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Key Points:

- Concentrations of dissolved organic matter (DOM) range widely among tributaries of Lake Michigan, peaking in wetland-dominated watersheds and during the fall season
- DOM is smaller in molecular weight and less aromatic in watersheds with little wetland land cover type and in the spring season, whereas alkalinity is positively correlated to urban land cover as well as underlying carbonate geology
- DOM composition varies more in time (i.e., among seasons) than does either organic carbon concentrations or alkalinity

Supporting Information:

Supporting Information may be found in the online version of this article.

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Seasonal and Spatial Variability of Dissolved Carbon Concentration and Composition in Lake Michigan Tributaries

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Abstract Dissolved organic matter (DOM) is a complex mixture of many compounds and its composition dictates numerous reactions in the environment. Large lakes and marine coastlines receive DOM from watersheds that differ widely in their land cover, with potential implications for both the quantity and composition of carbon inputs. Seasonal variation in DOM quantity and composition may also differ among tributaries and be mediated by land cover. Here, we quantify spatially (i.e., among tributary) and seasonal variation in DOM concentration, DOM composition based on ultraviolet-visible spectroscopy, and alkalinity across 101 tributaries of Lake Michigan, one of the world's largest lakes, using a synoptic sampling approach. Wetland land cover has the largest effect on DOM, producing high concentrations of DOM that are more aromatic and larger in apparent molecular weight. Seasonal variation is also pronounced, with concentrations and aromaticity of DOM peaking in fall across most tributaries. Watershed lithology and land cover both affect alkalinity, with higher values associated with the geography of carbonate bedrock and urbanized watersheds. Watershed land cover has a larger effect than season on all organic carbon parameters. However, seasonal variation is especially important for DOM composition. This disparity suggests that the environmental processing of DOM within river channels mediates its composition more than its concentrations. Considering the wide range of land cover and lithology around Lake Michigan and other large water bodies, accounting for both spatial and seasonal dynamics is essential for understanding controls on DOM delivery.

Plain Language Summary Tributaries carry important inputs of water, nutrients, and contaminants to the Great Lakes. We sampled >100 tributaries of Lake Michigan in each season to determine how the type of land surrounding each tributary affects the carbon it brings to Lake Michigan. We considered organic carbon concentration and composition, as well as alkalinity. Wetlands had the largest effect on organic carbon with tributaries from wetland-dominated areas having a higher concentration of organic carbon and organic carbon composition consistent with that originating from the land. Both land cover and geology impact alkalinity with the amount of carbonate species underlying the watershed increasing the alkalinity in the tributary. The season of sample collection is significant for organic carbon but not for alkalinity. Additionally, the season of sample collection has a greater impact on organic carbon composition than it does on concentration. These results yield information about how the broader carbon cycle may be affected as a result of changing landscape types.

1. Introduction

Dissolved forms of carbon represent a significant portion of the global carbon pool (Cole et al., 2007). Dissolved inorganic carbon (DIC) exists as carbonate species in water and is the major contributor to alkalinity in most natural waters (Stumm & Morgan, 1996), although it is important to note non-carbonate species can contribute to alkalinity in some cases (Golub et al., 2017; Hunt et al., 2011). DIC exchanges with carbon dioxide in the atmosphere and can be converted to and from dissolved organic matter (DOM) through a variety of processes (Granéli et al., 1996; Ward et al., 2017). DOM is a mixture of biologically derived molecules that are diverse in their molecular composition, size, and properties. The composition of DOM depends on

its original source (i.e., allochthonous inputs of terrestrial plant matter vs. autochthonous material from algae and microbes), as well as processing via chemical (Gonsior et al., 2009) or biological reactions (D'Andrilli et al., 2015). Anthropogenic pollution such as leaching from impervious surfaces or wastewater discharge can further diversify DOM composition (Bodhipaksha et al., 2017; Hosen et al., 2014).

DOM plays many key roles in aquatic environments, such as fueling microbial metabolism (Lovley et al., 1996; Ward et al., 2017) and absorbing ultraviolet light entering the water (Steinberg et al., 2004). It also mediates reactions that affect the fate of metals and organic contaminants through physical, chemical, and biological processes (Aiken et al., 2011; Raeke et al., 2017; Zhao et al., 2017). For example, DOM in surface waters can both decrease and enhance photochemical reactions that degrade persistent chemicals (Remucal, 2014). Importantly, the composition of DOM affects the rates and extent of many of these reactions (Berg et al., 2019; Maizel et al., 2017). The composition of DOM also represents an important component of water quality as a whole. DOM in drinking water sources can be problematic because reactions with disinfectants such as chlorine and chloramine from toxic by-products (Bulman & Remucal, 2020). Evidence shows these reactions are selective and the composition of DOM in source water affects by-product formation (Lavonen et al., 2013; Milstead & Remucal, 2021).

Despite being among the largest lakes on Earth (Forsyth et al., 2016), the Laurentian Great Lakes (hereafter Great Lakes) are strongly influenced by inflows of nutrients and carbon from tributaries (Marcarelli et al., 2019). Moreover, vast differences among tributaries in watershed land cover, discharge, and chemistry can create substantial differences in loads along the coastline of large lakes and seas (Gloege et al., 2020; Mooney et al., 2020). Indeed, the observed spatial heterogeneity of nearshore nutrients and microbial metabolism within the Great Lakes is at least partially attributable to disparities in tributary inputs (Marcarelli et al., 2019; Stephens & Minor, 2010). Recent work has addressed both spatial and temporal variation in the tributary loading of nutrients across many Great Lakes tributaries revealing that small watersheds can have an outsized influence on nearshore chemistry (Gloege, et al., 2020; Mooney et al., 2020). In contrast, variation in the quantity and composition of dissolved organic carbon inputs and in alkalinity has received less attention across the spectrum of land cover, bedrock geology, and seasonal dynamics.

The concentration of dissolved organic carbon ([DOC]) is much more commonly reported in surface waters than measurements of its composition. For example, previous research reports [DOC] in studies that take place over multiple years (Jane et al., 2017; Strock et al., 2017), as a result of spatial variability (Frost et al., 2006; Mulholland & Hill, 1997), as a function of the season (McCabe & Arnold, 2016), or variability due to a changing climate (Freeman et al., 2004; Schelker et al., 2012; Weyhenmeyer & Karlsson, 2009). However, only a subset of existing [DOC] studies also include measurements of DOM composition (e.g., Dalmagro et al., 2017; Table S1 in Supporting Information S1). While these studies provide useful data, an understanding of the variability in DOM composition across a wide spatial scale is critical for assessing its environmental reactivity.

Here we use ultraviolet-visible (UV-vis) spectroscopy to characterize DOM composition in tributaries of the Great Lakes. This technique is simple and inexpensive compared to other methods (Minor et al., 2014), allowing us to consider differences in DOM composition across our large data set. Additionally, UV-vis spectroscopy is the most commonly used technique for evaluating DOM composition and makes our results easily comparable to other studies (Chin et al., 1994). Furthermore, the development of relationships between more complex DOM characterization (e.g., high-resolution mass spectrometry and nuclear magnetic resonance spectroscopy) and UV-vis measurements make UV-vis analysis even more informative (Kellerman et al., 2015; Nebbioso & Piccolo, 2013).

Here we evaluate patterns of the concentrations and composition of dissolved organic carbon and of alkalinity reaching Lake Michigan during each season from 101 tributaries spanning its >2,000 km circumference that drain watersheds of vastly different size and land cover, likely making the relationships discovered in this study more applicable to other sites. Our primary objectives are to test how land cover and seasonality give rise to spatiotemporal heterogeneity in DOM and to investigate how land cover, seasonality, and lithology affect alkalinity. We hypothesize that land cover influences concentrations of both organic carbon concentration and composition, while alkalinity will additionally be affected by both land cover and geology. By sampling seasonally, we can evaluate whether land cover effects override major swings in

temperature and organic carbon inputs to control both the quantity and composition of DOM. Our goal is to use these broad gradients in watershed context and seasonal conditions to disentangle the drivers of DOM composition from [DOC] and alkalinity, thereby yielding generalizable insights.

2. Materials and Methods

2.1. Materials and Sample Collection

Tributaries surrounding Lake Michigan were sampled in July (n = 97) and October (n = 99) of 2016 and January (n = 63) and March (n = 99) of 2017. We used a synoptic sampling approach to maximize our spatial coverage while minimizing the temporal variability among individual tributaries in each season. This allowed us to capture broad differences in seasonal controls (e.g., overland flow, riparian vegetation, soil temperature) over spatial variability of carbon concentration and composition. Discharge was generally highest in the spring and fall and lowest in the summer during the sampling period relative to means for 2016–2018. However, because of the massive extent of the Lake Michigan coastline, there was inherent temporal variability among tributaries within a season that we could not control. The number of tributaries sampled during each season varied due to shifts inaccessibility (e.g., ice cover during January). Surface water was collected from the main stem of each tributary at the road crossing closest to the mouth using bridge sampling methods (Decker & Simmons, 2013). Samples were immediately filtered through 0.45 μm glass fiber filters and stored in amber glass vials at 4°C. All chemical analyses were performed within one month of sample collection except where noted.

All glassware was combusted at 450°C for 8 hr to mineralize any trace amounts of organic carbon. Potassium hydrogen phthalate (ACS grade) and sulfuric acid (concentrated, ACS grade) were purchased from Fisher Scientific and used as received. All dilutions or blanks were prepared with ultra-pure water from a Milli-Q water purification system maintained at 18.2 MΩ cm.

2.2. Analytical Techniques

A Shimadzu total organic carbon analyzer was used to measure [DOC]; the instrument was calibrated using known concentrations of potassium hydrogen phthalate as standards that were analyzed throughout the sequences. Each sample was injected four times and the results of the last three injections were averaged after confirming that the coefficient of variance was less than 10% for each sample. Similarly, deviations between standards and instrument response ranged from 2% to 10%. Alkalinity was measured using a Mettler Toledo G20 autotitrator that was calibrated with standards obtained from Aqua Solutions. Alkalinity was quantified by measuring the amount of 0.1 N H_2SO_4 required to reach an endpoint of pH 4.5 and is reported as $CaCO_3$ equivalents (Yakushev, 1999); the coefficient of variance of triplicate measurements was less than 5% using this technique. Ultraviolet-visible spectroscopy was used to measure the amount of light absorbed by the sample from 200 to 800 nm. A Shimadzu 2401PC recording spectrophotometer was used and spectra were collected in 1 nm intervals using a quartz cuvette with 1-cm pathlength. Water samples were referenced to ultra-pure water with absorbance from 700 to 800 nm subtracted. Samples whose absorbance values exceeded 1.5 at any wavelength were diluted with ultra-pure water. E_2:E_3 was calculated as the ratio of the absorbance at 250 nm to the absorbance at 365 nm and is inversely proportional to direct measurements of average molecular weight (Helms et al., 2008). Specific ultraviolet absorbance at 254 nm ($SUVA_{254}$) was calculated by dividing the absorbance at 254 nm by the concentration of dissolved organic carbon. $SUVA_{254}$ is positively correlated to the aromaticity of DOM measured by nuclear magnetic resonance spectroscopy (Weishaar et al., 2003).

It was necessary to rerun a subset of [DOC] samples that had been collected in the spring due to instrument malfunction. These samples had been frozen and thawed. To determine the effects of freezing and thawing on DOM analysis, 15 samples that had been successfully analyzed for both [DOC] and UV-vis spectroscopy in the spring were rerun after freezing and thawing and compared to their original values. Linear regression was performed that was then applied to the samples that only had their concentrations quantified after freezing and thawing. Further details and a demonstration of no preferential loss of carbon or change in optical properties is included in Text S1 in Supporting Information S1.

2.3. Data Analyses

We determined the watershed area, % agricultural, % barren, % herbaceous, % forest, % shrubland, % urban, and % wetland for each of the 101 tributaries in the study with the Great Lakes Aquatic Habitat Framework (GLAHF; Forsyth et al., 2016). A multiple linear regression (MLR) model was fitted to variation in each of our four carbon parameters: [DOC], alkalinity, $SUVA_{254}$, and E_2:E_3. Prior to any analysis, the four measurement types (i.e., [DOC], alkalinity, $SUVA_{254}$, and E_2:E_3) and watershed area were $\log_{10}$ transformed to meet model assumptions and to normalize the data. Each model included terms for the watershed area and three major land cover types (i.e., % agricultural, % urban, % wetland, which showed only modest collinearity and low variance inflation factors) as continuous independent variables. The season of sample collection was treated as a categorical independent variable to test for main effects of the season (e.g., differences in [DOC] between summer and winter), as well as interactive effects between season and continuous independent variables (e.g., percent agriculture within a watershed). When using a categorical independent variable with multiple levels in multiple linear regression, one of the levels is inherently set as the reference level for comparison (i.e., the fall season in this analysis; Greenacre & Primicerio, 2014). Only those tributaries that were sampled in all four seasons were included in this analysis ($n = 56$, 59, 55, and 53 for [DOC], E_2:E_3, $SUVA_{254}$, and alkalinity, respectively). Interactions were included to test whether the effects of each land cover type varied with watershed area or season. Bayesian information criterion (BIC) was used to select a final reduced model for each carbon parameter.

Simple linear regressions of all data from each carbon parameter against every land cover type were used to make our results comparable to previous studies. We used Tukey's HSD to test for significant differences among seasons.

To specifically address the hypothesis that geology plays an important role in driving alkalinity in tributaries of Lake Michigan, we characterized the proportion of bedrock as carbonate using geological maps from the GLAHF (Wang et al., 2015). We used MLR to test whether the watershed area, season, and lithology have effects on alkalinity. We represented lithology using a binary classification of whether carbonate bedrock underlies >50% of the watershed. This approach was selected because most watersheds were made up of either predominantly carbonate or non-carbonate (e.g., shale, sandstone) bedrock.

To directly compare spatial and seasonal variations of each of the four-carbon parameters, we calculated coefficients of variation for the standard deviation of untransformed means from each season across all tributaries ($CV_{seasonal}$) and compared them to coefficients of variation for untransformed means of each tributary calculated across all four seasons ($CV_{spatial}$; Equations 1 and 2). Further details of this calculation are described in Text S2 in Supporting Information S1.

$$CV_{spatial} = \frac{\text{standard deviation of tributary means}}{\text{mean of entire data set} * 100} \quad (1)$$

$$CV_{seasonal} = \frac{\text{standard deviation of seasonal means}}{\text{mean of entire data set} * 100} \quad (2)$$

To prevent bias, only those tributaries that were sampled in all four seasons were included in this analysis. All calculations and statistical analyses were performed in *R*.

3. Results and Discussion

3.1. Watershed Information

The watersheds surrounding Lake Michigan are diverse in terms of their size (3.1 km^2 to 16,469 km^2), predominant land cover, and geology. The three dominant types of land cover were urban (1.6%–79.1%), agricultural (0%–91.2%), and wetland (0.1%–78.9%); forest (0.9%–63.1%) and herbaceous (0%–21.4%) were sometimes common, while barren (0%–8.6%) and shrubland (0%–6.1%) classes were always rare. Generally, watersheds with extensive wetlands are located around the northwestern part of Lake Michigan, while agriculture and urban land cover dominate the southern and eastern areas (Figure 1). Underlying geology includes crystalline igneous (0%–38.3%), carbonate (0%–100%), crystalline metamorphic (0%–28.5%), iron formation (0%–0.1%), sandstone (0%–100%), shale (0%–100%), and water (0%–3.6%).

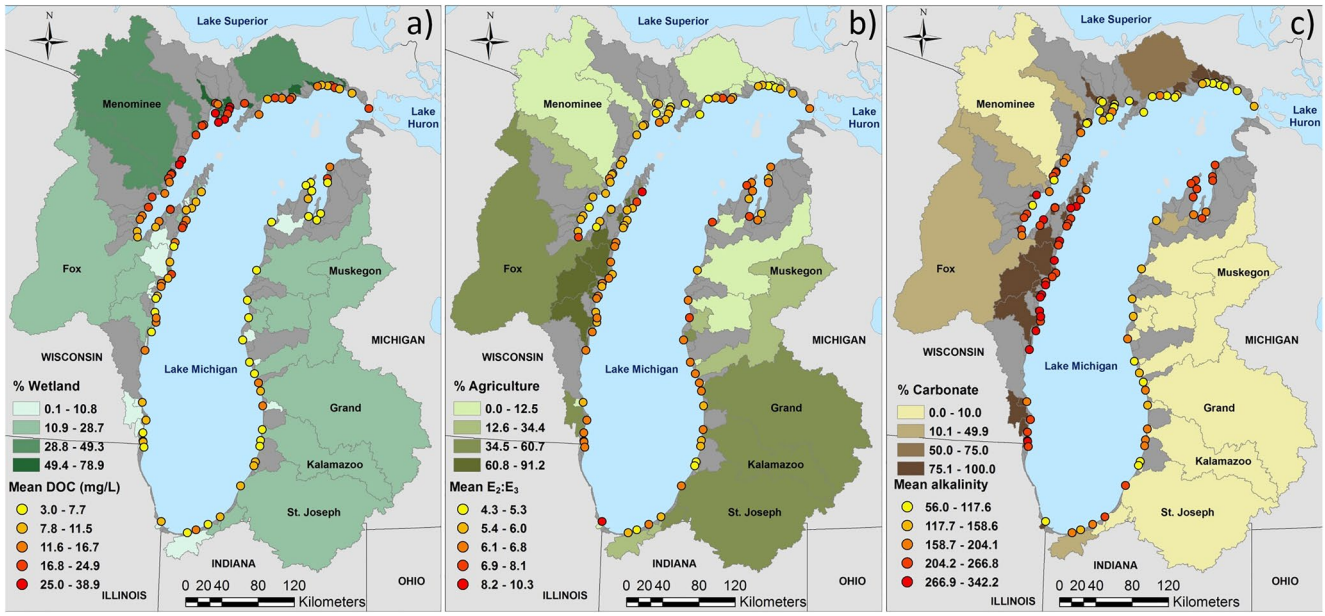

Figure 1. Maps of Lake Michigan tributaries and watersheds. Points represent tributaries sampled where the color corresponds to mean values of (a) dissolved organic carbon concentration in mg-C L^{-1}, (b) E_2:E_3, and (c) alkalinity in units of mg L^{-1} as $CaCO_3$ for all samples collected. Shading of the watersheds represents the (a) % wetland land cover, (b) % agricultural land cover, and (c) % carbonate of the quaternary geology.

3.2. Dissolved Organic Carbon

3.2.1. Spatial Variability

Dissolved organic carbon concentrations measured in the tributaries vary in space and by season. [DOC] ranges from 1.62 to 48.45 mg-C L^{-1} with a mean of 13.1 mg-C L^{-1} (n = 382). Generally, the highest [DOC] values are observed in the tributaries draining into the northwestern part of the lake (Figure 1a). Our [DOC] measurements fall within the ranges previously reported for tributaries of Lake Michigan (Frost et al., 2006; McElmurry et al., 2014) and other Great Lakes (Berg et al., 2019; Minor & Stephens, 2008).

Multiple linear regressions show that both land cover and the season of sample collection influence [DOC] in tributaries. Our reduced model includes terms for % agriculture, % urban, and % wetland in the watershed, as well as the season (Table S2 in Supporting Information S1). The % wetland in the watershed has the most significant positive effect on [DOC] (Figure 2a; Table S2 in Supporting Information S1). Slope coefficients for urban and agricultural land cover are nearly an order of magnitude less than that of wetland land cover (Table S2 in Supporting Information S1). The key contribution of wetland land cover to [DOC]

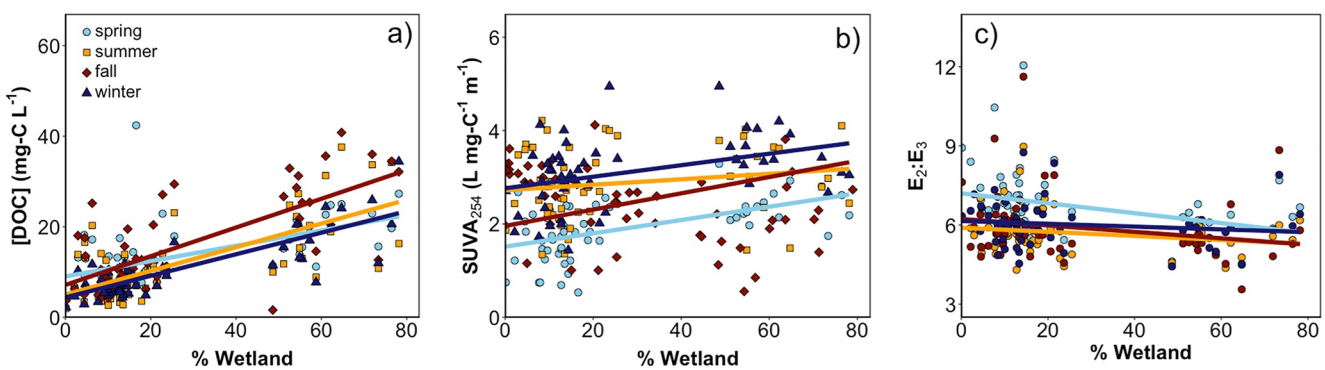

Figure 2. (a) Dissolved organic carbon concentration, (b) specific ultraviolet absorbance at 254 nm, and (c) E_2:E_3 versus % wetland in the watershed. Colors indicate the season. Only tributaries sampled in all four seasons are included in this plot. Slopes, intercepts, and statistics for these plots are given in Tables S3–S5 in Supporting Information S1.

is confirmed using simple linear regression; other land cover types were weakly negatively associated with [DOC] (Figure S3 in Supporting Information S1). Watershed area is not a significant predictor of [DOC] across tributaries (Table S2 in Supporting Information S1).

The primacy of wetlands as a source of DOM in watersheds is well established in the literature (e.g., Cawley et al., 2014; Clark et al., 2004; Dalmagro et al., 2017; Dillon & Molot, 1997; Eckhardt & Moore, 1990; Flint & McDowell, 2015; Frost et al., 2006; Hanley et al., 2013; Kortelainen & Saukkonen, 1995; Mattsson et al., 2005; Palviainen et al., 2016; Xenopoulos et al., 2003). It is noteworthy that this trend is also observed in this data set given the wide range of watershed sizes and landcover types considered, suggesting that this relationship may be universal in freshwater systems. Water draining from wetlands draws upon carbon fixed in both terrestrial and aquatic ecosystems, and the slow rates of flow through saturated soils and shallow standing waters allows ample opportunity for dissolution. There is less consensus about the role of other land cover types. We observe positive relationships between [DOC] and agriculture in the MLR model, in agreement with some studies (Graeber et al., 2012; Shang et al., 2018) but not others (McElmurry et al., 2014). Similarly, the positive relationship between [DOC] and urban land cover in our MLR models aligns with some earlier findings (Aitkenhead-Peterson et al., 2009; Alvarez-Cobelas et al., 2012; Hosen et al., 2014) but not others (McElmurry et al., 2014). The MLR in this study does not consider forest land cover, but there is no obvious association of [DOC] with forest (Figure S3 in Supporting Information S1). In other studies, % forest has been both positively (McElmurry et al., 2014) and negatively correlated to [DOC] (Frost et al., 2006; Graeber et al., 2012).

These inconsistencies across studies may be attributable to differences in sampling design, setting, and extent of comparisons (Table S1 in Supporting Information S1). For example, McElmurry et al. (2014) sampled surface runoff rather than stream channels. In addition, the types of statistics applied across data sets vary substantially with some groups using simple linear regressions (Aitkenhead-Peterson et al., 2009; Cawley et al., 2014; Eckhardt & Moore, 1990) and others using MLR (Alvarez-Cobelas et al., 2012; Clark et al., 2004; Dillon & Molot, 1997; Flint & McDowell, 2015; Frost et al., 2006; Graeber et al., 2012; Hanley et al., 2013; Mattsson et al., 2005; McElmurry et al., 2014; Shang et al., 2018; Xenopoulos et al., 2003). Even among the studies using MLR, the independent predictors tested and model selection methods vary widely (Table S1 in Supporting Information S1).

3.2.2. Seasonal Variability

Seasonality is also an important factor for [DOC], which in the tributaries increases in the order of winter < summer < spring < fall (Figure 3a; Table S10 in Supporting Information S1) with mean values of 10.6, 11.9, 13.5, and 15.5 mg-C L^{-1}, respectively. Median [DOC] values for the same seasons are 8.3, 7.5, 10.3, and 10.6 mg-C L^{-1}, respectively. MLR, which accounts for many additional factors, indicates that [DOC] in the summer and winter is significantly lower than in fall (Table S2 in Supporting Information S1). The different slopes of [DOC] among land cover types also affirm the importance of seasonality; the effect of wetlands was maximal in the fall compared to other seasons (Figure 2a).

Elevated [DOC] is frequently observed in the fall (Aulló-Maestro et al., 2017; Dawson et al., 2011; Flint & McDowell, 2015; Liu et al., 2014; Mattsson et al., 2015; McCabe & Arnold, 2016; Mulholland & Hill, 1997; Oni et al., 2014; McDowell & Fisher, 1976) as organic compounds leach from leaf litter and other plant detritus in the water following the growing season. In these tributaries, elevated discharge during the fall may also have contributed to higher [DOC]. The fall activities of fungi and bacteria may also contribute to releasing DOM into the water (Mulholland & Hill, 1997). Increases in the relative amount of terrestrial DOM are consistent with these hypotheses but cannot be assessed fully considering [DOC] alone. For example, the smaller amount of [DOC] observed in the winter samples may be consistent with either lower terrestrial inputs during this season or decreased microbial activity from autotrophs during the colder months.

3.3. DOM Composition

3.3.1. Spatial Variability

We observe a wide range of $SUVA_{254}$ values (0.35–4.95 L mg-C^{-1} m^{-1}) across Lake Michigan tributaries. The highest $SUVA_{254}$ values (i.e., >3.0 L mg-C^{-1} m^{-1}) are observed in tributaries draining into the northwest

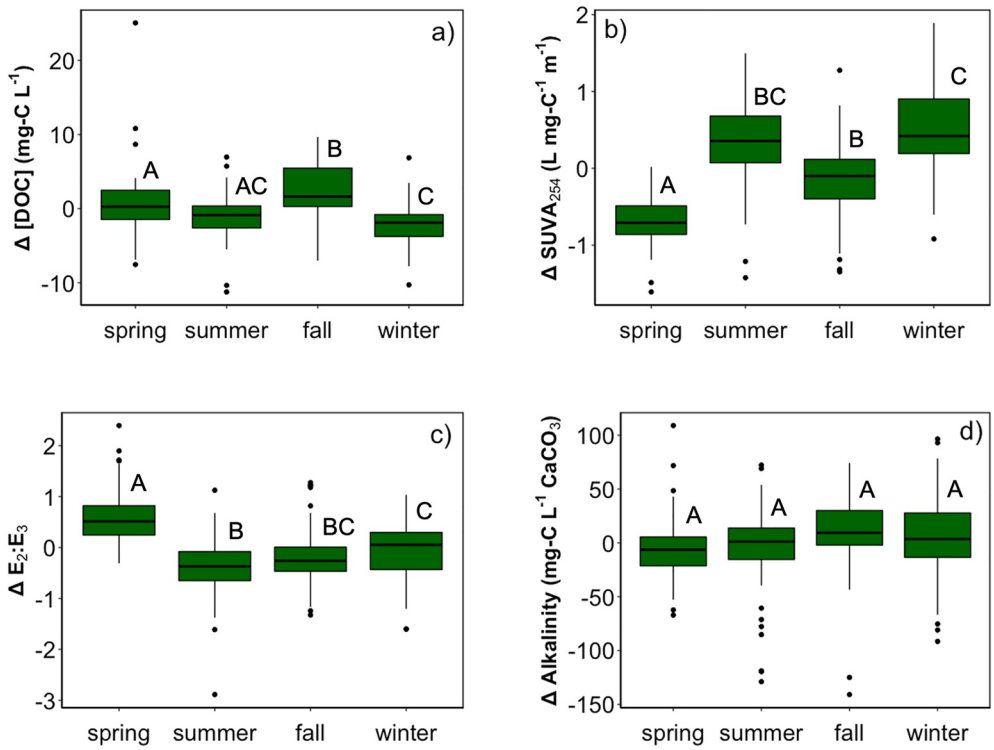

Figure 3. Differences (Δ) for (a) dissolved organic carbon concentration, (b) specific ultraviolet absorbance at 254 nm, (c) E_2:E_3, and (d) alkalinity calculated for the values in each season relative to the mean value in each individual tributary. Only data from tributaries sampled in all four seasons are included. Different letters indicate significant differences based on Tukey HSD comparisons.

part of the lake, where wetland land cover dominates (Figure S4 in Supporting Information S1). These high values are generally indicative of terrestrially-derived DOM that has not been heavily processed (Weishaar et al., 2003), although there are some cases of microbes producing DOM with $SUVA_{254}$ values of ~3.0 L mg-C^{-1} m^{-1} under limited conditions (Thompson & Cotner, 2020). We also observe a wide range of E_2:E_3 values (3.6–12.0), where the upper end of the spectrum suggests either DOM originating from aquatic ecosystems or heavily processed terrestrially-derived molecules (Helms et al., 2014). E_2:E_3 is highest in tributaries located on the eastern and western sides of the lake (Figure 1b). In the remainder of this manuscript, we will refer to DOM composition as determined using optical parameters as proxies for aromaticity and molecular weight; no direct or molecular level analyses were performed.

The preferred MLR model for $SUVA_{254}$ includes season, % agriculture, % urban, and % wetland, along with interaction terms between the watershed area and both % urban and % wetland (Table S6 in Supporting Information S1). Wetland has the strongest positive effects on $SUVA_{254}$ (Figure 2b; Table S6 in Supporting Information S1). Interestingly, agricultural and urban land cover also lead to increased $SUVA_{254}$, which may be attributable to terrestrially-derived DOM and/or limited opportunities for microbial processing. However, the negative interaction terms indicate that these relationships become less important as the size of the watershed, and therefore hydraulic residence time, increases (Table S5 in Supporting Information S1).

The strongest patterns in E_2:E_3 are attributable to seasonality, but wetland land cover and watershed size are significant correlates as well (Table S7 in Supporting Information S1). E_2:E_3 increases with wetland dominance in the MLR, which is contradictory to the hypothesis that wetland DOM is high in apparent molecular weight and is opposite the negative trends observed in simple linear regressions between E_2:E_3 and % wetland (Figure 2c and Figure S7 in Supporting Information S1). However, this positive term is an order of magnitude lower than any of the seasonal terms and there is also a significant negative interaction between wetlands and watershed areas, suggesting that the influence of wetlands on E_2:E_3 is attenuated in large watersheds (Figure 2c; Figure S7 and Table S7 in Supporting Information S1).

$SUVA_{254}$ and E_2:E_3 are generally inversely proportional to one another (Fichot & Benner, 2011), and that is the case for Lake Michigan tributaries. When considered by land cover classes, the expected inverse relationship applied to all types except the herbaceous land cover, which was uncommon in these watersheds (Figures S5 and S6 in Supporting Information S1). This opposing relationship is not obvious considering the MLR results alone as the MLR for $SUVA_{254}$ and E_2:E_3 include different terms (Tables S6 and S7 in Supporting Information S1). This result may be attributable to the fact that optical properties depend on both the source of the carbon and the extent of the environmental processing of DOM.

Overall, the optical properties describing the composition of DOM show less spatial variability than [DOC]. The literature supports our observation that terrestrially-sourced DOM is consistently and positively correlated to % wetland using UV-vis spectroscopy (Hanley et al., 2013) or fluorescence spectroscopy (Graeber et al., 2012; Singh et al., 2017; Williams et al., 2010). This observation is due to a large amount of plant-derived (i.e., allochthonous) carbon present in wetlands that are transferred into stream water. In addition, this organic carbon is fresh and therefore has had little opportunity to undergo environmental processing, which generally results in lower aromaticity and molecular weight (Helms et al., 2013; Minor et al., 2007). Terrestrially-sourced DOM has also been correlated to other land cover types in the literature including % agriculture using UV-vis (McElmurry et al., 2014) and fluorescence spectroscopy (Graeber et al., 2012), as well as to % forest using UV-vis (McElmurry et al., 2014) and fluorescence spectroscopy (Singh et al., 2017). Microbially-sourced (i.e., autochthonous) DOM or more environmentally processed DOM, which is represented with low $SUVA_{254}$ and high E_2:E_3 values in this study, has been correlated to % forest with fluorescence spectroscopy (Heinz et al., 2015), to % urban with both UV-vis (McElmurry et al., 2014) and fluorescence spectroscopy (Chen et al., 2017; Hosen et al., 2014; Lu et al., 2014), and to % agriculture with UV-vis spectroscopy (Shang et al., 2018; Table S1 in Supporting Information S1).

3.3.2. Seasonal Variability

Seasonality has important effects on both $SUVA_{254}$ and E_2:E_3. $SUVA_{254}$ values increase in the order of spring < fall < summer < winter (Figure 3b; Table S11 in Supporting Information S1), with mean values of 1.98, 2.49, 2.95, and 3.10 L mg-C^{-1} m^{-1}, respectively. The MLR for $SUVA_{254}$ similarly demonstrates that values in the spring are lowest and values in summer and winter are higher than those in the fall (Table S6 in Supporting Information S1). E_2:E_3 values increase in the order of summer < fall < winter < spring (Figure 3c; Table S12 in Supporting Information S1), with seasonal mean values of 5.70, 5.92, 6.02, and 6.71, respectively. In the MLR, values in spring are lower than those in the fall (Table S7 in Supporting Information S1).

Ours is among the first studies to analyze the seasonal dynamics of organic matter composition in parallel with a concentration across a wide range of streams (Table S1 in Supporting Information S1), particularly across such a large spatial scale, and shows clear evidence of seasonal variation in DOM composition as well as concentrations. Previous reports of seasonal variation in DOM composition have been mixed, ranging from no effects observed using fluorescence spectroscopy (Heinz et al., 2015), to decreasing $SUVA_{254}$ over the warm months (i.e., spring to fall; McCabe & Arnold, 2016; Müller et al., 2014), increasing absorbance during the spring snowmelt (Cao et al., 2016; Macdonald & Minor, 2013), and higher E_2:E_3 in the winter as compared to summer (Yates et al., 2016). Most likely, these variable seasonal patterns are due to complex interactions between land cover and climatic seasonality.

The seasonal dynamics of DOM optical properties may reflect a combination of carbon sources, environmental processing of organic carbon, and dilution by hydrological fluctuations. The relative variations in optical properties do not follow fluctuations in discharge, which were highest in the spring and fall and lowest in the summer relative to mean discharge for 2016–2018, but higher temporal resolution data is needed to thoroughly evaluate these relationships. High $SUVA_{254}$ values in the fall can be partially explained by leaching from newly-arrived leaf litter (Mulholland & Hill, 1997), though only a modest proportion of watershed area in Lake Michigan tributaries is vegetated with deciduous trees. Conversely, we observe high E_2:E_3 and low $SUVA_{254}$ in the spring when new plant growth is only just starting in this region, leaving DOM pools dependent on older, more processed forms of organic carbon. We also see the signature of microbial activity in the DOM composition proxies. Both heterotrophic respiration of DOM and autotrophic production of DOM generally produces DOM with lower molecular weight (i.e., higher E_2:E_3) and lower aromaticity (i.e., lower $SUVA_{254}$; Bai et al., 2017; Mulholland & Hill, 1997; Zhou et al., 2019), and we see these shifts

across most tributaries in the spring when terrestrial inputs are minimal but microbes are able to resume their activity under warming temperatures. Photobleaching could also result in decreased $SUVA_{254}$ and increased E_2:E_3 (Aulló-Maestro et al., 2017; Brinkmann et al., 2003; Cory et al., 2007; Helms et al., 2008, 2014; Macdonald & Minor, 2013; Minor & Stephens, 2008; Vodacek et al., 1997) and could be most influential around the time of our spring sampling when there is little canopy cover. However, if additional light exposure due to lack of canopy cover were the primary driving factor, low $SUVA_{254}$ and high E_2:E_3 would also be expected in the winter in tributaries without ice cover. Our winter results are also interesting because both optical properties showed high values, which could reflect either the dominance of small, aromatic compounds or large compounds that are not aromatic. Since no new terrestrial inputs are expected during the winter, these compounds are likely either microbially-derived or other highly recalcitrant compounds.

3.4. Alkalinity

Alkalinity is a measurement of the buffering capacity of water. Alkalinity is sometimes used as a proxy for dissolved inorganic carbon because carbonate species are the main buffering components in natural waters (Stumm & Morgan, 1996), particularly in highly alkaline systems with slightly alkaline pH values (i.e., along the western shore of Lake Michigan). However, non-carbonate species can contribute to alkalinity in some cases (Golub et al., 2017; Hunt et al., 2011) and it is important to note that alkalinity and DIC are not necessarily interchangeable terms.

In this study, alkalinity ranges from 11.6 to 468 mg L^{-1} as $CaCO_3$, with a mean of 197 mg L^{-1} as $CaCO_3$. Alkalinity significantly correlates with certain land cover types (Figure S8 in Supporting Information S1). The best MLR model includes terms for % agriculture, % urban, watershed area, and an interaction term between agriculture and watershed area (Table S8 in Supporting Information S1). We observe the highest alkalinity values along the western side of Lake Michigan (Figure 1c), where urban land cover predominates. The positive association between alkalinity and urban land cover may be augmented by weathering of concrete (Kaushal et al., 2017).

In addition to the influence of land cover on alkalinity, bedrock lithology also plays a mediating role because bicarbonate (i.e., the dominant buffer in most natural waters) can originate from watershed mineral weathering (Raymond & Hamilton, 2018). Watersheds that are dominated by carbonate bedrock have significantly higher alkalinity than those where shale and sandstone predominate (Table S9 in Supporting Information S1), in keeping with previous findings (Mosher et al., 2010). We find a negative statistical interaction between watershed area, which generally increases alkalinity, and our binary carbonate variable, presumably resulting from the diversity of bedrock lithologies in large watersheds (Figure 1c). Interestingly, there are some wetland-dominated watersheds located on the northern end of Lake Michigan that have high % watershed carbonate but low alkalinity (Figure 1c). These sites may have their limestone bedrock capped by sediment that limits dissolution and exchange with stream water. Collectively, these results demonstrate that carbonate weathering is an important control of alkalinity in tributaries.

Alkalinity increases in the order of spring < summer < winter < fall (Figure 3d; Table S13 in Supporting Information S1). However, the best MLR model does not include seasonal effects, nor were pairwise differences statistically significant. This further suggests that geology, rather than land cover or seasonality, is the main driver of alkalinity (Tables S8 and S9 in Supporting Information S1). The emergence of urban land cover as a correlate of alkalinity is presumably attributable to the dissolution of concrete, which appears to have no strong seasonal signal. In addition, in the geology MLR, carbonate material is positively correlated to alkalinity which also does not change with the season.

3.5. Spatial/Seasonal Comparison

One of the primary objectives of this study is to compare spatial versus seasonal variation in both concentration and composition of DOM and alkalinity in Lake Michigan tributaries. Our MLR models suggest that differences among watershed land cover have the most predictable effect on concentration parameters (i.e., [DOC] and alkalinity), while seasonality has a more consistent influence on DOM composition (i.e., $SUVA_{254}$ and E_2:E_3). In fact, only seasonal effects were statistically significant for E_2:E_3 when complex

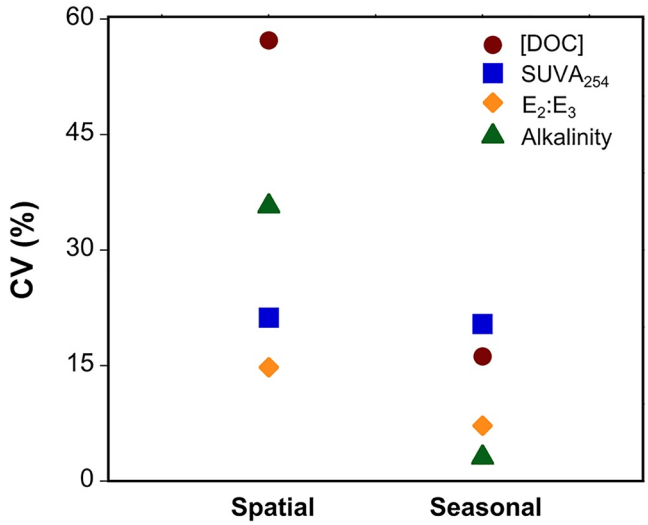

Figure 4. Coefficients of variation, $CV_{spatial}$, and $CV_{seasonal}$, for dissolved organic carbon concentration, alkalinity, specific ultraviolet absorbance at 254 nm, and E_2:E_3 measured in tributaries that were sampled in all four seasons. $CV_{spatial}$ is calculated as the standard deviation of tributary means divided by the mean of the entire data set. $CV_{seasonal}$ is calculated as the standard deviation of seasonal means divided by the mean of the entire data set.

interaction terms are excluded. To further assess organic carbon and alkalinity variation among watersheds and seasons, we compare coefficients of variation associated with our spatial versus seasonal observations.

For all four parameters tested, $CV_{spatial} > CV_{seasonal}$ (Figure 4). However, the difference in magnitude between spatial and seasonal CV is modest for the compositional parameters $SUVA_{254}$ and E_2:E_3. Thus, we infer that seasonal variation across sites creates almost as much variation in DOM composition as the myriad differences in the watershed area, land cover, human population density, and other factors. In contrast, dissolved organic concentrations and alkalinity are primarily a reflection of disparities among watersheds and show limited seasonal signals.

The differential partitioning of spatial and seasonal variation between carbon concentrations and composition is an important insight arising from our comprehensive synoptic sampling approach and underscores the distinction between carbon sourcing and carbon processing. Contrasts in carbon source among watersheds are presumably stable across seasons, such that land cover and its correlates drive most variation in DOM concentrations, and bedrock lithology and urban concrete strongly influence alkalinity. We recognize that microbial and plant production of DOM varies widely throughout the year due to temperature, seasonal tissue senescence (e.g., leaf fall), water availability, and other factors, so it is interesting that such seasonal dynamics create only modest signals in [DOC].

The comparable magnitude of seasonal- and watershed-scale variation in DOM composition suggests that substantial seasonal variation in the processing of DOM in aquatic environments is overlaid on the seasonality of carbon inputs. Our optical proxies for the aromaticity and size of organic carbon molecules show the clear seasonal variation that accords with differences in molecular weight and aromaticity. Although we have no data on process rates in these tributaries, the seasonal shifts in DOM composition are large enough to signify more than just fluctuations in the magnitude and source of inputs. A host of biological and chemical reactions convert DOM from one form to another, which would result in minor shifts in overall [DOC] but substantial changes in $SUVA_{254}$ and E_2:E_3. For instance, conversion of newly leached allochthonous DOM into more recalcitrant DOM could be important in the fall season when there are relatively large inputs of leaves from deciduous trees. Our seasonal measurements across the tributaries suggest that such DOM processing produces a strong signature in the annual cycle of dissolved carbon availability and composition across the Lake Michigan basin.

4. Conclusions and Implications

We have documented extensive spatial and seasonal variation in both the concentration and composition of carbon forms across Lake Michigan tributaries. Our results show that land cover, lithology, and other differences among watersheds play a strong role in dictating dissolved organic carbon concentrations, the optical properties of DOM, and alkalinity. In contrast, seasonal dynamics affect the composition of DOM more strongly than its abundance or alkalinity. By extending our sampling through all four seasons, we also detect complex interactions between watershed attributes and seasonality that will require further work to understand. Taken together, our extensive survey captures strong signals of both spatial and seasonal drivers of stream carbon dynamics, underscoring the fact that local-scale variation must be interpreted in light of both landscape and seasonal context. Nonetheless, the parallel patterns of land cover and seasonal influences across so many discrete watersheds suggest a strong capacity for generalization within this geographic region. Further, while our synoptic approach captured broad seasonal patterns of spatial carbon dynamics for nearly 100 tributaries, determining specific temporal drivers of carbon concentration and composition (e.g., discharge-concentration relationships for individual tributaries) would build upon the temporal patterns we have discussed. While challenging across the spatial scale of a Great Lake, increased

temporal frequency of sampling could further resolve the complex spatial and temporal controls on carbon concentration and composition (Wayland et al., 2003). Integrating carbon variability across all stages of a tributary hydrograph under other seasonal biotic and abiotic controls, such as riparian vegetation and soil temperature, respectively, would further our understanding of carbon dynamics in regions that experience seasonal climatic shifts.

As the land cover and weather seasonality are shifting across the globe, there is a pressing need to understand the implications for carbon processing (Williams et al., 2015). The dynamic and interactive effects of spatial (i.e., between watershed) and seasonal factors documented in this study underscore the complexity of environmental controls on aquatic carbon, yet the strong signals of land cover and seasonal succession also offer hope for interpreting and predicting future carbon processing. Both land cover and climate are changing throughout much of the Great Lakes basin (D'Orgeville et al., 2014; Radeloff et al., 2012), so corresponding changes in dissolved carbon concentrations and composition are to be expected. The strong influence of wetland areas on DOM is particularly noteworthy because these extensive, water-saturated environments are sensitive to climate change and local human activities. Ultimately, we must also consider the net effect of these changes on the Great Lakes themselves, whose coastal ecosystems are strongly affected by the chemistry of inflowing tributaries (Mooney et al., 2020). Indeed, the seasonal swings in DOM concentrations documented here should be sufficient to measure by remote sensing, creating the possibility of higher-frequency observations than are feasible using extensive field surveys like ours. Integrating mechanistic perspectives and large-scale observational studies, whether in situ or remotely sensed, is a critical frontier in predicting the dynamics of dissolved carbon sources and processing across heterogenous landscapes like the Lake Michigan basin.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

Supporting Information S1 including additional information about methods and model outputs is provided. Raw data are made publicly available as a.csv file through the MINDS@UW repository (http://digital.library.wisc.edu/1793/82308; DOI: https://doi.org/10.21231/s6k0-y614; no registration required; licensing: CC-BY-NC).

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References

Aiken, G. R., Hsu-Kim, H., & Ryan, J. N. (2011). Influence of dissolved organic matter on the environmental fate of metals, nanoparticles, and colloids. *Environmental Science & Technology*, *45*(8), 3196–3201. https://doi.org/10.1021/es103992s

Aitkenhead-Peterson, J. A., Steele, M. K., Nahar, N., & Santhy, K. (2009). Dissolved organic carbon and nitrogen in urban and rural watersheds of south-central Texas: Land use and land management influences. *Biogeochemistry*, *96*(1), 119–129. https://doi.org/10.1007/s10533-009-9348-2

Alvarez-Cobelas, M., Angeler, D. G., Sánchez-Carrillo, S., & Almendros, G. (2012). A worldwide view of organic carbon export from catchments. *Biogeochemistry*, *107*(1–3), 275–293. https://doi.org/10.1007/s10533-010-9553-z

Aulló-Maestro, M. E., Hunter, P., Spyrakos, E., Mercatoris, P., Kovács, A., Horváth, H., et al. (2017). Spatio-seasonal variability of chromophoric dissolved organic matter absorption and responses to photobleaching in a large shallow temperate lake. *Biogeosciences*, *14*(5), 1215–1233. https://doi.org/10.5194/bg-14-1215-2017

Bai, L., Cao, C., Wang, C., Xu, H., Zhang, H., Slaveykova, V. I., & Jiang, H.-L. (2017). Towards quantitative understanding of the bioavailability of dissolved organic matter in freshwater lake during cyanobacteria blooming. *Environmental Science & Technology*, *51*, 6018–6026. https://doi.org/10.1021/acs.est.7b00826

Berg, S. M., Whiting, Q. T., Herrli, J. A., Winkels, R., Wammer, K. H., & Remucal, C. K. (2019). The role of dissolved organic matter composition in determining photochemical reactivity at the molecular level. *Environmental Science & Technology*, *53*(20), 11725–11734. https://doi.org/10.1021/acs.est.9b03007

Bodhipaksha, L. C., Sharpless, C. M., Chin, Y. P., & MacKay, A. A. (2017). Role of effluent organic matter in the photochemical degradation of compounds of wastewater origin. *Water Research*, *110*, 170–179. https://doi.org/10.1016/j.watres.2016.12.016

Brinkmann, T., Sartorius, D., & Frimmel, F. H. (2003). Photobleaching of humic rich dissolved organic matter. *Aquatic Sciences*, *65*(4), 415–424. https://doi.org/10.1007/s00027-003-0670-9

Bulman, D. M., & Remucal, C. K. (2020). Role of reactive halogen species in disinfection byproduct formation during chlorine photolysis. *Environmental Science & Technology*, *54*(15), 9629–9639. https://doi.org/10.1021/acs.est.0c02039

Cao, X., Aiken, G. R., Spencer, R. G. M., Butler, K., Mao, J., & Schmidt-Rohr, K. (2016). Novel insights from NMR spectroscopy into seasonal changes in the composition of dissolved organic matter exported to the Bering Sea by the Yukon River. *Geochimica Cosmochimica Acta*, *181*, 72–88. https://doi.org/10.1016/j.gca.2016.02.029

Cawley, K. M., Campbell, J., Zwilling, M., & Jaffé, R. (2014). Evaluation of forest disturbance legacy effects on dissolved organic matter characteristics in streams at the Hubbard Brook Experimental Forest, New Hampshire. *Aquatic Sciences*, *76*(4), 611–622. https://doi.org/10.1007/s00027-014-0358-3

Chen, H., Liao, Z. L., Gu, X. Y., Xie, J. Q., Li, H. Z., & Zhang, J. (2017). Anthropogenic influences of paved runoff and sanitary sewage on the dissolved organic matter quality of wet weather overflows: An excitation-emission matrix parallel factor analysis assessment. *Environmental Science & Technology*, *51*(3), 1157–1167. https://doi.org/10.1021/acs.est.6b03727

Chin, Y. P., Alken, G., & O'Loughlin, E. (1994). Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances. *Environmental Science & Technology*, *28*(11), 1853–1858. https://doi.org/10.1021/es00060a015

Clark, M. J., Cresser, M. S., Smart, R., Chapman, P. J., & Edwards, A. C. (2004). The influence of catchment characteristics on the seasonality of carbon and nitrogen species concentrations in upland rivers of Northern Scotland. *Biogeochemistry*, *68*, 1–19. https://doi.org/10.1023/b:biog.0000025733.07568.11

Cole, J. J., Prairie, Y. T., Caraco, N. F., McDowell, W. H., Tranvik, L. J., Striegl, R. G., et al. (2007). Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget. *Ecosystems*, *10*(1), 171–184. https://doi.org/10.1007/s10021-006-9013-8

Cory, R. M., McKnight, D. M., Chin, Y. P., Miller, P., & Jaros, C. L. (2007). Chemical characteristics of fulvic acids from Arctic surface waters: Microbial contributions and photochemical transformations. *Journal of Geophysical Research: Biogeosciences*, *112*(4), 1–14. https://doi.org/10.1029/2006jg000343

D'Orgeville, M., Peltier, W. R., Erler, A. R., and Gula, J. (2014). Climate change impacts on Great Lakes Basin precipitation extremes. *Journal of Geophysical Research*, *119*(18), 10799–10812.

D'Andrilli, J., Cooper, W. T., Foreman, C. M., & Marshall, A. G. (2015). An ultrahigh-resolution mass spectrometry index to estimate natural organic matter lability. *Rapid Communications in Mass Spectrometry*, *29*, 2385–2401. https://doi.org/10.1002/rcm.7400

Dalmagro, H. J., Johnson, M. S., de Musis, C. R., Lathuillière, M. J., Graesser, J., Pinter-Júnior, O. B., & Cuoto, E. G. (2017). Spatial patterns of DOC concentration and DOM optical properties in a Brazilian troptical river-wetland system. *Journal of Geophysical Research: Biogeosciences*, *122*(8), 1883–1902. https://doi.org/10.1002/2017jg003797

Dawson, J. J. C., Tetzlaff, D., Speed, M., Hrachowitz, M., & Soulsby, C. (2011). Seasonal controls on DOC dynamics in nested upland catchments in NE Scotland. *Hydrological Processes*, *25*(10), 1647–1658. https://doi.org/10.1002/hyp.7925

Decker, C., & Simmons, K. (2013). *Surface water sampling* (pp. 1–22). USEPA Publication.

Dillon, P. J., & Molot, L. A. (1997). Effect of landscape form on export of dissolved organic carbon, iron, and phosphorus from forested stream catchments. *Water Resources Research*, *33*(11), 2591–2600. https://doi.org/10.1029/97wr01921

Eckhardt, B. W., & Moore, T. R. (1990). Controls on dissolved organic carbon concentrations in streams, southern Quebec. *Canadian Journal of Fisheries and Aquatic Sciences*, *47*(8), 1537–1544. https://doi.org/10.1139/f90-173

Fichot, C. G., & Benner, R. (2011). A novel method to estimate DOC concentrations from CDOM absorption coefficients in coastal waters. *Geophysical Research Letters*, *38*(3), 1–5. https://doi.org/10.1029/2010gl046152

Flint, S. A., & McDowell, W. H. (2015). Effects of headwater wetlands on dissolved nitrogen and dissolved organic carbon concentrations in a suburban New Hampshire watershed. *Freshwater Sciences*, *34*(2), 456–471. https://doi.org/10.1086/680985

Forsyth, D. K., Riseng, C. M., Wehrly, K. E., Mason, L. A., Gaiot, J., Hollenhorst, T., et al. (2016). The Great Lakes hydrography dataset: Consistent, binational watersheds for the Laurentian Great Lakes basin. *Journal of the American Water Resources Association*, *52*(5), 1068–1088. https://doi.org/10.1111/1752-1688.12435

Freeman, C., Fenner, N., Ostle, N. J., Kang, H., Dowrick, D. J., Reynolds, B., et al. (2004). Export of dissolved organic carbon from peatlands under elevated carbon dioxide levels. *Nature*, *430*(6996), 195–198. https://doi.org/10.1038/nature02707

Frost, P. C., Larson, J. H., Johnston, C. A., Young, K. C., Maurice, P. A., Lamberti, G. A., & Bridgham, S. D. (2006). Landscape predictors of stream dissolved organic matter concentration and physicochemistry in a Lake Superior river watershed. *Aquatic Sciences*, *68*(1), 40–51. https://doi.org/10.1007/s00027-005-0802-5

Gloege, L., McKinley, G. A., Mooney, R. J., Allan, J. D., Diebel, M. W., & McIntyre, P. B. (2020). Lake hydrodynamics intensify the potential impact of watershed pollutants on coastal ecosystem services. *Environmental Research Letters*, *15*, 1–28. https://doi.org/10.1088/1748-9326/ab7f62

Golub, M., Desai, A. R., McKinley, G. A., Remucal, C. K., & Stanley, E. H. (2017). Large uncertainty in estimating pCO_2 from carbonate equilibria in lakes. *Journal of Geophysical Research: Biogeosciences*, *122*, 2909–2924. https://doi.org/10.1002/2017jg003794

Gonsior, M., Peake, B. M., Cooper, W. T., Podgorski, D., D'Andrilli, J., & Cooper, W. J. (2009). Photochemically induced changes in dissolved organic matter identified by ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry. *Environmental Science & Technology*, *43*, 698–703. https://doi.org/10.1021/es8022804

Graeber, D., Gelbrecht, J., Pusch, M. T., Anlanger, C., & von Schiller, D. (2012). Agriculture has changed the amount and composition of dissolved organic matter in Central European headwater streams. *The Science of the Total Environment*, *438*, 435–446. https://doi.org/10.1016/j.scitotenv.2012.08.087

Granéli, W., Lindell, M., & Tranvik, L. (1996). Photo-oxidative production of dissolved inorganic carbon in lakes of different humic content. *Limnology and Oceanography*, *41*(4), 698–706. https://doi.org/10.4319/lo.1996.41.4.0698

Greenacre, M., & Primicerio, R. (2014). *Multivariate analysis of ecological data*. Fundacion BBVA.

Hanley, K. W., Wollheim, W. M., Salisbury, J., Huntington, T., & Aiken, G. (2013). Controls on dissolved organic carbon quantity and chemical character in temperate rivers of North America. *Global Biogeochemical Cycles*, *27*(2), 492–504. https://doi.org/10.1002/gbc.20044

Heinz, M., Graeber, D., Zak, D., Zwirnmann, E., Gelbrecht, J., & Pusch, M. T. (2015). Comparison of organic matter composition in agricultural versus forest affected headwaters with special emphasis on organic nitrogen. *Environmental Science & Technology*, *49*(4), 2081–2090. https://doi.org/10.1021/es505146h

Helms, J. R., Mao, J., Stubbins, A., Schmidt-Rohr, K., Spencer, R. G. M., Hernes, P. J., & Mopper, K. (2014). Loss of optical and molecular indicators of terrigenous dissolved organic matter during long-term photobleaching. *Aquatic Sciences*, *76*(3), 353–373. https://doi.org/10.1007/s00027-014-0340-0

Helms, J. R., Stubbins, A., Perdue, E. M., Green, N. W., Chen, H., & Mopper, K. (2013). Photochemical bleaching of oceanic dissolved organic matter and its effect on absorption spectral slope and fluorescence. *Marine Chemistry*, *155*, 81–91. https://doi.org/10.1016/j.marchem.2013.05.015

Helms, J. R., Stubbins, A., Ritchie, J. D., Minor, E. C., Kieber, D. J., & Mopper, K. (2008). Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter. *Limnology and Oceanography*, *53*(3), 955–969. https://doi.org/10.4319/lo.2008.53.3.0955

Hosen, J. D., McDonough, O. T., Febria, C. M., & Palmer, M. A. (2014). Dissolved organic matter quality and bioavailability changes across an urbanization gradient in headwater streams. *Environmental Science & Technology*, *48*(14), 7817–7824. https://doi.org/10.1021/es501422z

Hunt, C. W., Salisbury, J. E., & Vandemark, D. (2011). Contribution of non-carbonate anions to total alkalinity and overestimation of pCO_2 in New England and New Brunswick rivers. *Biogeosciences 8*, 3069–3076. https://doi.org/10.5194/bg-8-3069-2011

Jane, S. F., Winslow, L. A., Remucal, C. K., & Rose, K. C. (2017). Long-term trends and synchrony in dissolved organic matter characteristics in Wisconsin, USA, lakes: Quality, not quantity, is highly sensitive to climate. *Journal of Geophysical Research: Biogeosciences*, *122*(3), 546–561. https://doi.org/10.1002/2016jg003630

Kaushal, S. S., Duan, S., Doody, T. R., Haq, S., Smith, R. M., Newcomer Johnson, T. A., et al. (2017). Human-accelerated weathering increases salinization, major ions, and alkalinization in fresh water across land use. *Applied Geochemistry*, *83*, 121–135. https://doi.org/10.1016/j.apgeochem.2017.02.006

Kellerman, A. M., Kothawala, D. N., Dittmar, T., & Tranvik, L. J. (2015). Persistence of dissolved organic matter in lakes related to its molecular characteristics. *Nature Geoscience*, *8*(6), 454–457. https://doi.org/10.1038/ngeo2440

Kortelainen, P., & Saukkonen, S. (1995). Organic vs. minerogenic acidity in headwater streams in Finland. *Water, Air, and Soil Pollution*, *85*(2), 559–564. https://doi.org/10.1007/bf00476888

Lavonen, E. E., Gonsior, M., Tranvik, L. J., Schmitt-kopplin, P., & Ko, S. J. (2013). Selective chlorination of natural organic matter : Identification of previously unknown disinfection byproducts. *Environmental Science & Technology*, *47*, 2264–2271. https://doi.org/10.1021/es304669p

Liu, W., Xu, X., McGoff, N. M., Eaton, J. M., Leahy, P., Foley, N., & Kiely, G. (2014). Spatial and seasonal variation of dissolved organic carbon (DOC) concentrations in Irish streams: Importance of soil and topography characteristics. *Environmental Management*, *53*(5), 959–967. https://doi.org/10.1007/s00267-014-0259-1

Lovley, D. R., Coatest, J. D., Blunt-harris, E. L., Phillipst, E. J. P., & Woodward, J. C. (1996). Humic substances as electron acceptors for microbial respiration. *Nature*, *382*(1), 445–448. https://doi.org/10.1038/382445a0

Lu, Y. H., Bauer, J. E., Canuel, E. A., Chambers, R. M., Yamashita, Y., Jaffé, R., & Barrett, A. (2014). Effects of land use on sources and ages of inorganic and organic carbon in temperate headwater streams. *Biogeochemistry*, *119*(1–3), 275–292. https://doi.org/10.1007/s10533-014-9965-2

Macdonald, M. J., & Minor, E. C. (2013). Photochemical degradation of dissolved organic matter from streams in the western Lake Superior watershed. *Aquatic Sciences*, *75*(4), 509–522. https://doi.org/10.1007/s00027-013-0296-5

Maizel, A. C., Li, J., & Remucal, C. K. (2017). Relationships between dissolved organic matter composition and photochemistry in lakes of diverse trophic status. *Environmental Science & Technology*, *51*(17), 9624–9632. https://doi.org/10.1021/acs.est.7b01270

Marcarelli, A. M., Coble, A. A., Meingast, K. M., Kane, E. S., Brooks, C. N., Buffam, I., et al. (2019). Of small streams and Great Lakes: Integrating tributaries to understand the ecology and biogeochemistry of Lake Superior. *Journal of the American Water Resources Association*, *55*(2), 442–458. https://doi.org/10.1111/1752-1688.12695

Mattsson, T., Kortelainen, P., & Räike, A. (2005). Export of DOM from boreal catchments: Impacts of land use cover and climate. *Biogeochemistry*, *76*(2), 373–394. https://doi.org/10.1007/s10533-005-6897-x

Mattsson, T., Kortelainen, P., Räike, A., Lepistö, A., & Thomas, D. N. (2015). Spatial and temporal variability of organic C and N concentrations and export from 30 boreal rivers induced by land use and climate. *The Science of the Total Environment*, *508*, 145–154. https://doi.org/10.1016/j.scitotenv.2014.11.091

McCabe, A. J., & Arnold, W. A. (2016). Seasonal and spatial variabilities in the water chemistry of prairie pothole wetlands influence the photoproduction of reactive intermediates. *Chemosphere*, *155*, 640–647. https://doi.org/10.1016/j.chemosphere.2016.04.078

McDowell, W. H., & Fisher, S. G. (1976). Autumnal processing of dissolved organic matter in a small wooland stream ecosystem. *Ecosystems*, *57*(3), 561–569. https://doi.org/10.2307/1936440

McElmurry, S. P., Long, D. T., & Voice, T. C. (2014). Stormwater dissolved organic matter: Influence of land cover and environmental factors. *Environmental Science & Technology*, *48*(1), 45–53. https://doi.org/10.1021/es402664t

Milstead, R. P., Remucal, C. K. (2021). Molecular-level insights into the formation of traditional and novel halogenated disinfection byproducts. *ACS ES&T Water*, *1*(8), 1966–1974. https://doi.org/10.1021/acsestwater.1c00161

Minor, E., & Stephens, B. (2008). Dissolved organic matter characteristics within the Lake Superior watershed. *Organic Geochemistry*, *39*(11), 1489–1501. https://doi.org/10.1016/j.orggeochem.2008.08.001

Minor, E. C., Dalzell, B. J., Stubbins, A., & Mopper, K. (2007). Evaluating the photoalteration of estuarine dissolved organic matter using direct temperature-resolved mass spectrometry and UV-visible spectroscopy. *Aquatic Sciences*, *69*(4), 440–455. https://doi.org/10.1007/s00027-007-0897-y

Minor, E. C., Swenson, M. M., Mattson, B. M., & Oyler, A. R. (2014). Structural characterization of dissolved organic matter: A review of current techniques for isolation and analysis. *Environmental Science: Processes & Impacts*, *16*, 2064–2079. https://doi.org/10.1039/c4em00062e

Mooney, R. J., Stanley, E. H., Rosenthal, W. C., Esselman, P. C., Kendall, A. D., & McIntyre, P. B. (2020). Outsized nutrient contributions from small tributaries to a Great Lake. *Proceedings of the National Academy of Sciences*, *117*(45), 28175–28182. https://doi.org/10.1073/pnas.2001376117

Mosher, J. J., Klein, G. C., Marshall, A. G., & Findlay, R. H. (2010). Influence of bedrock geology on dissolved organic matter quality in stream water. *Organic Geochemistry*, *41*(11), 1177–1188. https://doi.org/10.1016/j.orggeochem.2010.08.004

Mulholland, P. J., & Hill, W. R. (1997). Seasonal patterns in streamwater nutrient and dissolved organic carbon concentrations: Separating catchment flow path and in-stream effects. *Water Resources Research*, *33*(6), 1297–1306. https://doi.org/10.1029/97wr00490

Müller, R. A., Kothawala, D. N., Podgrajsek, E., Sahlée, E., Koehler, B., Tranvik, L. J., & Weyhenmeyer, G. A. (2014). Hourly,daily, and seasonal variability in the absorption spectra of chromophoric dissolved organic matter in a eutrophic, humic lake. *Journal of Geophysical Research: Biogeosciences*, *119*. https://doi.org/10.1002/2014jg002719

Nebbioso, A., & Piccolo, A. (2013). Molecular characterization of dissolved organic matter (DOM): A critical review. *Analytical and Bioanalytical Chemistry*, *405*, 109–124. https://doi.org/10.1007/s00216-012-6363-2

Oni, S. K., Futter, M. N., Molot, L. A., & Dillon, P. J. (2014). Adjacent catchments with similar patterns of land use and climate have markedly different dissolved organic carbon concentration and runoff dynamics. *Hydrological Processes*, *28*(3), 1436–1449. https://doi.org/10.1002/hyp.9681

Palviainen, M., Lauren, A., Launiainen, S., & Piirainen, S. (2016). Predicting the export and concentrations of organic carbon, nitrogen, and phosphorus in boreal lakes by catchment characteristics and land use: A practical approach. *AMBIO A. Journal of the Human Environment*, *45*(8), 933–945. https://doi.org/10.1007/s13280-016-0789-2

Radeloff, V. C., Nelson, E., Plantinga, A. J., Lewis, D. J., Helmers, D., Lawler, J. J., et al. (2012). Economic-based projections of future land use in the conterminous United States under alternative policy scenarios. *Ecological Applications*, *22*(3), 1036–1049. https://doi.org/10.1890/11-0306.1

Raeke, J., Lechtenfeld, O. J., Seiwert, B., Meier, T., Riemenschneider, C., & Reemtsma, T. (2017). Photochemically induced bound residue formation of carbamazepine with dissolved organic matter. *Environmental Science & Technology*, *51*(10), 5523–5530. https://doi.org/10.1021/acs.est.7b00823

Raymond, P. A., & Hamilton, S. K. (2018). Anthropogenic influences on riverine fluxes of dissolved inorganic carbon. *Limnology and Oceanography Letters*, *3*, 143–155. https://doi.org/10.1002/lol2.10069

Remucal, C. K. (2014). The role of indirect photochemical degradation in the environmental fate of pesticides: A review. *Environmental Science: Processes & Impacts*, *16*, 628–653. https://doi.org/10.1039/c3em00549f

Schelker, J., Eklöf, K., Bishop, K., & Laudon, H. (2012). Effects of forestry operations on dissolved organic carbon concentrations and export in boreal first-order streams. *Journal of Geophysical Research: Biogeosciences*, *117*(1), 1–12. https://doi.org/10.1029/2011jg001827

Shang, P., Lu, Y. H., Du, Y. X., Jaffé, R., Findlay, R. H., & Wynn, A. (2018). Climatic and watershed controls of dissolved organic matter variation in streams across a gradient of agricultural land use. *The Science of the Total Environment*, *612*, 1442–1453. https://doi.org/10.1016/j.scitotenv.2017.08.322

Singh, S., Dash, P., Silwal, S., Feng, G., Adeli, A., & Moorhead, R. J. (2017). Influence of land use and land cover on the spatial variability of dissolved organic matter in multiple aquatic environments. *Environmental Science & Pollution Research*, *24*(16), 14124–14141. https://doi.org/10.1007/s11356-017-8917-5

Steinberg, D. K., Neson, N. B., Carlson, C. A., & Prusak, A. C. (2004). Production of chromophoric dissolved organic matter (CDOM) in the open ocean by zooplankton and the colonial cyanobacterium *Trichodesmium* spp. *Marine Ecology Progress Series*, *267*, 45–56. https://doi.org/10.3354/meps267045

Stephens, B. M., & Minor, E. C. (2010). DOM characteristics along the continuum from river to receiving basin: A comparison of freshwater and saline transects. *Aquatic Sciences*, *72*(4), 403–417. https://doi.org/10.1007/s00027-010-0144-9

Strock, K. E., Theodore, N., Gawley, W. G., Ellsworth, A. C., & Saros, J. E. (2017). Increasing dissolved organic carbon concentrations in northern boreal lakes: Implications for lake water transparency and thermal structure. *Journal of Geophysical Research: Biogeosciences*, *122*(5), 1022–1035. https://doi.org/10.1002/2017jg003767

Stumm, W., & Morgan, J. J. (1996). *Aquatic chemistry. Chemical Equilibria and rates in natural waters*. Wiley

Thompson, S. K., & Cotner, J. B. (2020). P-limitation drives changes in DOM production by aquatic bacteria. *Aquatic Microbial Ecology*, *83*, 35–46. https://doi.org/10.3354/ame01940

Vodacek, A., Blough, N. V., DeGrandpre, M. D., Peltzer, E. T., & Nelson, R. K. (1997). Seasonal variation of CDOM and DOC in the Middle Atlantic Bight: Terrestrial inputs and photooxidation. *Limnology and Oceanography*, *42*(4), 674–686. https://doi.org/10.4319/lo.1997.42.4.0674

Wang, L., Riseng, C. M., Mason, L. A., Wehrly, K. E., Rutherford, E. S., McKenna, J. E., Jr, et al. (2015). A spatial classification and database for management, research, and policy making: The Great Lakes aquatic habitat framework. *Journal of Great Lakes Research*, *41*(2), 584–596. https://doi.org/10.1016/j.jglr.2015.03.017

Ward, C. P., Nalven, S. G., Crump, B. C., Kling, G. W., & Cory, R. M. (2017). Photochemical alteration of organic carbon draining permafrost soils shifts microbial metabolic pathways and stimulates respiration. *Nature Communications*, *8*(1), 1–8. https://doi.org/10.1038/s41467-017-00759-2

Wayland, K. G., Long, D. T., Hyndman, D. W., Pijanowski, B. C., Woodhams, S. M., & Haack, S. K. (2003). Identifying relationships between baseflow geochemistry and land use with synoptic sampling and R-mode factor analysis. *Journal of Environmental Quality*, *32*, 180–190. https://doi.org/10.2134/jeq2003.1800

Weishaar, J., Aiken, G., Bergamaschi, B., Fram, M., Fujii, R., & Mopper, K. (2003). Evaluation of specific ultra-violet absorbance as an indicator of the chemical content of dissolved organic carbon. *Environmental Science & Technology*, *37*(20), 4702–4708. https://doi.org/10.1021/es030360x

Weyhenmeyer, G. A., & Karlsson, J. (2009). Nonlinear response of dissolved organic carbon concentrations in boreal lakes to increasing temperatures. *Limnology and Oceanography*, *54*(6), 2513–2519. https://doi.org/10.4319/lo.2009.54.6_part_2.2513

Williams, C. J., Frost, P. C., Morales-Williams, A. M., Larson, J. H., Richardson, W. B., Chiandet, A. S., & Zenopoulos, M. A. (2015). Human activities cause distinct dissolved organic matter composition across freshwater ecosystems. *Global Change Biology*, *22*(2), 613–626. https://doi.org/10.1111/gcb.13094

Williams, C. J., Yamashita, Y., Wilson, H. F., Jaffe, R., & Xenopoulos, M. A. (2010). Unraveling the role of land use and microbial activity in shaping dissolved organic matter characteristics in stream ecosystems. *Limnology and Oceanography*, *55*(3), 1159–1171. https://doi.org/10.4319/lo.2010.55.3.1159

Xenopoulos, M. A., Lodge, D. M., Frentress, J., Kreps, T. A., Bridgham, S. D., Grossman, E., & Jackson, C. J. (2003). Regional comparisons of watershed determinants of dissolved organic carbon in temperate lakes from the Upper Great Lakes region and selected regions globally. *Limnology and Oceanography*, *48*(6), 2321–2334. https://doi.org/10.4319/lo.2003.48.6.2321

Yakushev, E. (1999). *Alkalinity. Standard Methods for the Examination of Water and Wastewater*.

Yates, C. A., Johnes, P. J., & Spencer, R. G. M. (2016). Assessing the drivers of dissolved organic matter export from two contrasting lowland catchments. *U.K. Sciences of the Total Environment*, *569–570*, 1330–1340. https://doi.org/10.1016/j.scitotenv.2016.06.211

Zhao, L., Chen, H., Lu, X., Lin, H., Christensen, G. A., Pierce, E. M., & Gu, B. (2017). Contrasting effects of dissolved organic matter on mercury methylation by *Geobacter sulfurreducens* PCA and *Desulfovibrio desulfuricans* ND132. *Environmental Science & Technology*, *51*(18), 10468–10475. https://doi.org/10.1021/acs.est.7b02518

Zhou, Y., Zhou, L., He, X., Jang, K., Yao, X., Hu, Y., et al. (2019). Variability in dissolved organic matter composition and biolability across gradients of glacial coverage and distance from glacial terminus on the Tibetan Plateau. *Environmental Science and Technology*, *53*(21), 12207–12217. https://doi.org/10.1021/acs.est.9b03348