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Long-term changes in dissolved organic matter quality are unrelated to ecosystem recovery from acidification in the Adirondack region (New York, USA)

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Abstract Increasing concentrations of dissolved organic carbon (DOC) and changing dissolved organic matter (DOM) quality in surface waters, a phenomenon known as browning, have been observed at global scales with a range of implications for ecosystem structure and function, global carbon cycling and human health. Ecosystem recovery from chronic acidification resulting from rapid declines in acid deposition over recent decades has been the leading explanation for surface water browning. In this study, long-term dynamics of the quantity, quality, and seasonality of DOM in surface waters of an acid-resistant Adirondack lake and its forested watershed were investigated during a period of rapid regional changes in both acidic deposition and climate (1999–2018). Overall, we found that trends in DOM quality have occurred while the overall quantity and seasonality of DOC fluxes changed little during the same time frame. Lack of DOC trends was consistent with expectations for this acid-resistant ecosystem. Model reconstructions of DOM quality during this period indicated shifts towards a greater proportion of terrestrially-sourced DOM from the watershed, but with occasional 'pulses' of more microbially-processed DOM associated with periods of heavy rainfall and high discharge. Our findings suggest that ecologically meaningful changes in DOM quality may be occurring in acid-resistant ecosystems, aside from trends in DOC driven by ecosystem recovery from acid impairment.

Keywords Dissolved organic matter · Carbon cycling · Watershed processes · Acidic deposition · Fluorescence spectroscopy · Water quality · Adirondacks

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Introduction

Increasing concentrations and quality of dissolved organic matter (DOM) in surface waters, known as 'browning', has been a global-scale phenomenon with implications for ecosystem function and structure, human health, and global carbon cycling (Evans et al. 2004, 2024; Monteith et al. 2007; Clair et al. 2011; Lawrence et al. 2013; Driscoll et al. 2016; de Wit et al. 2023). Ecosystem recovery from chronic acidification, made possible by rapid declines in acid

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deposition over recent decades, has been the leading explanation for surface water browning (Driscoll et al. 2003; de Wit et al. 2007; Monteith et al. 2007, 2023; Evans et al. 2024). To date, the broadest-scale analysis of browning trends covering dozens of sites in eastern North America, western Europe, and Scandinavia, found that changes in SO_4^{2-} and Cl^- deposition, which drive decreases in solution ionic strength and increases in pH, along with indicators of catchment acid sensitivity, best explained historical trends in surface water dissolved organic carbon (DOC) concentrations (Monteith et al. 2007, 2023; Hruška et al. 2009; Lawrence and Roy 2021). The mechanism driving this change appears to result in shifts in the solubility of terrestrially derived DOC. These compounds tend to be phenolic, hydrophobic with low solubility (Qualls and Haines 1991). Elevated sulfate concentrations increase the acidity and ionic strength of soil solutions, decreasing the solubility of DOC (Ussiri and Johnson 2004), and therefore, with decreases in sulfate, the mobility of terrestrial DOM increases (Evans et al. 2024). Increased DOC export is thought to be primarily derived from organic soils, while mineral soils contribute less to browning of surface waters under decreased SO_4^{2-} inputs (Borken et al. 2011; Evans et al. 2012; Clarholm and Skylberg 2013).

Additional studies have indicated that other drivers, including decreases in nitrogen (N) deposition (Lloret and Valeila 2016), changes in land cover, climatic changes such as warming and increased runoff (Clark et al. 2010; Clair et al. 2011) and increases in atmospheric CO_2 could plan a role in the browning phenomenon. Historically elevated inputs of anthropogenic N may have suppressed decompositiomn of organic matter (OM) in forest ecosystems (Tonitto et al. 2014) via acidification effects and/or loss of soil microbial biodiversity (Davidson et al. 1998; Gilliam et al. 2019). With respect to climate, seasonal weather patterns exert fundamental controls on both DOC formation and terrestrial export to surface waters (Evans et al. 2004, 2006). Lastly, increasing atmospheric CO_2 has been linked to increased DOC flux from peatland soils in laboratory experiments (Freeman et al. 2004), indicating a potential feedback relationship between browning and climate change.

Overall, ecosystem recovery from acidification enhances the mobilization of DOC and DOM from organic soils (Borken et al. 2011) and may also affect the overall quality of DOM exported by forest watersheds (Clarholm and Skylberg 2013; San Clements et al. 2012, 2018). DOM represents an essential link between terrestrial and aquatic ecosystems due to its multifunctional role in watershed-surface water function and structure (Aitkenhead et al. 1999; Battin et al. 2008), including processes regulating the solubility and transport of metals through chelation (Possinger et al. 2020), soil and solution pH (Driscoll and Postek 1996; Fakhraei and Driscoll 2015), nutrient cycling and availability (Dittman et al. 2007; Groffman et al. 2018; Stetler et al. 2021), the production of photochemical oxidants (Wasswa et al. 2020), and the attenuation of light and thermal stratification of ponded waters with effects on biotic communities (Warren et al. 2016). Our understanding of whether changes in DOM, including source(s) and compositional properties, have been concomitant with trends in DOC (Monteith et al. 2007; Driscoll et al. 2016) is limited because DOM quality assays have rarely been part of long-term monitoring (Jaffé et al. 2008). However, a few studies have reported shifts in DOM quality in surface waters coinciding with changes in DOC quantity (SanClements et al. 2012, 2018; Evans et al. 2024; Rodriguez-Cardona et al. 2023). These investigations suggest that, for some waters, increases in DOC have resulted in more colored and higher molecular weight DOM.

In addition to specific UV absorbance ($SUVA_{254}$) and color, which have been widely used, fluorescence spectroscopy provides a detailed 'fingerprint' of surface water DOM sources and degree of microbial processing (Coble et al. 2014). Several indices have been derived from the fluorescence excitation–emission matrix (EEM), including the fluorescence index (FI; McKnight et al. 2001), humification index (HI), freshness index (FR or β/α; Wilson and Xenopoulos 2009), biological index (BI) and redox index (RI; Cory and McKnight 2005). Among these, FI can be used to differentiate between terrestrial and microbial sources of organic matter; FI is also closely related with $SUVA_{254}$ in representing spatial and temporal variation related to watershed position and seasonal timing (Jaffé et al. 2008). The RI represents the reduction–oxidation state of quinone-like compounds in DOM and provides an indicator of DOM solubility (Cory and McKnight 2005) which relates directly to mobilization and export. In particular, San Clements et al. (2012) reported that FI has increased in some lakes in Maine with concomitant increases in DOC. San Clements et al. (2018) found that FI decreased in streams draining watersheds in Maine and West Virginia that were experimentally manipulated by ammonium sulfate additions.

In this study, we report on 20 years of dynamics (1999–2018) in the quantity, quality, and seasonality of DOC/DOM in a remote forest watershed–lake ecosystem in the Adirondack Mountains of northern New York (USA), a region that has experienced among the most severe effects of chronic acidic deposition in North America. However, relative to most Adirondack ecosystems that have been acid-sensitive, Arbutus Lake and its forested catchment (Archer Creek Watershed) have been largely resistant to acid impairment due to base-rich parent materials and drainage characteristics. No trends in DOC concentration at the inlet or outlet streams of Arbutus Lake were observed over a ten-year period (1999–2009; Kang and Mitchell 2013), during which acidic deposition rapidly decreased (Sullivan et al. 2018). Meanwhile, most Adirondack streams and lakes experienced increasing DOC trends during that period (Lawrence et al. 2013; Driscoll et al. 2016). Here we revisited trends in DOC quantity at Arbutus, with an additional decade of water chemistry monitoring, to test three hypotheses. First, we expected that overall stability, or absence of trends, in lake and watershed DOC concentrations would continue through a second decade of monitoring (2009–2018), despite concurrent reductions in acid deposition. Second, we hypothesized that shifting weather patterns, including warmer winters with frequent/early thaws and increased summer storm intensity, may have driven changes in the seasonality of watershed and lake DOC fluxes. Third, we hypothesized that DOM quality changes may have been occurring regardless of DOC quantity remaining overall stable over the last two decades (1999–2018). For these purposes, we conducted novel analyses of the phenology (timing) of DOC loading and assessed recent changes and variability in DOM quality using model-based historical reconstructions of fluorescence indices from long-term monitoring data.

Weekly water chemistry records at the inlet and outlet of Arbutus Lake were analyzed for trends and temporal variability in DOC concentration and loading (which incorporated daily hydrological records) from 1999 to 2018. We also evaluated whether changes in seasonal timing of DOC loading occurred during the same period. Next, DOM quality was assessed with fluorescence spectroscopy and computation of DOM quality indices (LoRusso et al. 2020) for weekly samples collected during a full water year, in conjunction with ongoing water chemistry monitoring, at both inlet and outlet streams. Based on relationships between fluorescence indices and monitored stream chemistry parameters, statistical models were developed to generate historical predictions of DOC quality indices at a weekly resolution for the inlet and outlet streams from 1999 to 2018. These reconstructed time series of DOM quality indices were analyzed for seasonal dynamics, trends, and extreme values to evaluate whether changes in DOM quality and source may have occurred, regardless of trends (or lack thereof) in DOC quantity, over the 20-year period. Extreme values observed in DOM quality hindcasts were referenced to antecedent and concurrent weather conditions (e.g., cumulative precipitation) to identify potential causal factors. Lastly, results were compared between inlet (watershed processes) and outlet (in-lake processes) to draw insights on differential ecosystem responses to recent changes in acidic deposition and local climate.

Methods

Site description

Arbutus Lake is located on Huntington Wildlife Forest (HWF), a 6000-ha research and education facility located in the Adirondack Mountains, in the Towns of Newcomb and Long Lake, New York (44° 00″ N, 74° 13″ W). Arbutus Lake is a 49-ha drainage pond located < 3 km from the National Atmospheric Deposition Program (NADP) NY-20 site (Newcomb) where precipitation chemistry has been continuously monitored since 1978. Archer Creek is the primary inlet stream at the north end of Arbutus Lake and its 130-ha forested catchment is known as Archer Creek Watershed (Fig. 1). Continuous monitoring of stage height and discharge is conducted using a V-notch weir at the lake outlet and a H-flume weir on Archer Creek just upstream from the inlet. See Beier et al. (2021) for an overview of long-term monitoring programs at this site, which have generated the hydrological and stream chemistry datasets used in this study (adk-ltm.org).

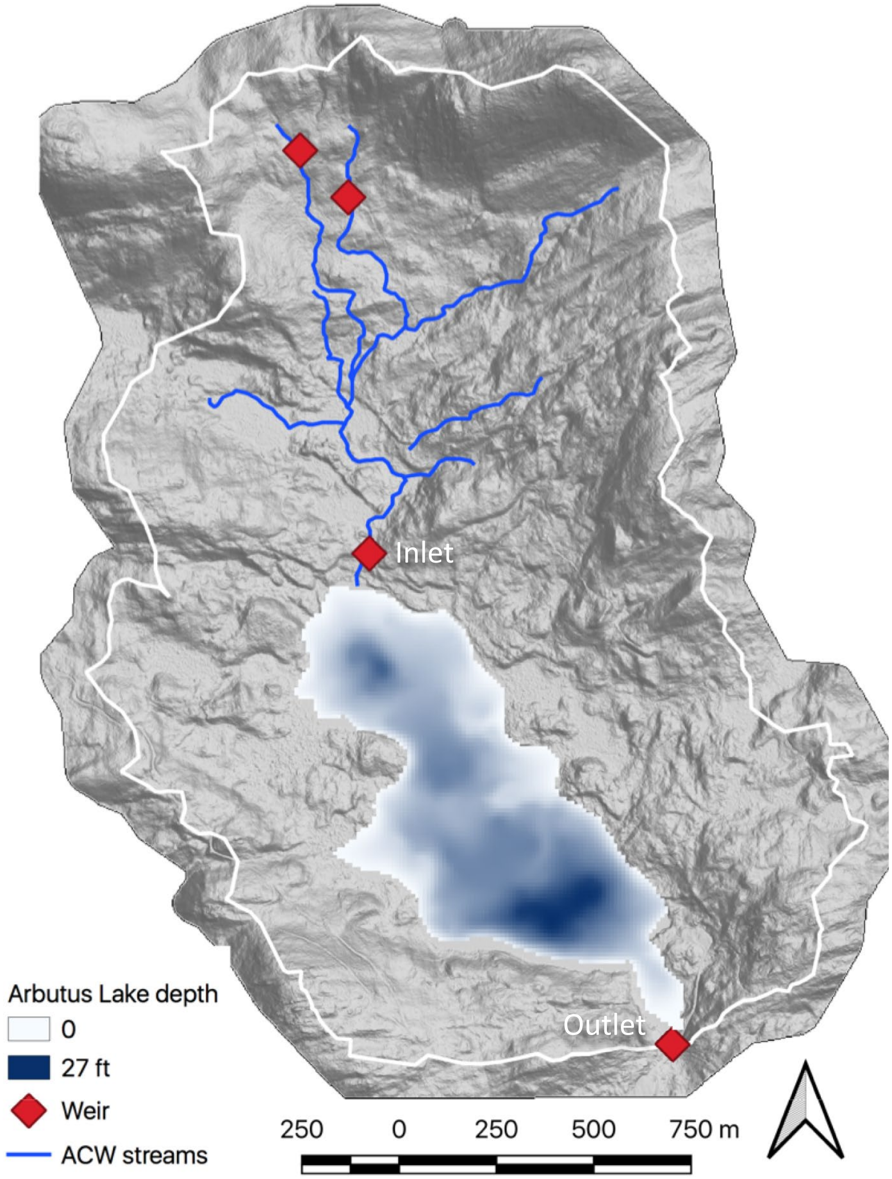

Fig. 1 Map of Arbutus Lake watershed and the long-term monitoring weirs at its inlet and outlet streams. The primary inlet, known as Archer Creek, and its major tributaries are depicted in blue. The entire lake catchment, estimated using the terrain model shown, is depicted by the white boundary line

Archer Creek Watershed (ACW) has a mean slope of 11% and a total relief of 225 m (Gomez et al. 2016). The catchment is located within the Anorthosite Massif igneous intrusion composed mostly of calcium-rich plagioclase feldspar, providing a moderately to very highly buffered parent material relative to the granitic till common in the Adirondack region (McHale et al. 2002). Surficial geology consists of glacial till that is 75% sand and < 10% clay with many boulders and cobbles (Christopher et al. 2006). Upland forest soils are Becket–Mundal sandy loams (Haplorthods) up to 1 m thick, while soils in wetlands and low-lying areas consist of Greenwood Mucky Peat deposits between 1 and 5 m in depth (Somers 1986). These lowland and wetland forests are mostly composed of eastern hemlock [*Tsuga canadensis* (L.) Carr], yellow birch (*Betula alleghaniensis* Britt.), speckled alder [*Alnus incana* (L.) Moench], red spruce (*Picea rubens* Sarg.) and balsam fir [*Abies balsamea* (L.) Mill]. Upland forests are uneven-aged, second-growth hardwoods consisting of American beech (*Fagus grandifolia* Ehrh.), sugar maple (*Acer saccharum* Marsh.), red maple (*Acer rubrum* L.), and yellow birch, along with mixed conifers including eastern white pine (*Pinus strobus* L.), hemlock and spruce. Local climate in Newcomb is cool and moist (MAT = 5.28 °C; MAP = 1105 mm) with precipitation distributed consistently throughout the year.

Sample collection and laboratory analysis

On a weekly basis from 1999 to 2018, surface water samples were collected from the inlet and outlet streams, just upstream of weirs. Samples were collected in brown polyethylene bottles and stored on ice until transport to the Biogeochemistry Laboratory at SUNY ESF (Syracuse, NY). Samples were filtered using a Durapore 0.45 µm polyvinylidene difluoride (PVDF) membrane and stored at 4 °C until analysis. Water chemistry analyses consisted of pH, acid neutralizing capacity (ANC), DOC, NO_3^-, SO_4^{2+}, Cl^-, NH_4^-, Na^+, K^+, Mg^{2+}, Ca^{2+}, Si, total Al, total N, DON, and total S. We used major ion data to calculate ionic strength (I, Eq. 1) to evaluate if changes in solution ionic strength coincided with changes in DOC.

$$I = 0.5 \sum c_i \left(z_i^2\right), \quad (1)$$

where I is solution ionic strength; c_i is the concentration of ionic solute i in mol/L; and z_i is the charge of ionic solute i.

In addition, duplicate weekly water samples collected from November 2016 to October 2017 were analyzed for fluorescence characteristics by LoRusso et al. (2020), as described below.

Absorbance and fluorescence spectroscopy

DOC concentration was determined using a Tekmar–Dohrmann Phoenix 8000 TOC analyzer. Optical information, including sample fluorescence and absorbance, was obtained using a Horiba Aqualog Steady-State spectrofluorometer. Using a 1 cm quartz cuvette, an excitation–emission matrix (EEM) was generated for each sample, with an excitation range of 240 to 550 nm and emission range of 247.68 to 830.02 nm. The fluorescence and absorbance indices were determined from the EEM using the MATLAB toolbox *DOMFluor* (Stedmon and Bro 2008).

These steps produced estimates of specific ultraviolet absorbance at a wavelength of 254 nm ($SUVA_{254}$), colored dissolved organic matter (CDOM), humic and fulvic acids, and several indices for each water sample: fluorescence (FI), humification (HI), biological (BI), freshness (FRI) and redox (RI). Hereafter we focus on SUVA, CDOM, FI and RI as primary indicators of DOM quality. FI allows for differentiation between terrestrial and microbial sources of DOM (McKnight et al. 2001; Cory et al. 2010) and was determined by calculating the ratio of emission at 470 nm and 520 nm at an excitation of 370 nm. RI is the sum of reduced quinone-like moieties divided by the total number of quinone-like moieties (Cory and McKnight 2005).

Time series decomposition and analysis

Mean monthly DOC time series observations were decomposed with the seasonal and long-term trends by applying a loess method (STL; Cleveland et al. 1990), using a 37-month window for trends and 23-month window for seasonality. This technique produced three component time series representing modes of temporal variance present within the raw time series: trend (low frequency), seasonal (periodic), and random (high frequency). The seasonal component was then subtracted from the raw time series to produce a complete (continuous) seasonally-adjusted time series for trend analysis, both for the full time series and on a monthly basis.

Trends were analyzed using non-parametric Mann–Kendall tests to identify significant deviation from a random walk over time; and Sen slopes, to estimate a linear rate of change over time. Both the seasonally adjusted (continuous and monthly-focused) time series and their corresponding trend components (extracted from the same raw time series) were analyzed with this approach. Although both statistics were calculated for all series, we focused on those with significant trends (M–K tau values indicating a non-random directionality) for estimating rates of change with Sen slopes.

Phenology of DOC loading

We evaluated changes in the phenology (or seasonality) of DOC loading at the inlet and outlet streams over the last two decades, using the following method. Weekly data were interpolated to daily resolution using 24-h discharge estimates (derived from 15-min stage height measurements) and these daily DOC loads were summarized by water year (October–September). We then identified the water-year dates when each of five percentile benchmarks (10%, 25%, 50%, 75%, 90%) of the cumulative annual DOC loads were reached. Each water year was analyzed separately to correct for interannual variation in total cumulative DOC loads. The benchmark dates were then compiled into annual time series to evaluate whether DOC loads were shifting to earlier or later times in the water year over the 2000–2018 period. Water years with 30 or more missing values for daily DOC load estimates were excluded from this analysis.

Historical DOC quality modeling

To generate continuous historical predictions (hindcasts) of DOM quality metrics (SUVA, CDOM) and indices (FI, BI, HI, FRI, RI) for the study period, we built multiple regression models using stream chemistry parameters (for which long-term records exist at the study sites) as predictors of DOM quality. Modeling was conducted separately for the inlet and outlet streams using the same sequence of steps: model selection, training, validation, and evaluation (prediction). Observations used for modeling were based on weekly sampling conducted during 2016–2017, when duplicate stream water samples were collected for DOM fluorescence analysis in tandem with ongoing monitoring of chemistry parameters. Linear relationships between water chemistry predictors and DOM indices were formalized in models, which were then evaluated for the historical period using long-term weekly chemistry records at each site (inlet and outlet).

For model selection and training, we used an information-theoretic approach to identify linear combinations of predictor variables that best explained the observed variance in each response variable, based on the data available. Predictor variables included pH, cations (Na^+, K^+, Mg^{2+}, Ca^{2+}), anions (SO_4^{2+}, NO_3^-, Cl^-), total S, total N, NH_4^+, dissolved Si, dissolved organic N (DON), and DOC. Response variables included SUVA, CDOM, and quality indices (FI, BI, HI, FRI, RI). We note that because these DOM indices are not 'measured' but estimated through a sequence of bench, computational, and statistical procedures, uncertainty estimates were not available.

First, a principal components analysis (on correlations) was conducted using all predictor and response variables, but run separately for the inlet and outlet to represent relationships among variables at each site. At this stage, two candidate predictors (total S, dissolved Si) were screened out due to excessive missing data. Next, using an additive (linear) multiple regression structure, we evaluated a set of candidate models based on all possible combinations of predictors with a maximum of six terms ($K = 6$) for each response variable at each site, without interactions among predictors. We then compared candidate models using AIC to select those within deltaAIC < 4 of the lowest-AIC model. All other candidates were withdrawn from further consideration.

Cross-validation was used to identify the single 'best' model among the final candidates for each DOM quality index at each site. We used a rolling-origin forecasting technique, which accounts for serial autocorrelation in time-series observations (Bergmeir et al. 2018), to generate estimates of root mean square error (RMSE), mean absolute error (MAE) and coefficient of variation (r^2) between observed values and model predictions. A combination of deltaAIC, MAE and r^2 were used to compare and select final models. Model RMSE was used to estimate a 95% confidence interval for model predictions. For prediction, final models were evaluated using the long-term weekly chemistry records available at each site from 1999 to 2019. The hindcasted DOM quality time series were then decomposed using the STL procedure and both the raw and seasonally adjusted hindcasts were analyzed for trends using non-parametric tests (Mann–Kendall and Sen slope). Confidence intervals (95% CI) were estimated for these trend statistics using a bootstrapping procedure with 5000 iterations. Extreme values in the hindcasts were flagged based on threshold values derived from the full time-series, and these weekly events were referenced against antecedent (7 days prior) and concurrent (7 days inclusive of date flagged with an extreme predicted value) cumulative precipitation inputs based on local weather data. Last, each seasonally adjusted hindcast was tested for presence of a 'breakpoint', indicative of a regime shift in mean and/or variance, using a standard normal homogeneity test (SNHT; Alexandersson 1986).

Results

Trends in DOC quantity

No meaningful trends were observed in either seasonally-adjusted stream DOC concentrations or estimates of monthly loading at Arbutus inlet and outlet over the last two decades (1999–2019; Fig. 2). Of the 26 DOC time-series tested, only two exhibited non-random (directional) patterns over time (Table 1). Both of these trends were at the lake outlet, where slight DOC increases during April have driven a very weak positive trend in DOC concentration overall. No trends in DOC concentration were observed at the inlet stream (i.e., watershed export), nor were any significant trends found for monthly DOC load estimates at either the inlet or outlet.

Phenology of DOC loading

Changes in the annual timing of DOC loading were more evident at the lake outlet than the inlet, where, since 1999, most benchmark dates for cumulative DOC loading have occurred later in the water

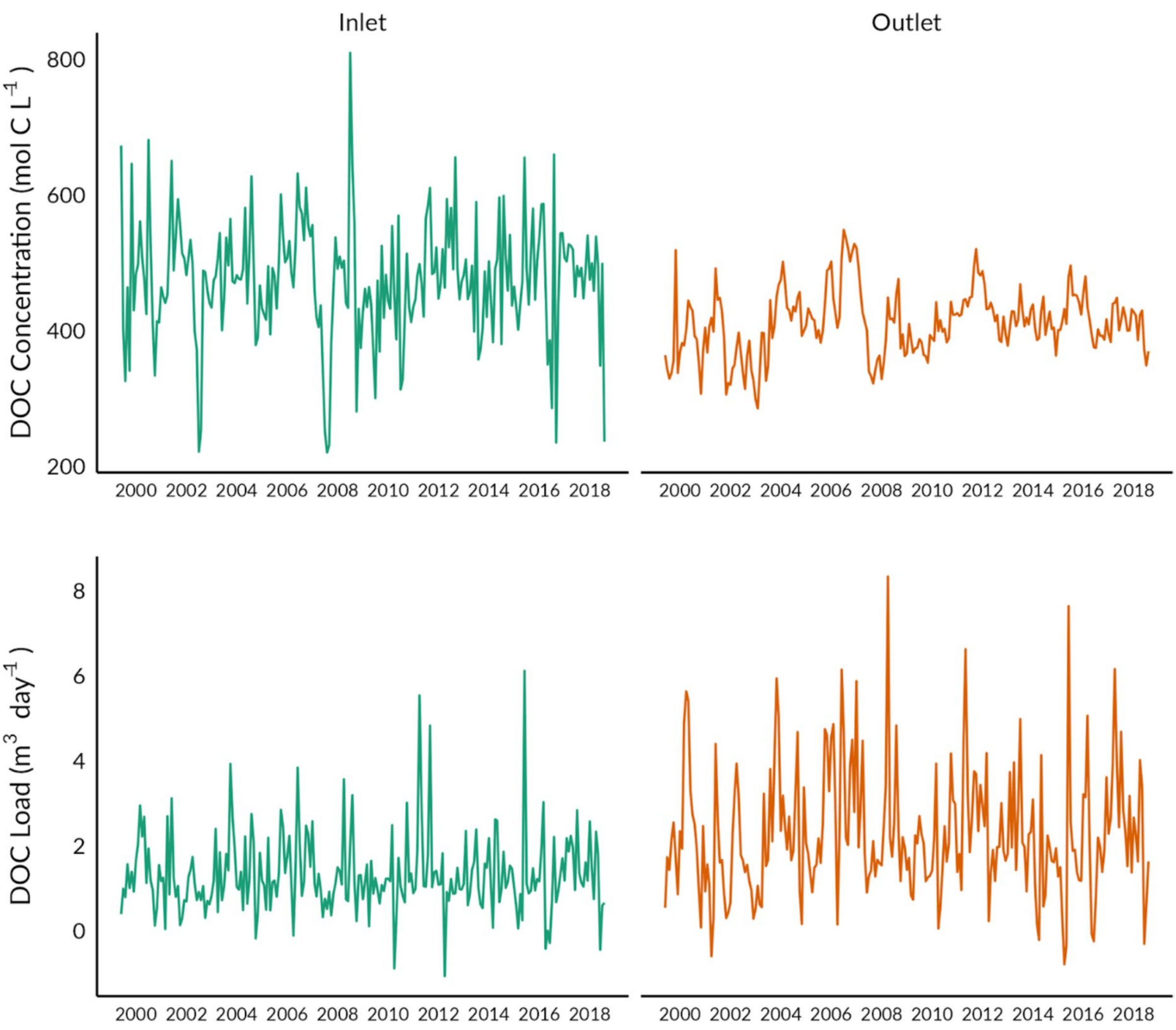

Fig. 2 Seasonally adjusted time-series of DOC concentration (top row) and estimated DOC loads (bottom row) at the inlet and outlet of Arbutus Lake (1999–2018). Weekly concentration data and daily load estimates were summarized to monthly means prior to time-series decomposition and seasonal adjustment. See Table 1 for trend statistics

Table 1 Analysis of trends in mean monthly DOC concentrations and estimated loads at inlet and outlet of Arbutus Lake, 1999–2018

		Inlet		Outlet	
	Time series	tau	Sen	tau	Sen
DOC concentration (umol C/L)	Full monthly	0.02	0.03 (0.36)	**0.14**	**0.15 (1.80)**
	Jan	0.01	0.01	0.24	4.42
	Feb	−0.02	−0.32	0.18	3.30
	Mar	0.01	0.06	0.17	1.25
	Apr	−0.23	−2.95	**0.33**	**1.82**
	May	−0.08	−1.19	0.12	0.88
	Jun	0.06	1.61	0.03	0.34
	Jul	0.17	6.23	0.26	4.21
	Aug	0.20	7.01	−0.01	−0.22
	Sep	−0.05	−0.44	0.16	2.17
	Oct	−0.13	−5.75	0.18	2.18
	Nov	−0.29	−5.86	−0.05	−1.11
	Dec	0.11	1.62	0.16	2.42
DOC load (mol-kg/day)	Full monthly	0.01	0.00	0.00	0.00
	Jan	0.11	0.01	0.22	0.06
	Feb	0.06	0.01	0.23	0.05
	Mar	−0.12	−0.02	0.09	0.04
	Apr	−0.18	−0.07	−0.05	−0.04
	May	−0.04	−0.01	−0.04	−0.04
	Jun	0.18	0.05	−0.01	−0.01
	Jul	0.26	0.04	0.19	0.04
	Aug	0.14	0.02	0.03	0.00
	Sep	−0.05	0.00	−0.18	−0.01
	Oct	−0.01	0.00	−0.15	−0.03
	Nov	−0.16	−0.02	−0.17	−0.05
	Dec	−0.05	−0.01	−0.04	−0.03

Weekly concentration data and daily load estimates were summarized to monthly means prior to time-series analysis. Sen slopes in parenthesis were converted to annual rates of change. Significant trends (tau, $p < 0.05$) are shown in bold

year (Fig. 3). Later seasonality of outlet DOC loading was evident at the 50% benchmark, i.e., the date when half of that water year's cumulative DOC load was reached, which shifted approximately 30 days from early March to early April. Meanwhile the 90% benchmark at the outlet shifted earlier by approximately 10 days, from early August to late July. By contrast, at the inlet there was little evidence of change in DOC loading, except for a slight shift later for the 90% benchmark. All of the time-series had substantial interannual variation, most notably at 50% and 90% benchmarks, which is probably due to the variable timing of spring snowmelt and summer rainfall events, respectively.

Modeling DOM quality via water chemistry parameters

Some qualitative insights on the biogeochemical controls on DOM quality at Arbutus were drawn from the model selection process itself, including the principal components analysis (Fig. 4). The PCA results indicated substantial differences between the inlet and outlet, most notably for the DOM indices: at the inlet, FI was closely associated with FRI, BI, NO_3^- and SO_4^{2+}, while at the outlet, FI was more closely associated with SUVA, CDOM, and RI. Based on final model forms (Table 2), pH and SO_4^{2+} predictors were included in all 7 inlet models, but only in 3 of 7 outlet

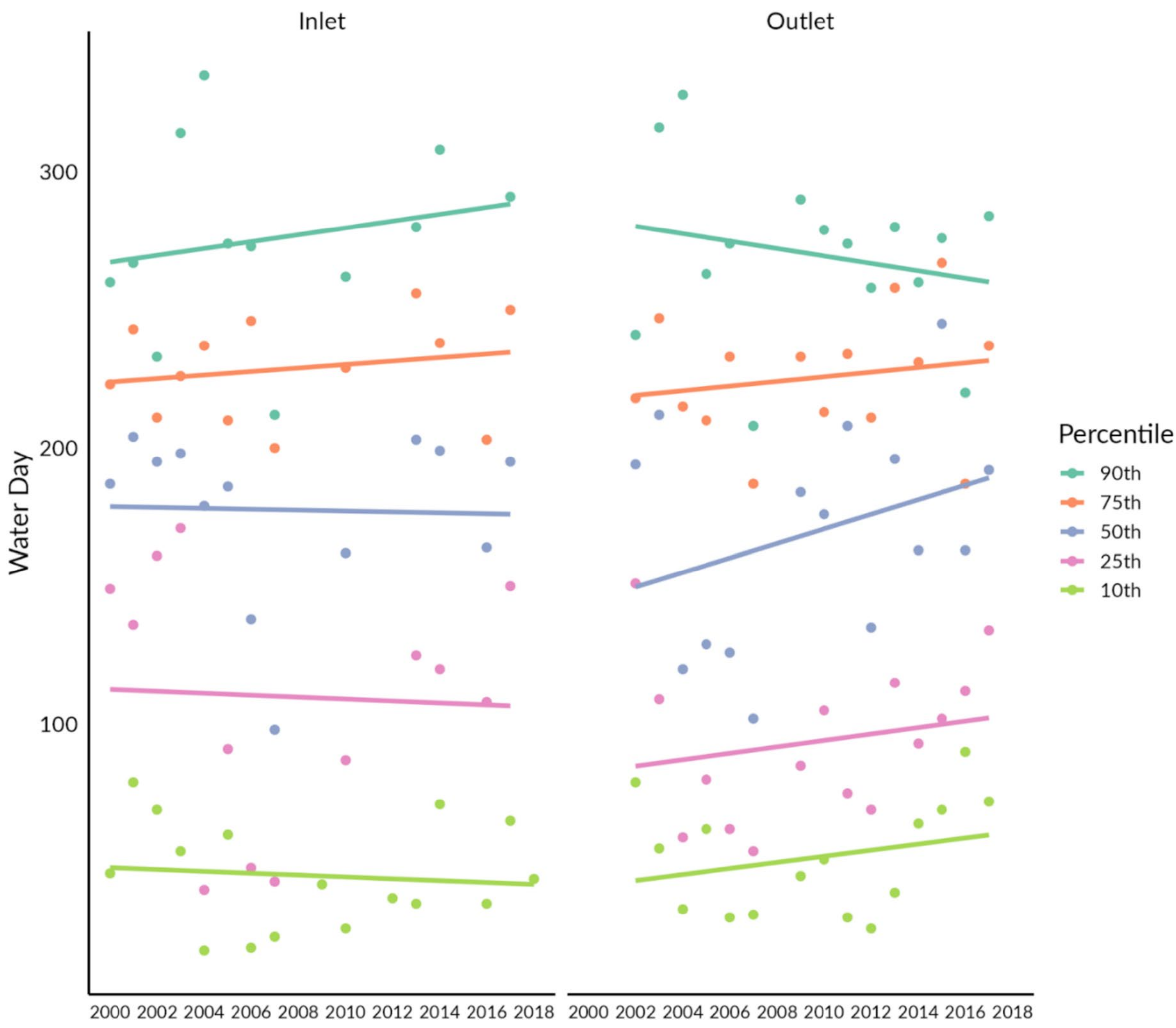

Fig. 3 Long-term changes in phenology (timing) of DOC loading at the inlet and outlet of Arbutus Lake. Weekly data were interpolated to daily resolution, summarized by water year (October–September) and the dates associated with five benchmarks (10%, 25%, 50%, 75%, 90%) of the cumulative yearly DOC loads were estimated. Linear models were fit to each series of benchmark dates to illustrate changes over time; positive slopes indicate the benchmark was reached later in the water year, negative slopes indicate benchmark was reached earlier

models, of DOM quality. Total Al was a predictor in 5 of 7 outlet models but was entirely absent from inlet models. Outlet models typically included combinations of multiple base cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) as predictors, while inlet models either lacked these predictors entirely (FI, RI, BI, FRI, HI) or included only one cation predictor each (SUVA, CDOM).

Historical dynamics of DOM quality

To recap, 14 models (7 indices × 2 sites) for predicting historical DOM quality at the inlet and outlet streams of Arbutus Lake were fitted and tested (Table 2) based on weekly water sampling from November 2016 to October 2017. Models varied in explanatory power (r^2) but had similar prediction errors (RMSE, MAE) when scaled to the mean response parameter values. Using these models, we

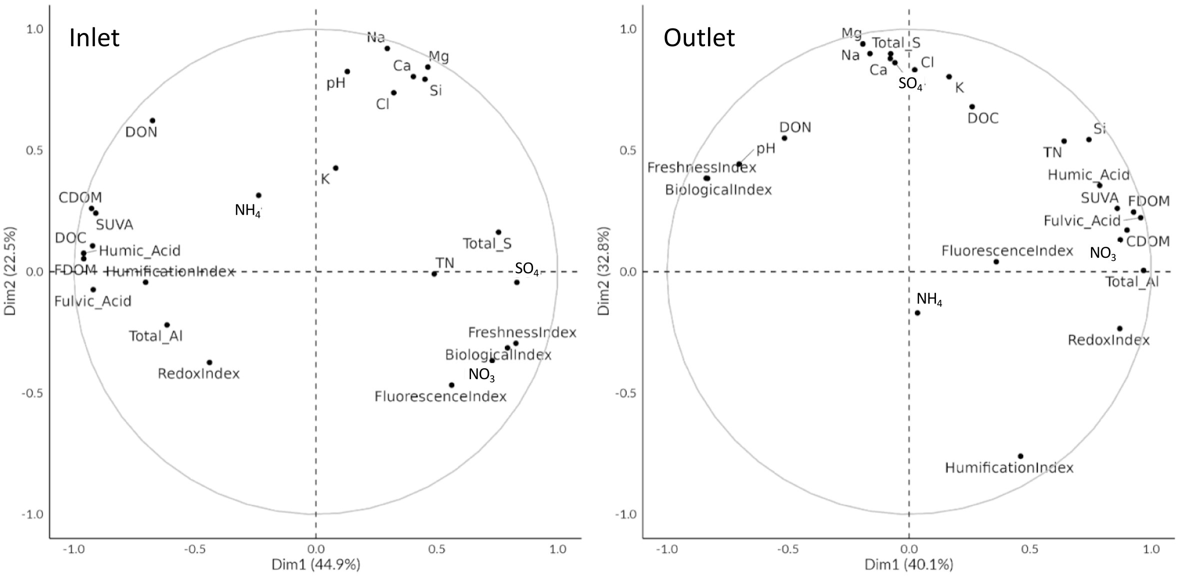

Fig. 4 Relationships among DOM quality indices and water chemistry parameters based on principal components analysis (on correlations). Observations were based on duplicate surface water samples collected at a weekly interval during the 2016–2017 water year at the inlet and outlet of Arbutus Lake (New York, USA). Cations and anions (e.g., SO_4^{2+}, NO_3^+, NH_4^+, Cl^-, Na^+, K^+, Mg^{2+}, Ca^{2+}) are labeled without superscripts, for visual clarity

Table 2 Summary of multiple regression models predicting DOC fluorescence indices based on stream chemistry parameters at the inlet and outlet of Arbutus Lake

Site	Model	RMSE	MAE	r^2
Inlet	SUVA ~ pH + K + NO_3 + SO_4 + DOC	0.012	0.010	0.98
	CDOM ~ pH + Na + SO_4 + DON + DOC	237.6	151.2	0.90
	Biological Index ~ pH + SO_4 + DOC	0.009	0.007	0.56
	Fluorescence Index ~ pH + SO_4	0.017	0.014	0.62
	Freshness Index ~ pH + SO_4 + DOC	0.010	0.008	0.59
	Humification Index ~ pH + NO_3 + SO_4 + DOC	0.010	0.008	0.36
	Redox Index ~ pH + SO_4 + DOC	0.010	0.006	0.24
Outlet	SUVA ~ Na + Mg + Ca + Total Al + Cl + DOC	0.010	0.007	0.77
	CDOM ~ NH_4 + Mg + K + Total Al + NO_3 + DOC	108.8	97.7	0.72
	Biological Index ~ Mg + K + Ca + Total Al + Cl + SO_4	0.009	0.008	0.69
	Fluorescence Index ~ pH + Cl	0.018	0.015	0.42
	Freshness Index ~ Mg + K + Ca + Total Al + Cl + SO_4	0.010	0.007	0.72
	Humification Index ~ pH + SO_4 + DOC	0.016	0.012	0.22
	Redox Index ~ pH + Na + Mg + K + Ca + Total Al	0.016	0.010	0.75

All observations used for model training and validation were based on surface water samples (n = 47) collected on a weekly basis during 2016–2017. Models were selected from a full candidate set (all possible linear combinations of all predictors) based on AIC. A rolling origin cross-validation technique was used to estimate model performance based on three metrics: RMSE (root mean square error), MAE (mean absolute error) and r^2 (predicted vs observed)

Table 3 Trends in reconstructed historical DOC quality indices (1999–2018) at Arbutus inlet and outlet, estimated from the a) raw time-series and b) seasonally adjusted time-series

a. Raw time-series predictions

Index	Site	n	tau	tau 95% CI	Sen slope	Sen 95% CI
SUVA	inlet	237	**0.25**	(0.20, 0.29)	4.43x10^{-4}	(3.59x10^{-4}, 5.14x10^{-4})
	outlet	236	**0.09**	(0.01, 0.14)	5.30x10^{-5}	(4.74x10^{-6}, 7.82x10^{-5})
CDOM	inlet	237	**0.14**	(0.09, 0.17)	2.57	(1.71, 3.02)
	outlet	237	0.08	(−0.03, 0.12)	0.53	(−0.18, 0.80)
FI	inlet	240	**−0.62**	(−0.62, −0.53)	−4.73x10^{-4}	(−5.19x10^{-4}, −4.56x10^{-4})
	outlet	240	**−0.35**	(−0.39, −0.31)	−1.51x10^{-4}	(−1.74x10^{-4}, −1.40x10^{-4})
RI	inlet	237	**−0.47**	(−0.52, −0.42)	−9.65x10^{-5}	(−1.03x10^{-4}, -8.50x10^{-5})
	outlet	240	**−0.18**	(−0.25, −0.14)	−1.08x10^{-4}	(−1.60x10^{-4}, -9.05x10^{-5})

b. Seasonally adjusted time-series

Index	Site	n	tau	tau 95% CI	Sen slope	Sen 95% CI
SUVA	inlet	237	**0.39**	(0.32, 0.45)	4.50x10^{-4}	(3.80x10^{-4}, 5.15x10^{-4})
	outlet	236	**0.07**	(0.00, 0.16)	3.84x10^{-5}	(1.80x10^{-6}, 7.73.x10^{-5})
CDOM	inlet	237	**0.25**	(0.19, 0.32)	2.48	(1.88, 3.00)
	outlet	237	0.06	(−0.03, 0.12)	0.39	(−0.19, 0.79)
FI	inlet	240	**−0.69**	(−0.73, −0.60)	−4.78x10^{-4}	(−5.12x10^{-4}, −4.50x10^{-4})
	outlet	240	**−0.38**	(−0.44, −0.35)	−1.49x10^{-4}	(−1.74x10^{-4}, −1.40.10^{-4})
RI	inlet	237	**−0.51**	(−0.59, −0.47)	−9.83x10^{-5}	(−1.05x10^{-4}, −8.73x10^{-5})
	outlet	240	**−0.21**	(−0.31, −0.17)	−1.03x10^{-4}	(−1.62x10^{-4}, −8.96x10^{-5})

Linear models were evaluated at a weekly resolution and predictions were averaged to monthly resolution prior to seasonal adjustment (using STL decomposition) and trend analysis. Significant trends (tau, $p < 0.05$) are shown in bold. Sen slopes are given as annual rates and 95% confidence intervals for Mann-Kendall tau and Sen slope estimates were based on 5000 bootstrap samples

produced hindcasts at a weekly resolution and estimated 95% confidence intervals (CI) for predictions based on estimated model RMSE via cross-validation. These time series were then analyzed for trends using Mann–Kendall and Sen tests, and the 95% CI of these test statistics was estimated via bootstrapping. In rare instances (< 10 out of over 3300 predictions), the models generated implausible predictions (e.g., negative values of indices) that were omitted from trend analyses (Table 3.), but for transparency were not scrubbed from the hindcast time-series plots (Figs. 5, 6, 7). Based on the PCA results and insights from model training, we hereafter focus on hindcasts of four DOM indices: SUVA, CDOM, FI and RI.

Historical SUVA dynamics at the inlet (Fig. 5) exhibited a long-term increasing trend (tau = 0.39, 95% CI: [0.32, 0.45], Table 3.) and consistent seasonal patterns in which higher values occurred mostly during summer. Based on a SUVA ≥ 0.6 threshold, 9 weekly SUVA predictions were flagged as SUVA peaks, mostly during summer in July (3) and August (3), and the rest in autumn (1 each in September, October, November). Timing of SUVA peaks did not consistently coincide with heavy rainfall or high-flow periods in the watershed. Four of the six SUVA peaks

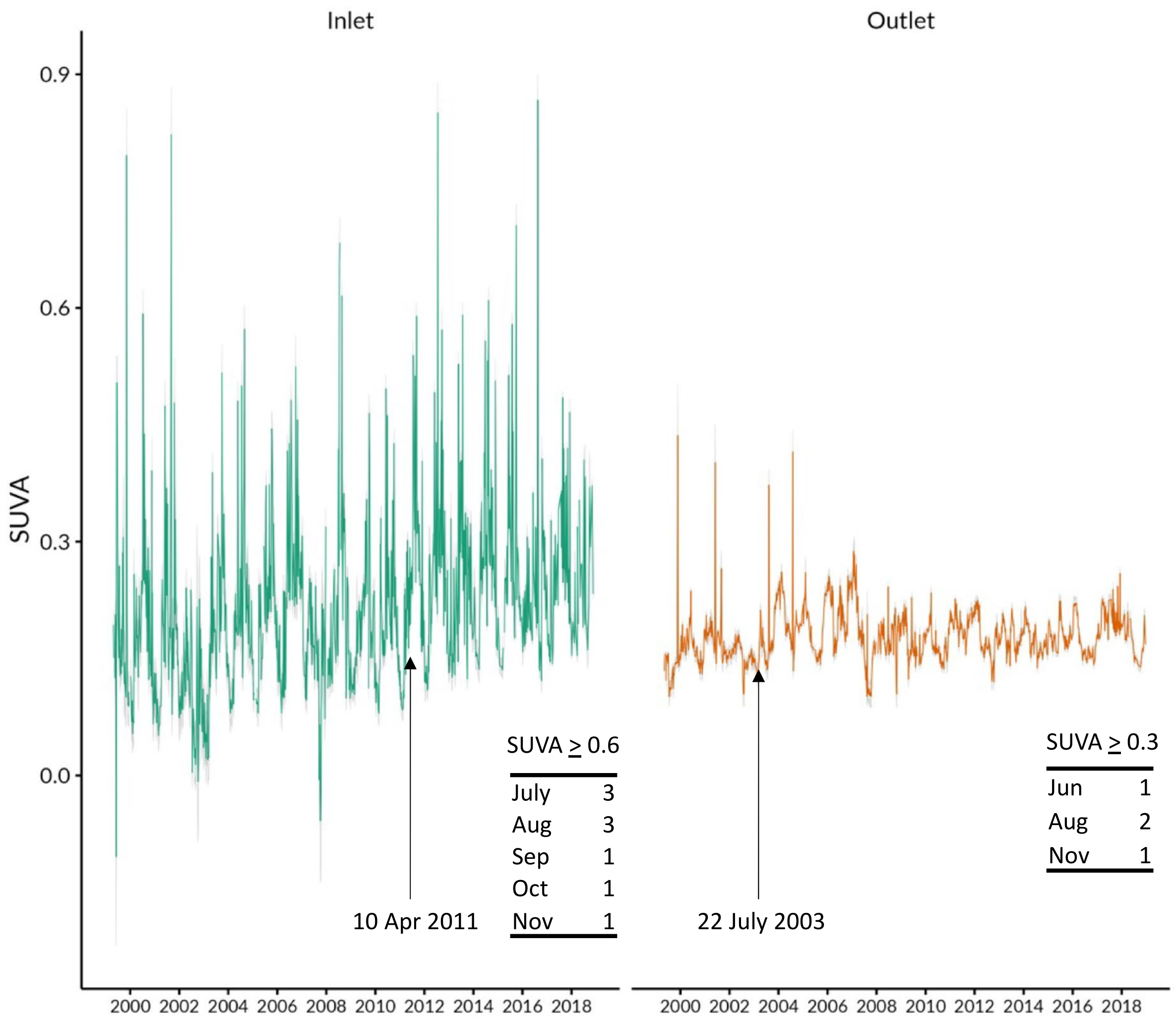

Fig. 5 Historical reconstruction of $SUVA_{254}$ of DOM collected at the inlet and outlet of Arbutus Lake, summarized to mean monthly values from 1999 to 2018, based on models using long-term water chemistry data (see Table 2). Gray shaded areas are 95% confidence intervals based on model error (RMSE) estimated by cross-validation, estimated breakpoints (based on SNHT tests) are noted by dates with vertical arrows, and inset tables show frequency of extreme values (if present) by month of occurrence in hindcasted time-series

flagged during the growing season (June–August) coincided with heavy rainfall; most notably, the two consecutive weeks of July 2008 with very high SUVA predictions (0.66–0.68) corresponded to 15.8 cm total rainfall over a 21-day period (inclusive of 1 week antecedent), or 147.6% of the mean total July precipitation of 10.7 cm (from 1986 to 2016). August peaks in 2014 and 2016 also coincided with rainfall amounts over 14-day periods that were equal to (100.8%, August 2014) or greater than (112.6%, August 2016) the mean total August precipitation of 9.76 cm. The remaining five SUVA peaks, including all those in autumn (September, October, November), occurred during nominally typical rainfall conditions. Very low SUVA (<0.1) estimates at the inlet occurred almost entirely in the winter (January, February, March) during typical low-flow conditions.

The SUVA hindcast of the lake outlet was less temporally variable than the inlet, both seasonally and over the full hindcast period. No significant trend

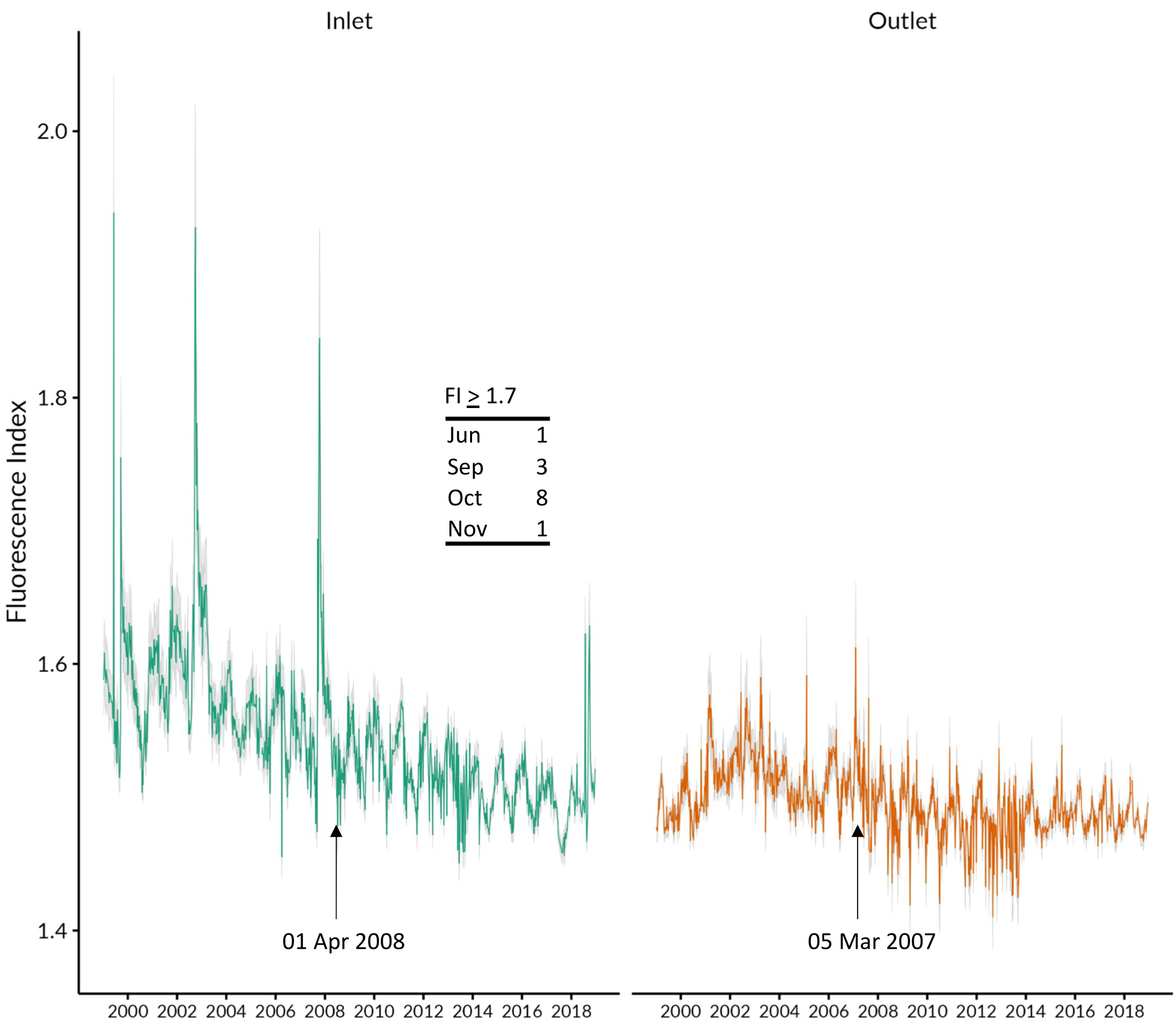

Fig. 6 Historical reconstruction of the fluorescence index (FI) of DOM quality at the inlet and outlet of Arbutus Lake, summarized to mean monthly values from 1999 to 2018, based on models using long-term water chemistry data (Table 2). Gray shaded areas are 95% confidence intervals based on model error (RMSE) estimated by cross-validation, estimated breakpoints (based on SNHT tests) are noted by dates with vertical arrows, and inset tables show frequency of extreme values (if present) by month of occurrence in hindcasted time-series

existed in the seasonally-adjusted SUVA historical time-series and there were no weekly SUVA predictions > 0.5 at the outlet. Only 4 weekly values of SUVA > 0.3 were predicted at the outlet for the entire period (1999–2018) and these occurred in July (1), August (2) and November (1). Breakpoint analysis identified a possible regime shift in 2003, specifically in April 2003 at the inlet, and July 2003 at the outlet.

The CDOM hindcasts tracked closely with the SUVA hindcasts, in terms of seasonal patterns and differences between inlet and outlet with respect to trends and variability (see Fig. S2 Supplemental Materials). Long-term CDOM trends at the inlet were similar to increasing SUVA trends, although weaker (less monotonic), while also like SUVA, no trends in CDOM were evident at the outlet (Table 3.). Most of the predicted CDOM peaks at the inlet occurred in summer and temporally coincided with SUVA peaks flagged in weekly predictions. Lastly, estimated breakpoints in the CDOM hindcasts were closely aligned with SUVA breakpoints at both inlet

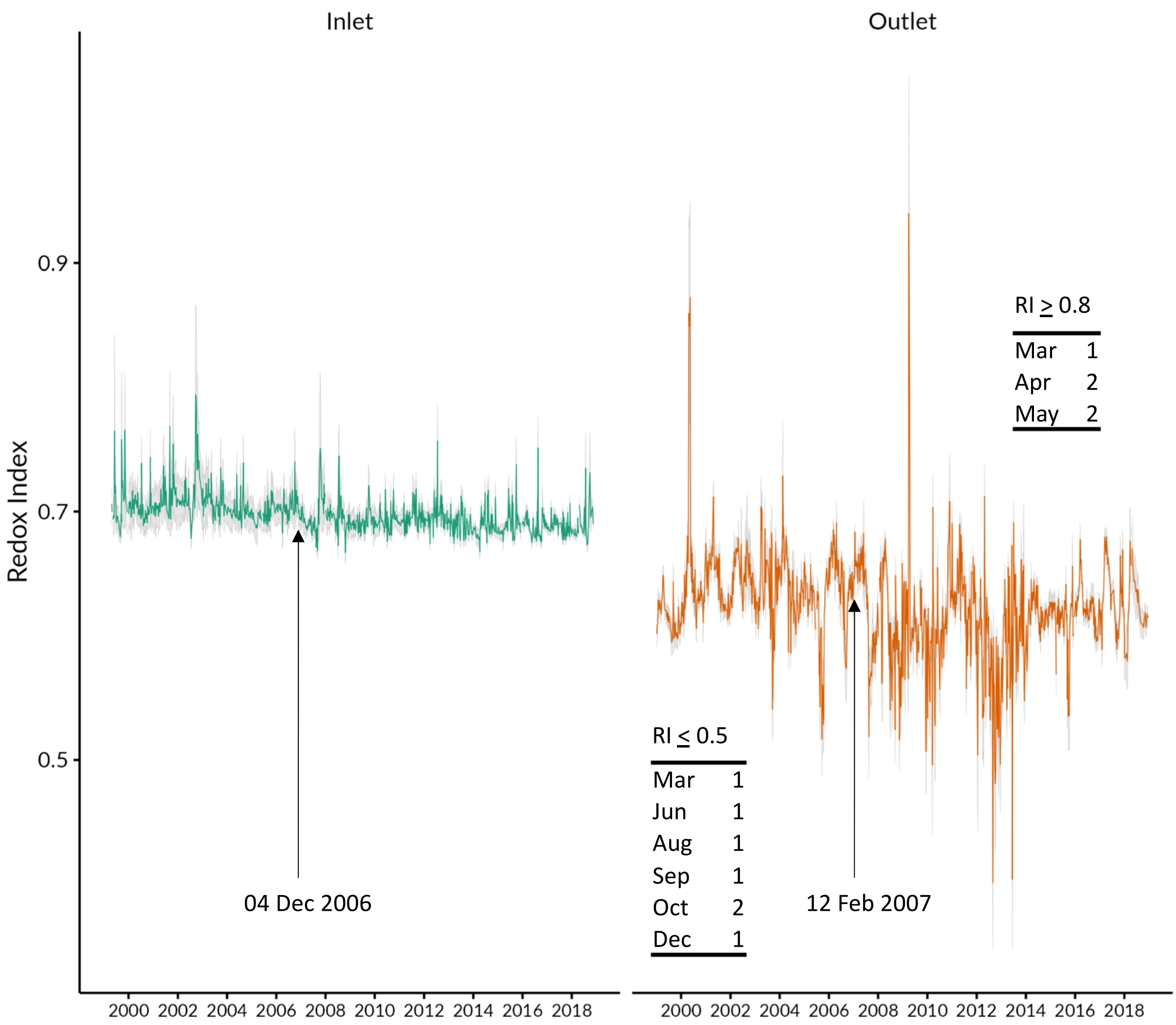

Fig. 7 Historical reconstruction of the redox index (RI) of DOM quality at the inlet and outlet of Arbutus Lake, summarized to mean monthly values from 1999 to 2018, based on models using long-term water chemistry data (Table 2). Gray shaded areas are 95% confidence intervals based on model error (RMSE) estimated by cross-validation, estimated breakpoints (based on SNHT tests) are noted by dates with vertical arrows, and inset tables show frequency of extreme values (if present) by month of occurrence in hindcasted time-series

(CDOM: June 2011, SUVA: April 2011) and outlet (same week of 22 July 2003).

The FI hindcasts exhibited seasonal patterns that cycled from winter maxima (more microbially-derived DOM) to summer minima (more terrestrially-derived DOM) through intermediate values in the spring and fall (Fig. 6). After seasonal adjustment of the hindcast, FI exhibited a long-term declining trend since 1999 that was strongly monotonic (tau = −0.69, 95% CI [−0.73, −0.60]), equating to a reduction in mean annual FI values from approximately 1.6 to 1.5. This trend indicated a shift to a proportionally greater DOM fraction from terrestrial versus microbial sources in the watershed. At the outlet, a similar seasonality and decreasing trend in FI was evident, but with less directionality and magnitude, than at the inlet (Table 3.). Potential breakpoints in the FI hindcasts were identified as April 2008 (inlet) and March 2007 (outlet).

Although FI exhibited the strongest monotonic decline among the DOM indices reconstructed from 1999 to 2018, several very high FI peaks (Fig. 6) were indicative of short-term pulses of microbially-sourced DOM at the inlet. Based on a FI ≥ 1.7 threshold, 13 weekly FI predictions were flagged as FI 'peaks' in the water years of 1999 (1 week each in June and September), 2002 (7 weeks in September, October, November) and 2007 (4 weeks in October). Timing of these peaks often coincided with one or more antecedent heavy rainfall events (defined as ≥ 0.64 cm day^{-1}) and periods of high stream discharge. The three highest-FI peaks at the inlet were during the growing season: 1 week in June 1999 (FI = 1.94, 95% CI [1.83, 2.04]), and two consecutive weeks in September 2002 (FI = 1.93, 95% CI [1.83, 2.02]; FI = 1.89, 95% CI [1.81, 1.98]). The June 1999 peak followed a week with 2.87 cm rainfall that coincided with the very end of snowmelt in the watershed. The September 2002 peak occurred during a 2-week period with 8.05 cm total rainfall, an amount equal to 89% of the mean total monthly rainfall for September (9.03 cm) based on 1986–2016 weather records (Demers 2020). Over half of this rainfall (4.24 cm) occurred in a single day (27 September 2002) that corresponded to the second-highest FI prediction (1.93) in the hindcast. Nine of the 10 remaining high FI peaks occurred in either 2002 or 2007 and all were associated with high antecedent precipitation during autumn. In 2002, the FI peak spanned seven consecutive weeks from late September through early November, during which 22.25 cm precipitation occurred, including 9 days with heavy rainfall. Similarly, in 2007, all four weeks of October had peak FI estimates that coincided with 17.91 cm total rainfall, an amount representing 164.5% of mean total October precipitation (1986–2016). We also noted that just 7 days of heavy rainfall accounted for roughly 75% of October 2007 total precipitation. Lastly, the September 1999 peak coincided with 14.58 cm total rainfall over 14 days, equal to 161% of the average total precipitation in September (9.03 cm).

Decreasing trends in the seasonally adjusted redox index (RI) hindcasts were observed for both sites, but more consistently at the inlet (tau = -0.51, 95% CI [-0.59, -0.47]) than the outlet (tau = -0.21, 95% CI [-0.31, -0.17]). Although a stronger RI trend at the inlet (relative to outlet) was consistent with the SUVA, CDOM and FI results, the RI hindcasts had much greater high-frequency variation at the outlet relative to the inlet (Fig. 7), in contrast with the other DOM indices. We note, however, that these differences in hindcast variability between inlet and outlet may reflect the fact that outlet models of SUVA, CDOM and FI had notably lower explanatory power (r^2) than inlet models, while the converse was true for RI models (Table 2). It follows that models that explained less variability would be less capable of predicting outlier and extreme values, although error metrics (RMSE, MAE) suggested overall similar prediction accuracy.

Discussion

Long-term stability of DOC quantity was consistent with previous observations and expectations based on the high pH buffering capacity of the Arbutus ecosystem, due in part to base-rich parent materials that are atypical in the Adirondack region (Beier et al. 2012). Kang and Mitchell (2013) did not detect any trends in DOC concentration at Arbutus during the first decade of intensive monitoring (1999–2010), a period encompassing rapidly decreasing SO_4^{2+} concentrations and increasing pH of precipitation (Sullivan et al. 2018) as well as surface water browning trends at regional (Lawrence et al. 2013; Driscoll et al. 2016) and global scales (Monteith et al. 2007).

Our results confirm that changes in DOC still have not emerged in a second decade of intensive monitoring at Arbutus (2011–2019), despite ongoing decreases in acid deposition concomitant with browning in surface waters elsewhere in the Adirondack region. The lack of browning trends in a well-buffered ecosystem like Arbutus that never experienced acidification, in the context of a chronically acidified region where the majority of lakes are browning (Driscoll et al. 2016), lends support to the acid recovery hypothesis (Monteith et al. 2007). Although atmospheric sulfate deposition and sulfate concentrations at Arbutus inlet and outlet trended consistently downward during this period (Beier et al. 2021), it does not appear decreasing sulfate has resulted in a detectable or significant increase in DOC mobilization and export. Moreover, the magnitude and rates of decrease in sulfate concentrations at Arbutus are similar to values measured for other lakes in the Adirondack region (Driscoll et al. 2016).

Montieth et al. (2023) found that precipitation ionic strength (estimated from electrical conductivity measurements) was the dominant driver of increases in DOC in headwater catchments in Europe. In contrast, drainage waters at Arbutus exhibited no change in DOC concentration or flux, despite significant decreasing trends in ionic strength at both the inlet ($n = 1033$; $tau = -0.328$, $p < 0.0001$; Sen slope $= -0.017$) and outlet ($n = 1009$; $tau = -0.500$, $p < 0.0001$; Sen slope $= -0.015$) during the 20-year study period. Similar to sulfate, marked decreases in ionic strength of circumneutral drainage waters have not coincided with changes in DOC concentration or load in the Arbutus ecosystem.

Alternatively, investigators have suggested that enhanced transport of DOC and DOM is associated with changes in the partitioning of higher molecular weight aromatic organic acids with soil surfaces. Increases in solution pH results in dissociation of these organic acids, thus increasing their mobility (Usirri and Johnson 2004; Evans et al. 2024), hence the lack of DOC increase at Arbutus may reflect well-buffered drainage waters that have experienced limited long-term changes in pH.

Overall, long-term dynamics estimated from DOM quality hindcasts (Table 3.) characterized a shift since 2000 towards more terrestrially-sourced carbon in surface waters at Arbutus. These trends—indicated by decreasing FI and increasing SUVA and CDOM—have been much more pronounced, in terms of both directionality and magnitude, at the inlet stream (watershed export) relative to the outlet stream (in-lake processes). This apparent long-term change in DOM quality of watershed export is consistent with recent evidence from regional (SanClements et al. 2012, 2018; Rodriguez-Cardona et al. 2023) to global scales (Evans et al. 2024). After seasonal adjustment, no trends in SUVA or CDOM were evident at the outlet, while these indices along with FI were also much less temporally variable (or 'noisy') at the outlet versus the inlet). Conversely, the hindcasts for redox, biological, and freshness indices exhibited greater temporal variability at the outlet. To some extent, these differences in temporal variability among hindcasts may reflect varying explanatory power of each model to predict outlier and extreme values. To the extent they represent reality, these differences in DOM quality dynamics between lake inflow and outflow likely reflect the in situ processing and production of DOM via plant, microbial, or photochemical activity, among other interacting factors and processes, including lake turnover (Jaffé et al. 2008; Rodriguez-Cardona et al 2023).

Moreover, the overall stability of DOC quantity in stream and lake water at Arbutus during a period of documented changes in regional climate (Dupigny-Giroux et al. 2018), does not lend support to the hypothesis that recent climatic changes, broadly speaking, have been a primary driver of browning in the Adirondack region. However, our results indicate how extreme precipitation events—which have become more frequent during the study period (Howarth et al. 2019) and are expected to continue to intensify in frequency and magnitude in the region (Dupigny-Giroux et al. 2018)—could have influenced short-term DOC fluxes from soils to surface waters, in terms of DOM quality and source. Precipitation extremes can lead to large C fluxes via transport of fresh, lignin-like DOM deeper into soils or to streams via bypass flow paths (Fröberg et al. 2007; Fenner and Freeman 2011; Strock et al. 2016; Raymond et al. 2016). Deep soil-saturating events may also connect microbial decomposers and sources of carbon in the soil macropore system, shifting the chemical quality of DOM to more microbially-derived content (Aitkenhead et al. 1999; Bailey et al. 2017; Kravchenko et al. 2021).

Our findings in the Arbutus watershed offer circumstantial evidence of the latter mechanism, which points to changing precipitation regimes as a potential driver of high-frequency variability in both quality and source of DOM in watershed exports (Possinger et al. 2020). Nearly all of the FI peaks predicted at Arbutus inlet—which indicated 'pulses' of microbially-derived DOM in the context of a longer-term ecosystem shift towards more terrestrially-derived material—coincided with periods of heavy rainfall and high watershed discharge. These peaks also mostly occurred after the end of growing season in late September and October, which suggests potential interactions with vegetation dynamics, i.e., fall senescence and dormancy leading to lower plant water uptake and overall deeper-saturated soils during heavy rain events. We noted that several well-documented summer storm events, including Tropical Storm Irene on 28 August 2011 (6.88 cm rainfall in 24 h), did not correspond with peaks or even above-average FI values in model hindcasts. An in-depth exploration of FI dynamics in response to precipitation extremes (among other types of climatic forcing) and in situ mediating factors may be justified, but would be best accomplished via long-term monitoring of DOM quality indices (as recommended by Jaffé et al. 2008) concurrently with other ecosystem dynamics, and not based on model predictions alone.

The apparent long-term change in DOM quality under conditions of no change in DOC concentration or flux for Arbutus Pond and watershed would seem to contrast with prior observations of browning in the literature (SanClements et al. 2012, 2018; Evans et al. 2024). However, in a detailed analysis of long-term patterns of changes in DOC, colored dissolved organic matter (CDOM), and surface water CO_2 partial pressure in lakes of southeastern Canada, Rodriguez-Cardona et al. (2023) found that there were no consistent long-term changes in CDOM in lakes with weak trends in DOC (below 0.05 mg C/L year^{-1}; 4.2 mol C/L year^{-1}) or concentrations below 0.42–0.50 mmol/L (5–6 mg C/L). Similar to Couturier et al. (2022), these studies suggest that lakes that have experienced shifts in CDOM do not necessarily exhibit changes in DOC. Rodriguez-Cardona et al. (2023) indicated that these conditions may reflect qualitative shifts in inflows of DOM rather than changes in DOC loading. Further, the coupling between changes in CDOM and DOC becomes stronger with a shorter hydraulic residence time of lakes, suggesting that a close hydrologic connection between watershed inflows and lake water is an important linkage between the terrestrial carbon cycle and changes in lake organic matter quality. Overall, these authors suggest that future studies distinguish between increases in lake DOC (organification) and DOM quality (browning) in their analysis.

Conclusion

Long-term dynamics of dissolved organic matter (DOM) quantity, quality and seasonality in surface waters of a remote Adirondack ecosystem (lake and its forest watershed) were investigated during a time of rapid regional changes in acid deposition and climate (1999–2018). Overall, we found that changes in DOM quality have outpaced any changes in DOC quantity and seasonality, which were largely stable during this time frame. Absence of DOC trends was consistent with expectations for this acid-insensitive ecosystem, while our model hindcasts of DOM quality during this time indicated shifts towards a greater proportion of terrestrially-sourced versus microbially-processed DOM. However, we also found circumstantial evidence that heavy rainfall events, especially those occurring outside of the active growing season, may drive short-term 'pulses' of microbially-processed material in watershed DOM export to the lake. Overall our findings suggest that meaningful changes in DOM quality could be occurring in other acid-insensitive ecosystems, regardless of the presence or absence of 'browning' trends in DOC driven by ecosystem recovery from acid impairment (or other factors). Although historical reconstructions of DOM quality can offer valuable insights, such inferences are limited by measurement and modeling uncertainties, which further supports the rationale for including analyses of DOM quality in long-term monitoring programs, especially where research foci include water quality, carbon cycling and/or ecosystem responses to external forcing.

Author contributions All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by S. Badri, N. LoRusso, M. Mahoney, J. Mills, P. McHale and C. Beier. The first draft of the manuscript was written by C. Beier and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Data availability All of the long-term monitoring data presented in this paper is currently available for download at adk-ltm.org. The DOM quality indices data used to train the hindcast models, and the reconstructed monthly DOM quality indices (model predictions) are available upon request.

Declarations

Conflict of interest The authors have no relevant financial or non-financial interests to disclose. The authors do not have any conflicts of interest related to this study and its results, including competing financial or non-financial interests (see below).

Ethical approval The study did not involve human participants or any other animals that require specific protocols for ethical research practice. Because the study did not involve human subjects, informed consent was not relevant here.

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