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Article

Land Use Overrides Stream Order and Season in Driving Dissolved Organic Matter Dynamics Throughout the Year in a River Network

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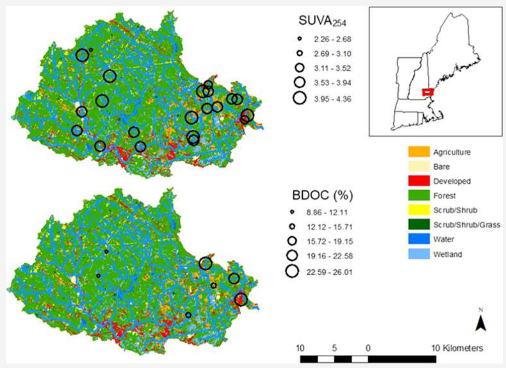
ABSTRACT: Anthropogenic land use has increased nutrient concentrations and altered dissolved organic matter (DOM) character and its bioavailability. Despite widespread recognition that DOM character and its reactivity can vary temporally, the relative influence of land use and stream order on DOM characteristics is poorly understood across seasons and the entire flow regime. We examined DOM character and 28-day bioavailable dissolved organic carbon (BDOC) across a river network to determine the relative roles of land use and stream order in driving variability in DOM character and bioavailability throughout the year. DOM in 1st-order streams was distinct from higher stream orders with lower DOC concentrations, less aromatic (specific ultraviolet absorbance at 254 nm ($SUVA_{254}$)), more autochthonous (fluorescence index), and more recently produced (β/α) DOM. Across all months, variability in DOM character was primarily explained by land use, rather than stream order or season. Land use and stream order explained the most DOM variation in transitional and winter months and the least during dry months. BDOC was greater in watersheds with less aromatic ($SUVA_{254}$) and more recent allochthonous DOM (β/α) and more development and impervious surface. With continued development, the bioavailability of DOM in the smallest and most impacted watersheds is expected to increase.



KEYWORDS: *dissolved organic carbon, dissolved organic matter, river network, stream order, land use, bioavailability, temporal*

1. INTRODUCTION

Riverine dissolved organic matter (DOM) is an important component of the global carbon (C) cycle with ~0.25 Pg C exported by rivers to the ocean each year.[1,2] DOM provides an energy source for microbial respiration, attenuates light penetration in the water column, binds and transports heavy metals and other organic pollutants,[3] and can represent a significant fraction of the total nutrient load.[4] DOM includes allochthonous (terrigenous), autochthonous (in-stream primary production), groundwater, and anthropogenic sources, which are considered important predictors of rates of microbial mineralization of DOM.[5−7] Microbes respire DOM as CO_2, contributing to greenhouse gas emissions from inland waters.[8] The smallest streams (1st and 2nd order; <10 km^2) exhibit some of the greatest variability in DOM character and land use[9] and account for disproportionately high contributions to CO_2 evasion.[10−12]

The River Continuum Concept (RCC) provides a long-standing paradigm that predicts how sources of DOM vary throughout a river network.[13] The RCC hypothesizes that DOM incorporated into stream food webs shifts from primarily allochthonous sources in headwaters to primarily autochthonous sources in higher-order streams, and this shift in source has been demonstrated in recent studies.[14,15] As a result of source shifts, the RCC predicts corresponding declines in the diversity of DOM from small streams to larger downstream rivers,[13] and research from relatively undisturbed forested streams supports these predictions.[9,16−21] Bioavailability of DOM is also expected to decrease with downstream river distance[15,22,23] because mineralization rates are typically driven by the optical and structural characteristics of DOM.[24,25] Globally, human land use change such as urbanization and agriculture has led to increased nutrient concentrations[26,27] and alterations in the flux, character, and bioavailability of DOM.[18,28−32] Predictions of DOM transformations within river networks have only recently incorporated variation in land use, and in human-dominated catchments, the hypothesized shifts in DOM character and bioavailability along a river network have been less pronounced, nonexistent, or have shown an alternative pattern than those originally hypothesized.[9,18,20,21] Because the smallest streams are often anthropogenically impacted,[9,18] the traditional DOM paradigm (more autochthonous and

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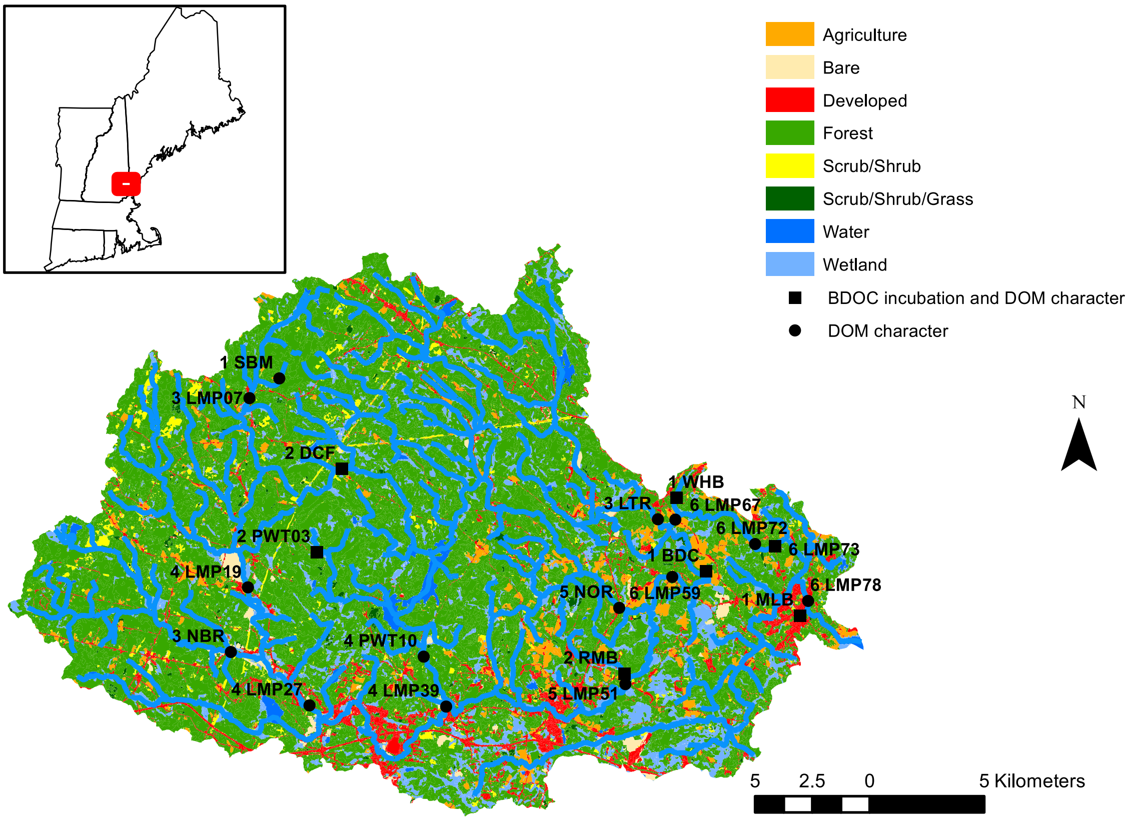

Figure 1. Map of study locations within the Lamprey River watershed in New Hampshire, U.S.A. Filled squares represent sites where BDOC and DOM characters were measured and filled circles represent sites where DOM character was measured. Site labels describe stream order followed by the site code (see Table 1 for details).

bioavailable DOM found in headwaters) can be disrupted by urban or agricultural land use.[9,18]

Hydrological connectivity of streams is also a critical predictor of DOM in river networks because it controls the delivery of terrestrial and anthropogenic DOM sources, downstream transport, and in-stream reactivity.[19,33−35] The pulse-shunt concept posits that short water residence time during large rain or snowmelt events limits in-stream biogeochemical processing by "shunting" DOM to higher-order rivers.[34] Dry periods with long water residence time can shorten transport distances, which enhances in-stream processing while disconnecting low-order streams from higher-order downstream rivers.[33] Longitudinal gradients of DOM can be highly sensitive to different flow conditions with lower flow conditions associated with more heterogeneous DOM due to enhanced biogeochemical processing.[33] Spatially and temporally extensive datasets across a land use gradient of individual river networks remain sparse[9,19] but are critical for understanding how anthropogenically influenced watersheds affect DOM character and its bioavailability across the entire flow regime.[33]

Here, we evaluate how temporal dynamics affect the relative importance of stream order and land use in driving temporal variability of DOM character and bioavailability using a spatially and temporally extensive dataset in the Lamprey River watershed, New Hampshire. Prior observations from this watershed showed that DOM homogenization occurred at the smallest scales (1st—2nd order; <10 km^2) and bioavailability in the mainstem did not differ with watershed sizes that ranged from 15.1 to 548.1 km^2 (3rd—6th order).[9] We extend these earlier evaluations with the inclusion of four additional years of DOM characterization using a wide range of optical indices and 28-day bioassays encompassing the smallest and most heterogeneous streams. We hypothesized that land use, rather than Strahler stream order, would explain greater variability in DOM dynamics across the watershed. However, we expected that land use and stream order would have less influence on DOM in drier months as streams become less hydrologically connected to terrestrial DOM inputs and residence times in the stream channel increase. Finally, we hypothesized that DOM bioavailability would vary with land use in 1st- and 2nd-order streams. This extensive dataset of DOM character and bioavailability over time and space allows us to explore some of the most fundamental questions about how DOM functions at the river network scale across wide ranges in flow regimes.

2. METHODS

2.1. Study Sites. The Lamprey River watershed is a 548 km^2 watershed (Figure 1; Table 1), with ongoing weekly to monthly monitoring across 21 locations spanning 1st to 6th order since 2011 for DOM character[9] and 1999 for solute concentrations.[36,37] Within the Lamprey River watershed, the greatest variability in background nitrogen concentrations occurs within the smallest headwaters,[9] and thus, we selected small headwater streams to evaluate the effects of inorganic N concentrations on bioavailability (Table 1). We measured bioavailable fractions of dissolved organic carbon (BDOC) across 7 locations within the Lamprey River watershed including six headwater streams: Burley Demerit Creek (BDC), Moonlight Brook (MLB), Wednesday Hill Brook

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Table 1. Study Site Characteristics for BDOC Incubations and DOM Character Locations[a]

stream name	site code	wat. area (km^2)	stream order	For. (%)	Ag. (%)	Dev. (%)	Wet. (%)	CN	NO_3-N (mg L^{-1})	NH_4^--N (μg L^{-1})	DON (mg L^{-1})	TDN (mg L^{-1})
						BDOC Incubation and DOM Character						
Burley Demeritt Creek	BDC	0.3	1	36.3	49.2	4.1	9.1	61.5	2.16	76	1.09	3.33
Moonlight Brook	MLB	0.9	1	48.8	2.7	43.1	3.4	57.8	0.84	51	0.05	0.92
Wednesday Hill Brook	WHB	1.0	1	66.2	7.2	15.6	7.0	40.8	0.88	9	0.13	1.06
Pawtuckaway	PWT03	2.6	2	82.6	0.0	0.8	16.1	50.2	0.01	16	0.34	0.37
Rum Brook	RMB	4.9	2	59.8	9.2	11.3	15.9	43.8	0.19	26	0.21	0.43
Dowst Cate Forest	DCF	7.0	2	76.9	1.8	2.0	11.9	43.2	0.11	14	0.28	0.38
Lamprey River	LMP73	479.2	6	72.1	3.4	5.8	12.3	43.6	0.14	39	0.20	0.39
						DOM Character						
Saddleback Mountain	SBM	0.3	1	98.6	0	0	0	42.0	0.01	9	0.07	0.09
Lamprey River	LMP07	15.1	3	89.0	2.6	0.5	2.8	40.9	0.05	13	0.16	0.22
North Branch	NBR	41.5	3	78.0	7.7	2.3	6.7	42.2	0.06	11	0.20	0.26
Little River	LTR	51.7	3	78.3	3.6	2.6	6.8	42.5	0.11	17	0.19	0.31
Pawtuckaway	PWT10	25.5	4	82.2	1.5	0.7	4.4	42.4	0.06	19	0.18	0.25
Lamprey River	LMP19	80.1	4	78.7	6.3	1.1	4.8	42.5	0.09	13	0.17	0.27
Lamprey River	LMP27	144.3	4	77.0	6.5	1.8	6.4	42.4	0.09	12	0.18	0.28
Lamprey River	LMP39	197.9	4	73.2	6.6	4.1	7.4	43.6	0.14	15	0.20	0.34
North River	NOR	128.9	5	78.4	7.0	1.7	5.9	42.9	0.06	13	0.21	0.28
Lamprey River	LMP51	251.7	5	72.6	6.9	4.2	7.5	46.0	0.25	24	0.20	0.48
Lamprey River	LMP59	396.6	6	74.0	7.3	3.4	7.1	42.0	0.16	17	0.20	0.37
Lamprey River	LMP67	469.3	6	73.7	7.4	3.4	7.3	43.6	0.15	18	0.21	0.37
Lamprey River	LMP72	476.9	6	73.6	7.6	3.4	7.3	43.6	0.15	27	0.28	0.46
Lamprey River	LMP78	548.1	6	71.7	7.9	3.6	8.6	44.6	0.13	24	0.21	0.37

[a]Nitrogen concentrations reflect the mean background concentration across incubation dates, with concentrations for DOM character reflected by mean background concentration across the period of record (2011−2019). The curve number represents mean watershed values extracted from GCN250 under average antecedent runoff conditions (ARCII). Abbreviations were used as follows: watershed area (Wat. area), forested (For.), agricultural (Ag.), developed (Dev.), wetland (Wet.), curve number (CN).

(WHB), Pawtuck-away (PWT03), Rum Brook (RMB), and Dowst Cate Forest (DCF), and one mainstem location (LMP73) (Figure 1). The six headwater streams represent 1st- and 2nd-order streams as defined by the Strahler stream order. The mainstem location is a 6th-order stream. Discharge was monitored during the incubation period at BDC, DCF, WHB,[38] and throughout the study at LMP73 (USGS 01073500). Where discharge was not available, we estimated discharge based on specific discharge (m^3 s^{-1} km^{-2}) from the downstream USGS gaging station (USGS 01073500).[9]

2.2. Stream Chemistry Analyses. All samples were analyzed for dissolved organic carbon (DOC), total dissolved nitrogen (TDN), nitrate (NO_3^-), and ammonium (NH_4^+) following previously reported methods.[9] Dissolved organic nitrogen (DON) was calculated as the difference between TDN and the sum of inorganic N (NO_3^--N + NH_4^+-N). Briefly, DOC and TDN were quantified with a Shimadzu TOC-VCSH or TOC-LCSH (Shimadzu Corporation, Kyoto, Japan) with a TNM-1 Total Nitrogen Module,[39] NO_3^- was measured by ion chromatography with suppressed conductivity detection (Dionex 1000 ICS with AS40 autosampler; Sunnyvale, CA), and NH_4^+ was measured using a discrete automated colorimetric analyzer (SmartChem 200; Unity Scientific, Brookfield, CT).

2.3. DOM Quantity and Character. Weekly to monthly monitoring of DOM quantity and character (fluorescence and absorbance; hereafter referred to collectively as DOM) were determined across 21 sites in the Lamprey River network from June 2011 until 2019.[9] Stream water was filtered in the field with pre-combusted Whatman GF/F 0.7 μm filters and stored in amber glass bottles that were pre-combusted at 450 °C for 6 h. Samples were kept cold at 4 °C until analysis. In addition to incubation samples, monthly monitoring within this river network includes optical DOM indices. Fluorescence excitation emission matrices (EEMs) were determined with a Jobin-Yvon Horiba Fluormax-3 fluorometer (Jobin-Yvon Horiba, France).[9] Room-temperature samples were placed in a 1 cm quartz cuvette and excited from 240 to 450 nm at 2.5 nm intervals; emissions were determined at each excitation wavelength from 350 to 550 nm at intervals of 1 nm. Beginning in June 2015, the EEM range was expanded to scan from 300 to 600 nm emission at 1 nm intervals to allow for the determination of additional indices; excitation intervals remained the same. EEMs were corrected for blank Milli-Q water samples analyzed daily and inner filter effects.[40] EEMs for each sample were normalized to the area under the Raman peak. UV absorbance data were collected with a Shimadzu photodiode array detector with HPLC that scanned from 200 to 700 nm at 1 nm intervals. Three reference standards were quantified daily, and used to validate instrument performance including: Pony Lake fulvic acid and Suwanee River fulvic acid (International Humic Substances Society), and quinine sulfate.

Specific ultraviolet absorbance at 254 nm ($SUVA_{254}$ L mg C^{-1} m^{-1}) was determined by dividing the absorbance of a DOM sample at 254 nm by the DOC concentration.[28,41] $SUVA_{254}$ is positively correlated with C aromaticity.[41] We determined several commonly reported DOM indices from this library of EEMs. T280 has been associated with

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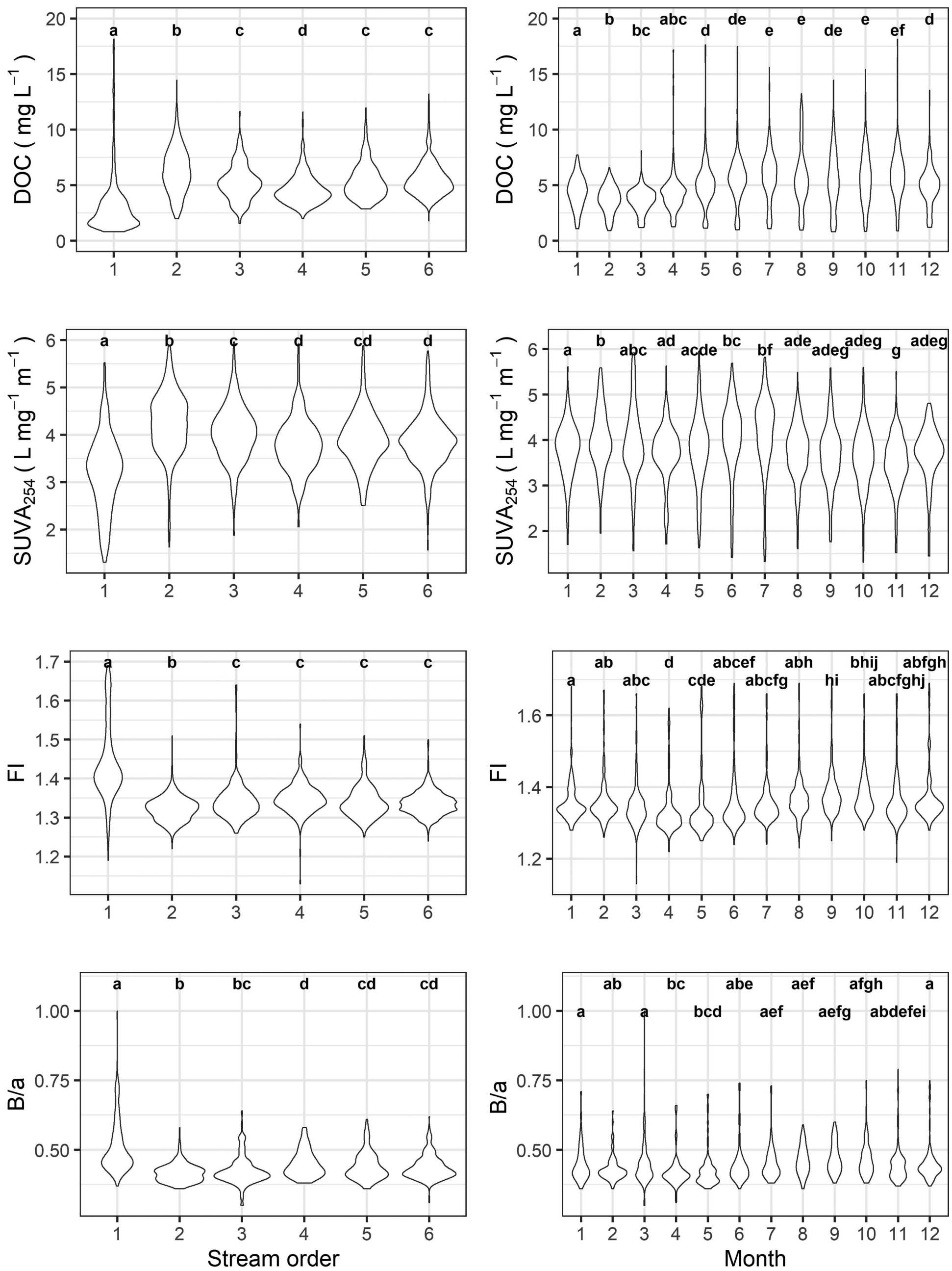

Figure 2. DOM in first-order streams within the Lamprey River network is characterized by less aromatic C (as indicated by lower $SUVA_{254}$), a distinct autochthonous-like source (as indicated by higher FI), and lower quantities of carbon (DOC), associated with more recently produced DOM (β/α) than higher-order streams. These results incorporate 8 years of DOM measurements across 21 locations in the river network for SUVA, FI, and DOC (2011−2019) and 4 years (2015−2019) for S_R, β/α, and HIX (see Figure S4 for S_R and HIX). Different lowercase letters denote statistically significant differences across stream order or month. Different lowercase letters denote statistically significant differences.

autochthonously derived DOM[42,43] and is the fluorescence intensity at 280 nm excitation and 350 nm emission.[44] The fluorescence index (FI) refers to the ratio of emission intensities at 470 and 520 nm at an excitation of 370 nm[45] and is a proxy for DOM source with higher values associated with microbially (autochthonously) derived DOM and lower values associated with terrestrially derived DOM. The freshness index (β/α) is the ratio of two fluorescing components β/α with β as more recently derived DOM and α as highly decomposed DOM.[46] β/α provides an indication of the relative contribution of recently microbially produced DOM.[28] The slope ratio (S_R) is the ratio of the slope of the 275−295 nm to the 350−400 nm region and is considered a proxy for molecular weight with higher values associated with lower molecular weight.[47] The humification index (HIX) was calculated using the normalized equation and is the ratio of the area of the emission spectrum at 435−480 nm to the sum of the emission area from 300 to 345 and 435 to 480 nm at an excitation wavelength of 255 nm. Higher HIX values (range 0 to 1) are associated with an increasing degree of humification and more structurally complex DOM.[48]

2.4. Bioavailable Dissolved Organic Carbon Incubations. We determined bioavailable DOC (BDOC) for 7 sites within the Lamprey River watershed using 28-day laboratory incubations that were conducted twice per season for a one-year period (July 2016 through June 2017). Sampling dates coincided with ongoing monthly monitoring within the watershed.[9,36] The incubation methodology followed previously described recommendations.[49] The loss of DOC through net bacterial production and respiration is quantified during the 28-day incubation. On each incubation date, we collected 250 mL of unfiltered water from each site in pre-rinsed, acid-washed HDPE bottles and placed the samples on ice. Within 6−8 h, we filtered stream water through 0.7 μm pre-combusted GF/F filters. A microbial inoculum was not required because filtration through 0.7 μm allows for some bacteria to pass through the filter.[49] We immediately set up the incubation with 12 replicates per site, adding 30 mL of filtered water into each 40 mL pre-combusted amber glass vial. We capped and shook all vials and then loosened the caps to allow airflow before placing vials in an incubator at 20 °C. We covered the samples with a box to ensure that they were incubated in the dark and regularly shook samples to prevent anoxia. Nutrient amendments to prevent nutrient limitation were not applied because we sought to determine microbial lability under ambient nutrient levels, consistent with prior studies.[6,50] On days 0, 7, 14, and 28, we shook all vials and sacrificed triplicate samples for chemical analysis. We immediately acidified the sample with concentrated HCl for analysis of DOC concentrations.

2.5. Geospatial and Statistical Analyses. Human population density (population km^{-2}) and housing units (number km^{-2}) were determined from US Census data (2010). Septic and sewer densities were determined by Trowbridge et al.[51] Percent impervious surface for 2010 was determined from NH GRANIT, and watershed land use was determined from NOAA 2016 land cover database.[52] United States Department of Agriculture (USDA) curve numbers were extracted from GCN250 under average antecedent runoff conditions (ARCII),[53] clipped to each watershed boundary to determine the mean watershed area. USDA curve numbers incorporate hydrologic soil groups, land use, treatment, and hydrologic condition information to estimate runoff with higher values associated with greater runoff potential during events.

To evaluate the utility of the RCC to understand how shifts in DOM character vary temporally, we applied a two-way analysis of variance (ANOVA) to test for significance in DOM character as a function of stream order and month. When significant, we applied Tukey's honest significant difference (HSD) test to identify significant differences among variables. Pearson's correlation was used to evaluate relationships among land use and DOM character. We used redundancy analysis to simultaneously determine the effects of land use (forested, agriculture, developed, wetland, septic density, impervious surface, and curve number) and stream order (x matrices; predictor variables) on DOM character (y matrix; response variable). Redundancy analysis was performed on the overall dataset and individually by month to examine temporal variability in relative contributions of land use and stream order. Redundancy analysis was performed with the vegan package in R (version 4.1.1; R Foundation for Statistical Computing, Vienna, Austria), modeled with 1000 permutations, and considered significant at $p < 0.001$ to provide a more conservative level of significance. All variables were scaled, by dividing individual values by their respective root-mean-square values, prior to analysis. Percent developed land was log-transformed prior to analysis to meet the assumption of a normal distribution.

To assess whether DOC mineralization varied temporally across incubation dates, we used a full factorial two-way repeated measures ANOVA with date and site as factors and % BDOC as the response. When ANOVA revealed a significant date and site interaction, we also ran a one-way ANOVA for each date independently to determine differences among means. We used Tukey's HSD post hoc analysis to describe significantly different treatment effects.

To determine predictors of BDOC (%) across all sites and dates, we used repeated measures linear regression analysis and included DOM indices ($SUVA_{254}$, FI, β/α, T280, S_R, HIX), DOC, NO_3, NH_4, DON, TDN, and PO_4 concentrations, watershed size, stream order, human population density, housing density, septic density, %impervious service, and land use as predictors. Repeated measures linear regression was performed in JMP 15 (SAS Institute, Cary, NC). BDOC was square-root-transformed for all analyses. Other variables were transformed when necessary (Table S3).

3. RESULTS

3.1. Temporal Variation in DOM Character: Stream Order vs. Land Use. DOM character and quantity varied significantly with stream order and by month for all metrics examined with significant interactions among stream order and month for concentrations of DOC and optical properties FI and β/α (Figure 2; Table S1). FI was consistently greater in 1st order than all other stream orders for all months (Figure S3), B/α was greater in 1st order for all months except September (Figure S1), and DOC concentration was greater in 1st order for all months except March and April (Figure S2). These results indicate that at the annual scale DOM responses to stream order are relatively consistent throughout the year with few exceptions. Generally, in late summer/early fall, DOC concentrations were elevated, and DOM was less aromatic, more recently produced (β/α), and more autochthonous (FI) with fewer differences in the degree of humification (HIX) and molecular weight (S_R).

Overall DOM in 1st-order streams was distinct from other stream orders as it was lower in DOC concentration, less aromatic ($SUVA_{254}$), more derived from autochthonous sources (FI), more recently produced (β/α), less structurally complex, lower in the degree of humification (HIX), and lower in molecular weight (S_R) (Figures 2 and S4). For concentrations of DOC, and optical measures including FI, $SUVA_{254}$, and β/α, 1st-order streams differed from all other stream orders, and 2nd-order streams also differed significantly from all other size classes examined, except β/α did not differ between 2nd- and 3rd-order streams. For HIX and S_R, 1st order differed from other stream orders except between 1st and 4th orders for HIX. For both HIX and S_R cases, 2nd order differed significantly from 4th-order streams. DOM character also differed significantly by month with DOM in late summer and early fall often distinct from spring months (Figures 2 and S4). Despite statistical significance, relatively small changes may not represent meaningful differences given the limitations of optical descriptors of DOM. For example, FI was originally considered significant when it differs by 0.1[54] although corrected spectra likely have reduced this difference further.[55] Statistical significance from 2nd to third order (FI of 1.32 vs 1.34) may thus not represent a meaningful difference in DOM properties between the two stream orders.

First- and 2nd-order streams also have the greatest variation in watershed land use, which was a strong predictor of DOM

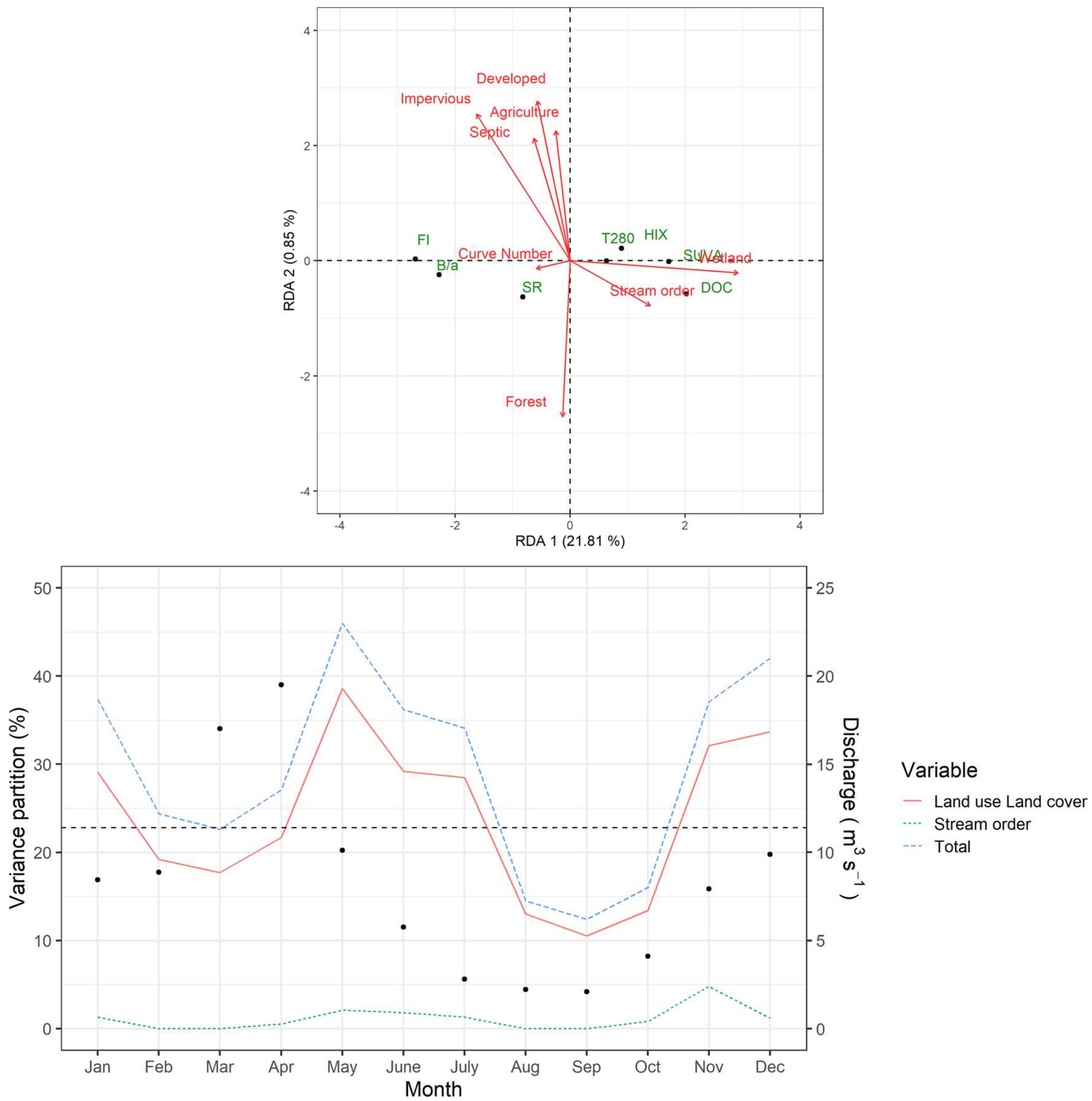

Figure 3. Redundancy analysis with stream order and land use to predict the distribution of DOM character in the Lamprey River watershed for the overall model. Variance partition results by month for monthly redundancy analyses. Monthly discharge (m^3 s^{-1}) averaged over the period of the record shown in filled circles. The horizontal dashed line represents the total variance explained by the overall model.

character (Table S2). Developed land and impervious cover were positively correlated with concentrations of TDN and NO_3, as well as FI, and β/α while negatively correlated with concentrations of DON, DOC, and $SUVA_{254}$. Agricultural land was associated with increases in NO_3 and TDN but not DOM (concentration or character). TDN and NO_3 were negatively correlated, and DOC concentration was positively correlated with forested land. NO_3, FI, β/α, and S_R were negatively correlated and DON, DOC, $SUVA_{254}$, HIX, and T280 were positively correlated with wetlands.

Redundancy analysis revealed that 22.8% of the variability in DOM character was explained by land use and stream order, which partitioned into most of this variability attributed to land use alone (18.6%) with only a small percentage attributed to stream order alone (0.9%), and 3.3% explained by both (Figure 3). The first axis, RDA 1, accounted for 21.8% of the variability and represented a land use gradient from impervious cover associated with high FI and β/α to wetland land cover associated with high DOC concentrations and $SUVA_{254}$.

When partitioned by month, redundancy analysis revealed that the majority of the variability in DOM character was attributed to land use every month of the year. Land use and stream order explained the most variation during May, December, January, and November (Figure 3). In May, land use and stream order explained 46.0% of the variation in DOM with 38.6% attributed to land use and 2.1% attributed to stream order alone. Total variation explained remained elevated from May through July as discharge continued to decline following its peak in April. In November, 37.1% of variation in DOM character was explained by these predictors and land use alone explained 32.1% while stream order explained 4.8% (Figure 3). The driest months of the year (lowest discharge) were associated with the least percent of total variation in DOM explained, with stream order associated with none of the variation in August and September and land use explaining 10.5 to 13.0%. Stream order explained a maximum of 4.8% of the variability in DOM character in November, followed by 2.1% in May. Stream order did not

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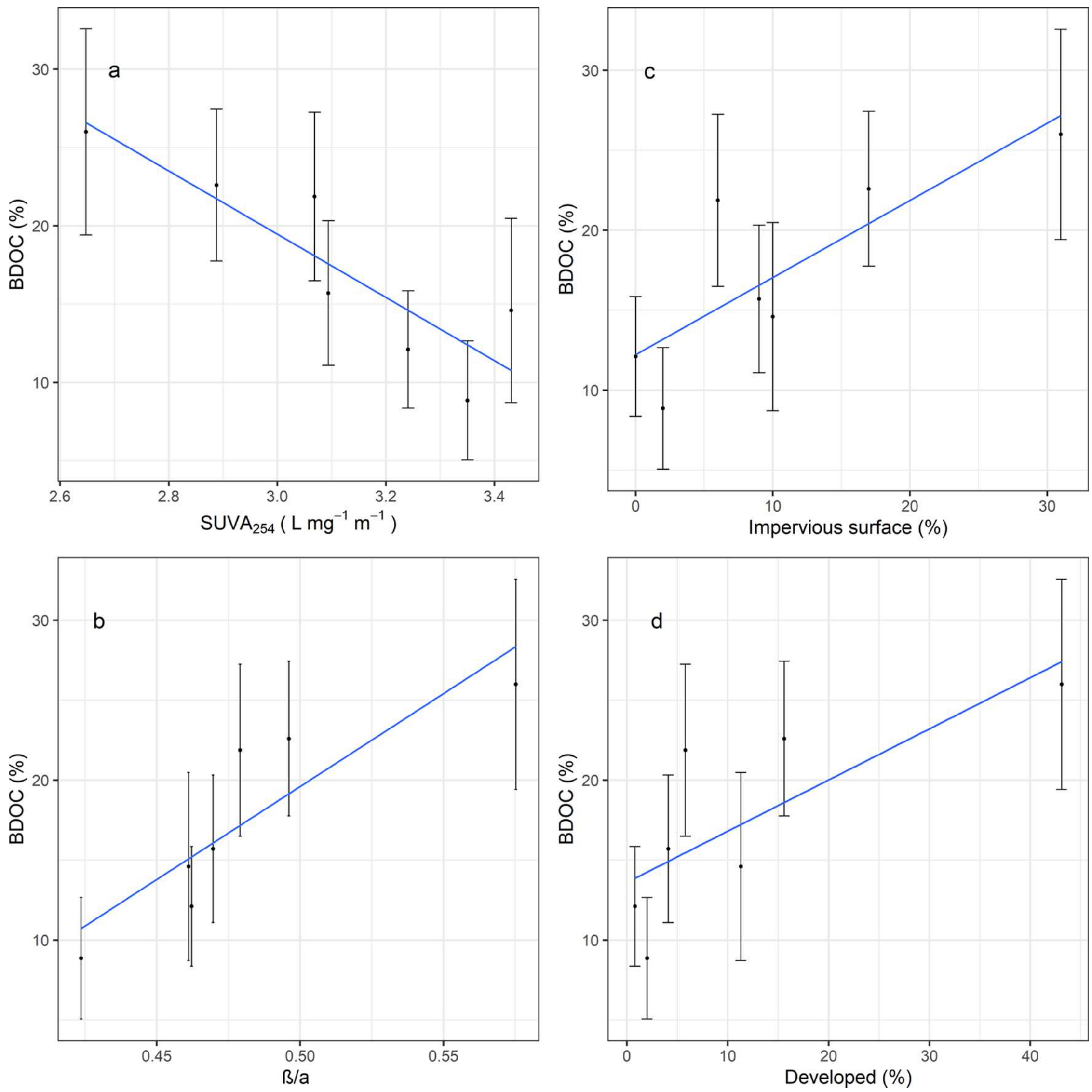

Figure 4. BDOC varied as a function of DOM character and land use. (a) 28-day BDOC (%) decreased with increasing $SUVA_{254}$. (b) BDOC increased with β/α. (c) BDOC increased with the impervious surface. (d) BDOC increased with the developed area. Error bars represent the standard error of 28-day BDOC across 8 dates (twice per season) in a single year.

explain any of the variability during February, March, August, and September.

3.2. BDOC. Mean BDOC across all sites and dates was 0.87 mg L^{-1}, comprising on average 17.4% of DOC. Across all 7 locations, mean annual BDOC (%) ranged from 8.9% (forest and wetland-dominated DCF) to 26.0% (highly developed MLB), with the least and greatest both occurring in the smallest (1st- and 2nd-order) streams. BDOC was significantly greater in 1st- than 2nd-order streams (Supporting Information Figure 6).

Across all sites and dates, BDOC (%) varied significantly by site (F = 5.783, DF = 2, n = 6, p = 0.0004) and date (F = 49.47, DF = 2, n = 7, p < 0.0001) with a significant interaction (site x date: F = 1.563, DF = 37, n = 42, p < 0.0001). BDOC (%) was significantly greater in February than all other dates and significantly lower in July and April than in August. Across all dates, BDOC was significantly greater at the highly developed MLB (greatest β/α) than the two least developed sites PWT03 and DCF (lowest β/α). BDOC at LMP, which has one of the highest septic densities, was significantly greater than forest and wetland-dominated DCF, while BDOC was similar among all other sites.

Overall, watersheds with the greatest human imprint produced stream biogeochemistry with a higher percentage BDOC (Figure 4; Table 1), but temporal variability in this relationship was observed among sampling events.[50] The most developed site (MLB) exhibited the highest %BDOC on half of all incubation dates. A site with 17.1% agriculture and high septic tank density (WHB) and the mainstem location (LMP) exhibited the highest %BDOC on 3 of 8 dates. An entirely forested site revealed the greatest %BDOC on a single incubation date in September, which was similar to the most developed site (MLB).

Across the entire year, BDOC in the Lamprey River network increased in streams with less aromatic C ($SUVA_{254}$), more recent allochthonous DOM (β/α), and more developed land use and impervious surface (Figure 4). We found tht BDOC (%) was negatively related to $SUVA_{254}$ ($F_{1,7}$ = 12.668; p = 0.02; r^2 = 0.39) and positively related to β/α ($F_{1,7}$ = 8.322; p = 0.03, r^2 = 0.41), developed land ($F_{1,7}$ = 6.539, p < 0.05; r^2 =

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0.42), and impervious surface ($F_{1,7}$ = 7.191, p = 0.04; r^2 = 0.42). All other individual predictors were not statistically significant (Table S3).

4. DISCUSSION

4.1. Temporal Variation in DOM Character and Bioavailability across Land Use and Stream Order. The importance of temporal variability in controlling DOM quantity, character, and reactivity has been widely acknowledged,[9,33,34,56−59] but no studies have examined the relative importance of land use and stream order on DOM across seasons and the entire flow regime over multiple years. We utilized an extensive multiyear dataset of weekly to monthly sampling to describe how DOM varied across 21 locations within a river network. Our analysis revealed that land use exerted a greater control on DOM character than stream order in every month of the year, demonstrating that snapshots from a limited number of dates[16−18] may be suitable to characterize DOM dynamics in heterogenous subwatersheds. Despite this strong predictive ability of land use and stream order to explain variability in DOM character, the relationships vary considerably throughout the year. This suggests that the strength of relationships among the various optical properties of DOM as well as its biological lability may vary considerably within a site based on hydrologic conditions and season. In our study watershed, the predictors of DOM characteristics were least influential during the driest months and most influential during transitional (May, November) and winter (December, January) months. The development of more general or universal relationships between DOM properties and proximal drivers such as land use or stream order thus needs to be based on year-round sampling across a wide range of watershed conditions and types.

As rivers reach a critical flow threshold, river reaches may become independent of upstream DOM sources and instead more reflective of local in-stream sources and processes.[33] Our data support this concept, as the primary predictors of DOM characteristics (land use and stream order) explained less of the variation in DOM during the driest months of the year. Dry periods are characterized by long water residence time, shortened longitudinal transport per unit time, less lateral hydrological connectivity with terrestrial and anthropogenic DOM sources, and a greater contribution of groundwater sources.[20,33,60] Our results support the conclusion that these physical drivers have important implications for DOM quality, providing further support for the general principle that DOM quality can be significantly altered by in-stream processes. First, during the driest months of August and September, only 12.4−14.5% of variation in DOM was explained, and it was exclusively attributed to land use. Second, September was the only month when DOM in 1st-order streams was not more recently produced (β/α) than in 2nd−6th-order streams and β/α was an important predictor of bioavailability. The anthropogenic land uses that drive bioavailability (impervious surface and developed land area) were not laterally connected during September. BDOC was often greatest in a highly developed watershed (MLB), but variability in BDOC was not explained by land use in September. In September, the highest BDOC (27% of DOC) occurred in both an entirely forested site (PWT03) and a highly developed watershed (MLB). Our extensive spatial and temporal sampling of DOM character and bioavailability taken together with prior research suggests that long residence time in a river network results in a fundamental alteration of DOM properties and bioavailability.[20,33,61]

Transitions from shoulder seasons (spring, fall) have been identified as critical in controlling "hot moments" of biogeochemical processing in temperate watersheds[56,58] but are also vulnerable to a changing climate.[62,63] These transitional periods provide important windows into the effects of land use and stream order on DOM, as they are times when the effects of these drivers are most evident (37−46% of variance explained) in a river network. The transitional months are characterized by moderate discharge and temperatures, and enhanced resource availability (light, nutrients, and organic matter),[58] and thus appear to provide optimal conditions for transporting allochthonous and anthropogenic sources of DOM while also allowing sufficient residence time for in-stream processing. Stream order explained its maximal amount (4.8%) of variation in DOM in November, and likely this was due to the timing of leaf-fall in the basin, coupled with increased flow from summer and early autumn lows that enhance longitudinal connectivity from lower to higher order. Regional canopy closure typically occurs at the end of May[62] with leaf senescence in early October,[63] and these changes are apparent in the hydrograph (Figure S5). Our observations indicate that despite stream order's minimal influence on DOM variability, its influence is greatest in the post-leaf-fall period. In contrast, land use remains a highly influential predictor of DOM characteristics into the winter, coinciding with a peak in DOM bioavailability. The timing of field sampling is thus key to capturing the full variability of DOM across a heterogeneous landscape.

The pulse-shunt concept posits that snowmelt and large events "shunt" DOM from headwaters to higher-order rivers without the opportunity for biogeochemical processing,[34] and our results provide empirical support for this concept by revealing that bioavailability was greater in the mainstem (LMP73) than in 1st- and 2nd-order streams during these high flow periods. Spring snowmelt has been associated with the export of large loads of labile, terrestrially derived DOM across stream orders.[64] Consistent with the pulse-shunt concept, we found that only during the wettest months typically associated with snowmelt (March and April) were DOC concentrations similar among stream orders. However, DOM character in 1st-order streams was still more recently produced, more autochthonous, and less aromatic than in higher-order streams during these high flow months. This suggests that across stream orders only DOC concentrations were affected by high flow months and not DOM character. Others have also reported homogeneous spatial distribution of terrestrially derived DOM during periods of high flow, which was attributed to short water residence times and high longitudinal connectivity throughout the river network.[33,65] We also found that DOM was less recently produced and indicative of allochthonous sources during these high flow periods.

4.2. Land Use Controls BDOC across Most Anthropogenically Impacted Low-Order Streams. Bioavailability is often inferred from the DOM character, which shows strong relationships with urban or agricultural land use,[28,50] but seldom has BDOC been measured across a river network influenced by anthropogenic land use. Our earlier evaluation within this river network found that BDOC did not vary predictably with stream order (3rd to 6th) in the mainstem.[9] In this study, BDOC was greater in 1st- than in 2nd-order streams reflecting the greater variation in land use and DOM character that occurs within these smallest streams. Our findings reveal the importance of sampling across space and time in a river network to incorporate variation in land use. Our results consistently show that land use, rather than stream order, explains variability in DOM character and its bioavailability. Furthermore, given the high degree of variation that occurs from 1st- to 2nd-order streams, we recommend that future analyses should not aggregate stream order classifications (e.g., 1st to 3rd and 4th to 6th order) because aggregation will mask the variability within the river network.

Land use also appears to control the directionality of the relationship between $SUVA_{254}$ and BDOC. Among headwaters and a single location in the mainstem, we observed a strong negative relationship between bioavailability and $SUVA_{254}$, whereas in our earlier analysis with only mainstem sites, we observed a positive correlation (r = 0.33, p < 0.01).[9] In the earlier study, samples were filtered through a 0.7 μm GF/F filter followed by a 0.2 μm filter and then frozen prior to setting up the incubation where a single microbial inoculum was introduced, and nitrogen and phosphorus were added to incubation vials.[9] These methodological differences limit direct comparisons across studies, but within each study, we expected the directionality of this relationship to be consistent. Although strong relationships of DOM bioavailability with $SUVA_{254}$ have been previously shown to be both positive[23,66,67] and negative,[5−7] urban land use gradients have consistently shown that bioavailability is negatively related to $SUVA_{254}$.[50,68] We attribute the shift in directionality to the high degree of variation in land use and corresponding changes in DOM character that occur in 1st- and 2nd-order streams (wetlands and forested: 39−98.6%), which does not occur in the mainstem (wetlands and forested: >80%).

Although we do not have sufficient information to identify the tipping point in human land use that reverses the relationship between $SUVA_{254}$ and bioavailability, such a reversal is likely to have profound effects on our ability to model the fate of DOM in river networks with simple optical proxies or remotely sensed DOM character.[69,70] High-frequency fluorescence DOM sensors can be effective proxies for DOC concentration, bioavailability, and optical DOM character ($SUVA_{254}$, S_R, FI) and are rapidly becoming incorporated into monitoring programs.[69−71] Our results suggest that site-specific relationships will be required to interpret relationships among various descriptors of DOM character and bioavailability, which limits the ability to make broad-scale inferences at regional or global scales. Further exploration of these relationships within and across river networks would provide essential information for modeling the fate of DOM at broad spatial scales.

With continued land use change over time, the bioavailability of DOM in the smallest and most impacted watersheds is expected to increase. Impervious cover in the suburban Lamprey River watershed ranges from 0.1 to 31.3% in our study subwatersheds, similar to values known to elicit changes in water quality along urban gradients.[50,75] Within the Lamprey watershed, bioavailability was greater when DOM was more recently produced and of autochthonous origin (β/α), a result that is further validated by its low C aromaticity ($SUVA_{254}$). This moderately impacted suburban watershed that exhibits the same trends as highly impacted urban watersheds and indicates that nonpoint source pollution is dramatically altering DOM[50] and stream biogeochemical cycles in suburban as well as urban areas.

Few studies have identified impervious cover as an important predictor of BDOC,[50] and our results indicate that it should be further explored as an important driver even in moderately impacted watersheds. Impervious cover reflects the degree of urbanization and is often associated with significant changes in water quality, including less complex and more bioavailable DOM character[28,50] and salinization of freshwaters.[72−77] Anthropogenic activities also shift DOM stoichiometry[78] and directly contribute novel sources of DOM such as organic fertilizers or sewage runoff,[79,80] ultimately affecting bioavailability. With increases in impervious cover and novel DOM sources causing the most pronounced changes in the smallest streams, integrating anthropogenic land use into existing paradigms is essential to gaining a fundamental understanding of how DOM functions at river network scales.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.1c06305.

Table S1 reports statistical results for two-way ANOVA as predictors of DOM character. Table S2 includes correlations between land use and water quality. Table S3 reports results from repeated measured linear regression as predictors of BDOC. Figure S1 shows how B/α varied as a function of stream order for each month Figure S2 shows how DOC varied as a function of stream order for each month. Figure S3 shows how FI varied as a function of stream order for each month. Figure S4 shows how S_R and HIX varied by month and stream order. Figure S5 depicts the mean daily discharge during the BDOC incubation period. Figure S6 compares mean annual BDOC as a function of stream order (PDF)

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Notes

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