (with less absorptivity; McKnight et al., 1994) is more prevalent in stream water originating from lakes compared to streams flowing from watersheds without lakes.

In summary, we found stream water DOM concentrations were strongly related to watershed morphology, landcover, and the type of wetlands found in the watershed. The best fit regression model using a combination of variables from these three categories explains about 70 % of among stream variation in DOM concentration. In comparison, % wetland area, when considered alone, explained only 18 % of among stream variation in DOM concentrations. DOM M_w and ε_{280} were also significantly related to the landscape predictors used in this study. In general, less variation was explained in these DOM properties than in DOM concentrations by landscape characteristics. Our results thus suggest that the DOM concentration and chemistry in streams is controlled by multiple processes (DOM loading, degradation, and dilution) that vary across large and heterogeneous watersheds. The stronger connections between landscape variables and DOM concentration (compared to DOM physicochemical properties) indicate relatively fast in-stream processing alters the structure but not the quantity of DOM being transported through streams in this watershed. Future work needs to explicitly address the mechanisms that account for these patterns of DOM quantity and physicochemistry as they relate to composition and structure of the landscape.

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