Linking CDOM patterns in Cayuga Lake, New York, USA, to terrigenous inputs

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Abstract

Lacustrine patterns of the light absorption of colored dissolved organic matter (a\textsubscript{CDOM}) and its composition proxies were resolved and linked to concurrent conditions of tributary inputs for Cayuga Lake, New York. We analyzed fixed-frequency samples of the lake at 3 sites and runoff event-based samples at the mouths of 3 gauged tributaries over a 7 month interval and measured dissolved organic carbon (DOC) and a\textsubscript{CDOM} over the visible wavelengths (400–700 nm) and at 254 nm. The tributaries are demonstrated to be enriched in a\textsubscript{CDOM} and DOC, with widely different proxy conditions compared to the lake, which further diverge during runoff events. DOC, a\textsubscript{CDOM}, and the composition proxies for the tributaries had significant, and mostly strong, dependencies on flow rate, described by power-law relationships. The differences in the composition proxies indicated lower contributions of CDOM to the DOC pool, reduced aromaticity, decreased molecular size of CDOM, and decreased amounts of humic versus fulvic acids in the lake compared to the tributaries, all accepted signatures of photobleaching. Dynamics of a\textsubscript{CDOM} in the upper waters of the lake depended primarily on composition (e.g., color quality) and secondarily on a quantity metric (DOC), as demonstrated in a 2-component linear least-squares regression format. Signatures of linkages between the terrestrial inputs and in-lake a\textsubscript{CDOM} patterns and the effects of photobleaching include (1) the preferential in-lake loss of a\textsubscript{CDOM} relative to DOC, estimated from budget calculations; (2) the intermediate characteristics resolved at a near-shore site adjoining multiple tributary inflows; and (3) the magnitude and character of the dynamics observed at the pelagic sites.

Key words: CDOM, composition proxy, DOC, flow weighted concentrations, light absorption, multiple linear regression, photodegradation

Introduction

Absorption, a light-attenuating process, is an important determinant of the underwater and emergent light fields, quantified by the absorption coefficient (a, m\textsuperscript{-1}). As an inherent optical property (IOP), a is an intrinsic property, independent of the geometry of the light field (Kirk 2011). The magnitude and spectral character of a depends on the concentrations and composition of light-absorbing, optically active constituents (OACs), which all have strong wavelength (\lambda) dependencies (Babin et al. 2003, Binding et al. 2008, Perkins et al. 2013). The a(\lambda) is commonly partitioned into 4 additive components (Prieur and Sathyendranath 1981, Babin et al. 2003):

\[ a(\lambda) = a_\phi(\lambda) + a_{\text{NAP}}(\lambda) + a_{\text{CDOM}}(\lambda) + a_w(\lambda), \] (1)

corresponding to phytoplankton (\phi), nonalgal particles (NAP), colored dissolved organic matter (CDOM), and water (w), respectively. In the open oceans, a_\phi is dominant in the blue (in particular) and green spectral regions, and a_{\text{NAP}} and a_{\text{CDOM}} covary (Morel 1988). In coastal and inland waters, however, the various components are generally not correlated, and a_\phi is not

Although the number of partitionings of $a(\lambda)$ in lacustrine systems remains modest, the importance, if not dominance, of $a_{\text{CDOM}}$ in the blue spectral region seems to be common (Binding et al. 2008, Perkins et al. 2009, 2013, Nguy-Robertson et al. 2013). Quantification of $a_{\text{CDOM}}(\lambda)$ levels and dynamics is important to advance the capabilities of mechanistic remote sensing (e.g., semianalytical) retrieval algorithms (Binding et al. 2012, Mouw et al. 2013). CDOM is the colored component of the dissolved organic matter (DOM) pool (Rochelle-Newall et al. 2014) composed of a heterogenous array of humic substances and commonly partitioned according to fulvic and humic acids (Carder et al. 1989). The $a_{\text{CDOM}}$ can be viewed as having 2 components: (1) the amount of dissolved colored constituents (e.g., mass) and (2) their respective color potencies (color imparted per unit mass). Within the visible wavelengths (400–700 nm), $a_{\text{CDOM}}$ decreases exponentially with increasing wavelengths and is usually described by the model (Twardowski et al. 2004):

$$a_{\text{CDOM}}(\lambda) = a_{\text{CDOM}}(\lambda_r) e^{-S_{\text{CDOM}}(\lambda - \lambda_r)},$$

(2)

where $a_{\text{CDOM}}(\lambda_r)$ is the CDOM absorption at the reference wavelength, $\lambda_r$ (440 nm commonly adopted; Kirk 2011), and $S_{\text{CDOM}}$ (nm$^{-1}$) is the slope of the $a_{\text{CDOM}}(\lambda)$ spectrum. Measures of $a_{\text{CDOM}}(440)$ and $S_{\text{CDOM}}$ have been widely adopted as proxies for CDOM concentration and composition, respectively (Carder et al. 1989, Blough and Green 1995, Twardowski et al. 2004, Kirk 2011). The value of $S_{\text{CDOM}}$ is particularly sensitive to the protocols adopted for its determination from spectra (Twardowski et al. 2004). CDOM is influenced by both source and sink processes; however, lacustrine monitoring of $a_{\text{CDOM}}(\lambda)$ has rarely been conducted with the temporal and spatial resolution to analyse the effects of such processes. CDOM is subject to photochemical and microbial degradation (Moran et al. 2000, Vahatalo and Wetzel 2004) as well as adsorption to particles and subsequent deposition (Kirk 2011). Although there are both autochthonous (associated with primary production and coupled decomposition) and allochthonous (e.g., terrigeneous) sources of CDOM, it is generally accepted that watershed inputs dominate in lacustrine systems (Davies-Colley and Vant 1987, Perkins et al. 2009, Kirk 2011). Efforts to link the magnitude, dynamics, and characteristics of external inputs of CDOM and the $a_{\text{CDOM}}(\lambda)$ metric from watersheds to those of receiving lakes have generally been lacking.

The DOM pool of lotic systems has received substantial research attention in the context of chemical characterization, biogeochemical processes, and ecosystem function (Cole and Caraco 2001, Urban et al. 2005, Minor and Stephens 2008). Potential implications for downstream lentic systems have often been identified, including the underwater light field (Minor and Stephens 2008, Yang et al. 2013), although these have generally not been pursued, and visible wavelengths for $a_{\text{CDOM}}$ have not been studied. Much of this stream and river research has focused on dissolved organic carbon (DOC), the primary proxy of DOM. CDOM measurements at multiple wavelengths, mostly outside of the visible wavelengths, have served as diagnostic metrics, or proxies, of DOC composition in a number of lotic system studies (Minor and Stephens 2008, Spencer et al. 2010, Yang et al. 2013). For example, the ratio of $a_{\text{CDOM}}(254)$ (ultraviolet wavelength) to DOC (SUVA$^{254}$), a reliable metric of percent aromaticity of the DOM pool (Weishaar et al. 2003), has been integrated into a number of studies as an indicator of composition (Hood et al. 2005, Spencer et al. 2008, Fellman et al. 2009). The ratio of $a_{\text{CDOM}}$ values at 250 to 365 nm ($E_{254}/E_440$) has been used as a proxy of molecular size of DOM (De Haan and De Boer 1987, Peuravuori and Pihlaja 1997), the ratio of 465 to 665 nm as an indicator of aromaticity (Chin et al. 1994), and the ratio of absorption spectral slopes from 2 wavelength intervals in the UV as a metric of molecular weight (Helms et al. 2008).

Changes in DOC and CDOM levels during high flow (runoff) events have been reported in several stream and river studies (Coyne et al. 2005, Striegel et al. 2005, Inamdar et al. 2006, Yang et al. 2013). Parallel measurements of proxies have suggested concurrent changes in composition may occur (Hood et al. 2005, Fellman et al. 2009, Spencer et al. 2010, Yang et al. 2013). Such dynamics in terrestrial inputs offer challenges for robust temporal resolution of stream inputs and establishing linkages between these inputs and $a_{\text{CDOM}}$ patterns in receiving lakes. Based on a large DOC dataset for streams from 30 small forested watersheds in the eastern United States that featured increased monitoring coverage during intervals of high flow and continuous flow measurements, Raymond and Saiers (2010) reported 86% of DOC exported annually was during runoff events. Such features support the need for emphasis on tributary $a_{\text{CDOM}}$ dynamics during runoff events to quantify terrigenous inputs and advance the coupling with patterns in receiving lakes.

The overarching goal of this study is to advance the linkage between lacustrine patterns of $a_{\text{CDOM}}$ and its composition proxies with those of terrestrial sources, based on analysis of detailed concurrent lake and tributary measurements for Cayuga Lake, New York, made over a 7 month period. Elements of the presentation include: (1) resolution of in-lake patterns of $a_{\text{CDOM}}$, DOC, and proxies of their composition; (2) evaluation of the importance of $a_{\text{CDOM}}$ both as a component of $a$ (e.g., reference $\lambda = 440$ nm) and in influencing light penetration (e.g., attenuation coefficient).
in the lake; (3) resolution of the dynamics of $a_{\text{CDOM}}$, DOC, and proxies of their composition for multiple tributaries over a robust range of stream flows; (4) development of $a_{\text{CDOM}}$-flow and composition proxy-flow relationships and estimates of loads and volume-weighted values for the tributaries; (5) analysis of the contrasting conditions for $a_{\text{CDOM}}$, DOC, and composition proxies in the tributaries versus the lake; and (6) development of approximate $a_{\text{CDOM}}$ and DOC budgets for the upper waters of the lake. This is the first simultaneous linkage of $a_{\text{CDOM}}$ magnitude and its composition proxies for a large lake and its tributaries.

**Methods**

**System description**

Cayuga Lake (42°41′30″N, 76°41′20″W) is the fourth easternmost of the New York Finger Lakes and has the second largest surface area (172 km$^2$) and volume (9.4 × 10$^9$ m$^3$) (Fig. 1; Schaffner and Oglesby 1978). Its mean and maximum depths are 55 m and 133 m, respectively. It is an alkaline, hardwater, mesotrophic (Effler et al. 2010) lake with a warm monomictic stratification regime (Oglesby 1978). The average retention time of the lake (completely mixed assumption) is about 10 years (Schaffner and Oglesby 1978), with a net transport from south to north. Three streams that enter the southern end of the lake—Fall Creek, Cayuga Inlet, and Six Mile Creek—contribute nearly 40% of the total inflow (Fig. 1). The southernmost 2 km of the lake that receives these inflows is shallow (≤6 m) and is termed “the shelf.”

Fall Creek is the largest tributary to the lake, with a watershed area nearly 18% of the total (Table 1). This stream and 3 others—Cayuga Inlet, Six Mile Creek, and Salmon Creek—had continuous flow gauges proximate to their mouths (Fig. 1) during the study period of 2013. Fall Creek has the longest record of flow measurements, 89 years. Agricultural land use is particularly high in the Salmon Creek watershed (68%) but is also important in Fall Creek (Table 1). Land use conditions in the ungauged portion of the Lake’s watershed are generally similar (Table 1). The largest ungauged tributary has a watershed area 9% of the total; the next largest of the other 30 ungauged streams is 3%.

**Sampling and field measurements**

Sampling and field measurements for the southern half of the lake and the 4 gauged tributaries were conducted concurrently over the April through October interval of 2013. Three sites positioned along the lake’s primary axis, including one on the shelf (site 2) and 2 pelagic sites (depths >100 m) extending to mid-lake (sites 3 and 5; Fig. 1), were monitored. Sites 2 and 3 were sampled biweekly in April, May, and October and weekly for the June through September interval. Site 5 was monitored biweekly throughout the April through October interval. Near-surface (0.5 m) lake samples (triplicate at site 5) were collected at all 3 sites in glass containers for laboratory analysis, kept cool and dark, and processed and analyzed within 24 hours.

Stream samples were collected near the mouths of the 4 gauged tributaries (Fig. 1, Table 1). Stream sampling had 2 components: (1) biweekly fixed frequency sampling, and (2) runoff event sampling. The percentage of total flow (Q) for the study interval monitored, based on the daily average flows for the days of sample collection, ranged from 36 to 45% (Table 1). Runoff event collections were made with automated sampling equipment that could be triggered by changes in the stream stages or remotely, based on near-real-time flow data from gauged sites posted online by the United States Geological Survey (USGS). Samples were selected for analysis according to the goal of providing a robust representation of the event hydrographs.
Spectral measurements of absorption \([a_w(\lambda), \text{m}^{-1} \cdot \text{t-w}]\) relative to pure water over the 400–730 nm interval at a resolution of 4 nm were made \(\text{in situ}\) at the 3 lake sites, concurrent with sample collection, with an ac-s spectral attenuation and absorption meter (25 cm path length; WetLabs). Instrument calibration and adjustments of \(a_w\) were conducted as specified by the manufacturer (WetLabs 2006). Adjustments for the effects of temperature were made according to Pegau et al. (1997).

Scalar irradiance \((I)\) was measured with a spherical quantum photosynthetically active radiation (PAR, 400–700 nm) sensor (LiCor, LI-1935A) attached to a metal frame and lowered with a winch at a rate of \(\sim 0.3 \text{ m s}^{-1}\). These measurements were conducted for sites 2, 3, and 5, and an additional 5 locations along the lake’s primary axis, extending the entire length of the lake (Fig. 1). The attenuation, or extinction, coefficient for scalar irradiance \((k_z; \text{m}^{-1})\) was determined as the slope of the regression of the natural logarithm of \(I\) on depth \((z)\).  

**Laboratory measurements**

Methods for measurement of \(a_{\text{CDOM}}(\lambda)\) were compliant with those specified for satellite ocean color calibration/validation activities (Mitchell et al. 2003). Values of \(a_{\text{CDOM}}\) were determined through spectrophotometric scans (Perkin Elmer, Lambda 35) of filtered water (0.2 µm pore size Millipore membranes) in a 10 cm quartz cuvette, from 400 to 700 nm, using deionized water as reference. A baseline correction was made by subtracting the average absorbance value for the 685–700 nm range from all the spectral values (Binding et al. 2008, Perkins et al. 2013). The spectra were described with an exponential model (equation 2; Twardowski et al. 2004). Values of \(S_{\text{CDOM}}\) were estimated through a nonlinear regression fitting approach (Twardowski et al. 2004) over the 400–500 nm wavelength interval (Perkins et al. 2010, 2013).

DOC was measured according to the persulfate-ultraviolet oxidation method (5310 C; APHA 1992) on filtered (0.7 µm, Merck Millipore) water samples. The magnitude of \(a_{\text{CDOM}}\) at 254 nm (or UV 254; 0.2 µm filter) was determined according to a standard method (USEPA method 415.3; Potter and Wimsatt 2005). SUVA 254 was calculated as the ratio of paired \(a_{\text{CDOM}}(254)\) and DOC measurements.

**Data analysis, loading, and budget calculations**

Three ratios were calculated: (1) \(a_{\text{CDOM}}(440):\text{DOC}\), (2) \(\text{SUVA}_{254}\), and (3) \(a_{\text{CDOM}}(254):a_{\text{CDOM}}(400)\) \((E_{254})\). The first was intended to represent the magnitude of CDOM at a widely adopted reference wavelength (Kirk 2011) per unit of DOC. The second ratio depicts the aromaticity of the DOC pool. The \(E_{254}\) ratio was adopted as a second composition proxy, in addition to \(S_{\text{CDOM}}\) of \(a_{\text{CDOM}}\). Concentration-flow \((Q)\) and ratio–Q relationships were evaluated for the 4 gauged tributaries in a power-law equation format (log-log plots) and tested for performance. The extent of differences in these relationships between the tributaries was evaluated using the Homogeneity-of-Slopes model (StatSoft, Inc. 2003). The Mann-Whitney rank sum test was used to evaluate differences between nonnormally distributed datasets.

Loading rates of \(a_{\text{CDOM}}(440)\) (e.g., \(\text{m}^2 \text{s}^{-1}\)) and DOC (g s\(^{-1}\)) were calculated as the product of these metrics and stream \(Q\) (daily average) based on the continuous flow measurements at each of the 4 tributaries. Adjustments for the intervening portion of the watershed between the mouth and the gauge were made for each stream (3–25%). Loading estimates were made with FLUX software (Walker 1987; FLUX 32 Load Estimation Software, v3.03 Method 6) designed to support such efforts for the common case of combining continuous flow measurements with more temporally limited constituent observations. The adopted protocol (Method 6) used direct estimates of loads for the days of \(a_{\text{CDOM}}\) and DOC monitoring (observed loads). Loads for days without measurements were based

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**Table 1.** Features of gauged tributaries in Cayuga Lake including watershed area, land use, monitoring coverage and associated flow, and \(a_{\text{CDOM}}\) loading.

<table>
<thead>
<tr>
<th>Tributary</th>
<th>Watershed Area (%)</th>
<th>Land* Use (%)</th>
<th>Number of Samples</th>
<th>% Flow (of total)</th>
<th>% High* Flow (a_{\text{CDOM}}) Load</th>
<th>% High* Flow DOC Load</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fall Creek</td>
<td>17.7</td>
<td>48, 40, 0, 11</td>
<td>64</td>
<td>45</td>
<td>70.5</td>
<td>65.4</td>
</tr>
<tr>
<td>Cayuga Inlet</td>
<td>12.9</td>
<td>29, 55, 0, 15</td>
<td>46</td>
<td>45</td>
<td>80.3</td>
<td>75.6</td>
</tr>
<tr>
<td>Salmon Creek</td>
<td>12.5</td>
<td>68, 23, 1, 7</td>
<td>59</td>
<td>36</td>
<td>79.4</td>
<td>74.9</td>
</tr>
<tr>
<td>Six Mile Creek</td>
<td>7.2</td>
<td>21, 63, 0, 15</td>
<td>43</td>
<td>41</td>
<td>77.0</td>
<td>63.7</td>
</tr>
<tr>
<td>Unmonitored</td>
<td>49.7</td>
<td>60, 25, 1, 14</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

* land use percentages separated by commas indicate agriculture, forest, other rural, and urban uses, respectively.

* those loads received when \(Q\) was greater than the mean.
on the In transformed $a_{\text{CDOM}}$–Q and DOC–Q relationships and interpolated residuals (observed loads minus the constituent–Q relationship loads). The daily load estimates between days of observed loads were calculated as the sums of the $a_{\text{CDOM}}$–Q and DOC–Q-based values plus the interpolated residuals.

Volume-weighted $a_{\text{CDOM}}$ DOC, and composition proxy values were calculated for the 4 gauged tributaries by dividing the estimated total load by the total flow for the study period. Two flow strata were adopted to partition runoff event contributions to $a_{\text{CDOM}}$ and DOC loading, demarcated by the mean Q for the study period. This flow corresponded approximately to the upper quartile for the long-term record of Fall Creek. Loads for Qs greater than this threshold were attributed to runoff events.

These rare concurrent lake and tributary $a_{\text{CDOM}}$ and DOC datasets, including inputs during major runoff events, despite the incomplete coverage of the watershed, support a first set of approximate paired budget calculations for these components for the epilimnion of a lake, as described by:

$$\text{external load} = (\Delta \text{lake content}) + \text{(export)} + \text{(in-lake losses)}.$$ (3)

The 4 components of the budget have units of kg for DOC and m³ for $a_{\text{CDOM}}$ (440). The budgets were calculated for the April–October study interval. There are approximations and uncertainties embedded in each of these calculated terms. The change ($\Delta$) in lake content was calculated as the product of the change in concentration over the study period and the volume of the epilimnion (average depth of 10 m, corresponding volume of $1.4 \times 10^8$ m³). The export was calculated as the product of the estimated sum of the tributary inflows (i.e., assumed to equal export) for the study period and the study average concentration at pelagic site 5 (assumed equivalent to outflowing water). The sum of the tributary inflows was calculated by adjusting the sum of the gauged inflows by the portion of the overall lake watershed not gauged (~50%; i.e., adjustment factor of 2). The in-lake losses were calculated as a residual according to the above budget (equation 3). The corresponding approximate estimates of fractions of the fate of the external loads (partitioned according to $\Delta$ lake content, export, and in-lake losses) are presented.

Results

Lake patterns and relationships

The time series of daily average flows in Fall Creek for the study period (Fig. 2a), along with the historic mean, are presented to provide hydrologic context for the in-lake patterns of $a_{\text{CDOM}}$ and its characteristics. The total flow for the interval ranked 32nd highest of the 89-year record. Flow was elevated at the onset of sampling in April. Multiple runoff events occurred, the largest in late June, mid-July, and early August. The August event had a return interval of 2 years.

The dynamics of $a_{\text{CDOM}}$ (440), DOC, and the composition proxies are compared for sites 2 and 3 (Fig. 2b–h). The depicted temporal, and in some cases spatial, variability should be considered in the context of the performance of analytical results for triplicate lake samples; median coefficient of variation (cv) values (n = 12) were 4.3, 2.9, and 2.4% for $a_{\text{CDOM}}$ (440), DOC, and $a_{\text{CDOM}}$ (254), respectively. Spatially, the greatest differences were observed between sites 2 and 3. Conditions at site 5 were generally similar to those at site 3 and are represented here only in the comparison of average values and variability ($\pm$1 standard deviation) for the 3 sites (bar charts of Fig. 2b–h). Values for $a_{\text{CDOM}}$ (440) ranged from ~0.2 to 0.5 m⁻¹ at site 2, and 0.17 to 0.35 m⁻¹ at site 3 (Fig. 2b). Levels of $a_{\text{CDOM}}$ (440) at site 2, which adjoins the mouths of 3 substantial tributaries, were usually higher and generally more variable than at site 3 (see cv values in % on bar charts, Fig. 2). On average, $a_{\text{CDOM}}$ (440) at site 2 was 21.6% greater than at site 3, with a median value that was significantly greater (p = 0.002; Mann-Whitney rank sum test). Some $a_{\text{CDOM}}$ peaks at site 2 were observed after runoff events, but these did not always coincide with the timing of smaller increases at site 3. General increases in these metrics occurred at both sites over the high runoff interval of late June through August.

The contribution of $a_{\text{CDOM}}$ (440) makes to $a_{\text{lw}}$ for the blue wavelengths is depicted by the ratio $a_{\text{CDOM}}$ (440)/$a_{\text{lw}}$ (440) (Fig. 2c). Average values exceeded 0.5 for all 3 sites, although wide variations (~0.3–0.8) occurred. Average values of the ratio were not significantly different for the 3 sites (p = 0.67, one-way ANOVA). Peaks in the ratio values did not track those for $a_{\text{CDOM}}$ (440) in all cases. The important role of $a_{\text{CDOM}}$ in regulating light penetration in the lake is indicated indirectly by the strong dependence of $k_{\text{t-w}}$ on $a_{\text{CDOM}}$ (440) (Fig. 3a; $r^2 = 0.77$, p < 0.001), and more directly by the dependence of $k_{\text{t-w}}$ on $a_{\text{CDOM}}$ (440) (Fig. 3b, $r^2 = 0.35$, p < 0.001).

Variations in DOC in the lake were smaller than for $a_{\text{CDOM}}$ (Fig. 2d), with generally higher levels of both DOC and $a_{\text{CDOM}}$ after mid-July. The highest DOC value was observed in early July (3.2 mg L⁻¹). The relationship between $a_{\text{CDOM}}$ (440) and DOC for the 3 locations was not strong; only 29% of the variability in $a_{\text{CDOM}}$ (440) was explained by differences in DOC according to linear least-squares regression (p < 0.001; inset Fig. 4a, Table 2). The average DOC at site 2 was only slightly greater than at sites 3 and 5, and the averages were not significantly...
different (p = 0.61, one-way ANOVA). Accordingly, the ratio $a_{\text{CDOM}}$(440):DOC, or the color per unit DOC, varied substantially, particularly at site 2 (Fig. 2e). Increases in the ratio seemed to be qualitatively linked to runoff events, although the increase at site 2 starting in late July remained elevated, with only modest variations through mid-September. A modest gradient in $a_{\text{CDOM}}$(440):DOC extended from the southern end to the pelagic sites; the ratio was ~12% greater (significant, p = 0.01, Mann-Whitney rank sum test) at site 2 than at site 3.

The other 3 composition proxies—SUVA$_{254}$ (Fig. 2f), S$_{\text{CDOM}}$ (Fig. 2g), and E$_2$:E$_4$ (Fig. 2h)—also varied temporally, although SUVA$_{254}$ and S$_{\text{CDOM}}$ were less variable than $a_{\text{CDOM}}$:DOC. Decreases in S$_{\text{CDOM}}$ and E$_2$:E$_4$ were observed when $a_{\text{CDOM}}$ increased in several instances. SUVA$_{254}$ levels were significantly higher at site 2 than sites 3 and 5 (p = 0.048 and 0.034, respectively, t-test), and E$_2$:E$_4$ tended to be lower at site 2, but not significantly (p = 0.107 and 0.144, respectively, t-test). There were no significant differences in S$_{\text{CDOM}}$ among any sites (p = 0.32, one-way ANOVA). The extent to which the composition proxies were predictors of $a_{\text{CDOM}}$ in the lake differed substantially (Fig. 4b–d). Differences in S$_{\text{CDOM}}$ explained 33%
of the variability observed in \(a_{\text{CDOM}}(440)\) according to linear least-squares regression (Fig. 4b; \(p < 0.001\)). The ratio \(E_2:E_4\) performed the best, explaining 56% of the variability in \(a_{\text{CDOM}}(440)\) (Fig. 4c; \(p < 0.001\)). Both of these relationships were negative, with decreases in the proxy as \(a_{\text{CDOM}}(440)\) increased. SUV A\textsubscript{254} was not a significant predictor of \(a_{\text{CDOM}}(440)\) variations in the lake (Fig. 4d). The extent to which relationships among the 4 proxies (including \(a_{\text{CDOM}}(440):\text{DOC}\)) existed in the upper waters of the lake varied. No significant relationships between SUV A\textsubscript{254} and \(a_{\text{CDOM}}(440):\text{DOC}\), and SUV A\textsubscript{254} and the \(a_{\text{CDOM}}\) composition proxies \(S_{\text{CDOM}}\) and \(E_2:E_4\), were observed. The \(a_{\text{CDOM}}\) proxies were reasonably good predictors of changes in the \(a_{\text{CDOM}}(440):\text{DOC}\) ratio. Differences in \(S_{\text{CDOM}}\) (Fig. 4e) and \(E_2:E_4\) (Fig. 4f) explained 36 (\(p < 0.001\)) and 57% (\(p < 0.001\)) of the observed variability in \(a_{\text{CDOM}}(440):\text{DOC}\), respectively, according to linear least squares regression. A strong positive relationship existed between these 2 \(a_{\text{CDOM}}\) composition proxies (Fig. 4g; \(r^2 = 0.56, p < 0.001\)).
Stream dynamics and relationships

The low analytical error for triplicate Salmon Creek samples (median cv values of 2.7, 2.3, and 2.6% for \(a_{\text{CDOM}}(440)\), DOC, and \(a_{\text{CDOM}}(254)\), respectively) supports the representativeness of the temporal variability and differences among the streams reported here. Large variations in \(a_{\text{CDOM}}(440)\) (Fig. 5b) and DOC (Fig. 5c) occurred in each of the tributaries over the study interval, as illustrated here for Fall Creek. The timing of the dynamics for this stream suggests a positive linkage of DOC and \(a_{\text{CDOM}}\) inputs with runoff events, when considered at the time scale of the entire study interval (Fig. 5a). Short time-scale variations are illustrated for Salmon Creek for the largest runoff event in early August, which also includes representation of the dynamics of the 4 composition proxies (Fig. 6). The temporal patterns of \(a_{\text{CDOM}}(440)\) (Fig. 6b), DOC (Fig. 6c), the \(a_{\text{CDOM}}(440):\text{DOC}\) ratio (Fig. 6d), and SUVA\(_{254}\) (Fig. 6e) tightly tracked that of the hydrograph (Fig. 6a). By contrast, the patterns for \(S_{\text{CDOM}}\) (Fig. 6f) and \(E_2:E_4\) (Fig. 6g) were somewhat less responsive and instead had an inverse pattern compared to the hydrograph, demonstrating decreases with increasing flow.

Significant dependencies on \(Q\), in a power-law format, were resolved for \(a_{\text{CDOM}}\), DOC, and the composition proxies for these streams (Fig. 7, Table 2), with 3 exceptions: significant relationships with \(Q\) were not observed for \(S_{\text{CDOM}}\) in Cayuga Inlet and Six Mile Creek, and in \(E_2:E_4\) for Six Mile Creek. The best fit regression lines of all significant power-law relationships are presented, but only the data for Salmon Creek are shown (as the selected example). The metrics for which the relationships were the strongest were \(a_{\text{CDOM}}(440)\) and \(a_{\text{CDOM}}(440):\text{DOC}\) (Table 2). Most of the \(a_{\text{CDOM}}\) and DOC loads (76.3 and 69.7%, respectively) from the 4 tributaries were delivered during runoff events (days when flows were greater than the study average). Rising versus falling limb signatures were observed for certain events and tributaries (Fig. 6); however, the effects from differences between events overwhelmed these such that significantly

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**Fig. 5.** Time-series for Fall Creek for the April–October interval of 2013: (a) daily average flow rate (\(Q\)), (b) \(a_{\text{CDOM}}(440)\), and (c) DOC. Average values with ± 1 standard deviation limits are presented for runoff event days for which multiple measurements were made.

**Fig. 6.** Time-series for Salmon Creek during a runoff event in 2013: (a) flow rate (\(Q\)), measured at 15 minute intervals; (b) \(a_{\text{CDOM}}(440)\); (c) DOC; (d) \(a_{\text{CDOM}}(440):\text{DOC}\); (e) SUVA\(_{254}\); (f) \(S_{\text{CDOM}}\) and (g) \(E_2:E_4\).
different rising and falling limb relationships for the entire study period did not emerge. The occurrences of significant differences in the Q relationships among the tributaries, evaluated by the Homogeneity-of-Slopes model (StatSoft, Inc. 2013), were limited (n = 3).

DOC was a strong positive predictor of \( a_{\text{CDOM}}(440) \) in the tributaries, with differences in DOC explaining 83% (p < 0.001) of the variability in \( a_{\text{CDOM}}(440) \) (Fig. 4a). Negative dependencies of \( a_{\text{CDOM}}(440) \) on the composition proxies of \( S_{\text{CDOM}} \) (Fig. 4b; \( r^2 = 0.26, p < 0.001 \)) and \( E_2:E_4 \) (Fig. 4c; \( r^2 = 0.47, p < 0.001 \)) were observed. A positive dependency prevailed for \( \text{SUVA}_{254} \) (Fig. 4d; \( r^2 = 0.36, p < 0.001 \)). These relationships were generally not significantly different among streams (Homogeneity-of-Slopes model). Significant relationships were found between the composition proxies with the exception of \( \text{SUVA}_{254} \). Negative dependencies of \( a_{\text{CDOM}}(440):\text{DOC} \) on both \( S_{\text{CDOM}} \) (Fig. 4c; \( r^2 = 0.30, p < 0.001 \)) and \( E_2:E_4 \) (Fig. 4f; \( r^2 = 0.50, p < 0.001 \)) were observed. The 2 \( a_{\text{CDOM}} \) proxies of \( S_{\text{CDOM}} \) and \( E_2:E_4 \) were positively correlated (Fig. 4g).

### Linkages between the lake and its tributaries, and multiple component \( a_{\text{CDOM}} \) models

The relative variations in \( a_{\text{CDOM}}(440) \), DOC, \( a_{\text{CDOM}}(440):\text{DOC} \), and \( \text{SUVA}_{254} \) were substantially greater in the monitored tributaries than in the lake (Fig. 8). The flow-weighted concentrations and composition proxy metric values for the streams were generally similar to the median values (Fig. 8). These flow-weighted values were widely different from lake levels, with the exception of \( S_{\text{CDOM}} \) (Fig. 8e). Values of \( a_{\text{CDOM}}(440) \) (Fig. 8a), DOC (Fig. 8b), \( a_{\text{CDOM}}(440):\text{DOC} \) (Fig. 8c), and \( \text{SUVA}_{254} \) (Fig. 8d) were higher in the tributaries than in the lake, and \( E_2:E_4 \) (Fig. 8f) was lower in the tributaries. Although differences in certain of these attributes were observed among the tributaries, such as the somewhat higher \( a_{\text{CDOM}}(440) \) levels in Fall Creek, these were modest relative to those between the tributaries and the lake. The differences between the lake sites (Fig. 2) were smaller than for the streams (Fig. 8).

The relationships between \( a_{\text{CDOM}} \) and DOC, \( a_{\text{CDOM}} \) and composition proxies, and among the proxies converge for the lake and the tributaries (Fig. 4) only in the broadest sense of being consistently positive or negative. The trajectories of these dependencies, described by linear regression statistics, differed greatly. Moreover, DOC was a much stronger predictor of \( a_{\text{CDOM}} \) over the wider ranges encountered in the tributaries (Fig. 4a). A significant \( a_{\text{CDOM}}-\text{SUVA}_{254} \) relationship prevailed for the tributaries but not in the lake (Fig. 4d). Despite the different trajectories, the performances for the other relationships were similar for the lake and the streams (Fig. 4b, c, and e–g).

Multiple linear regression analysis was applied in an effort to explain better the dynamics in \( a_{\text{CDOM}}(440) \) in both the tributaries and the lake, adopting DOC as a predictor \((x_1)\) of the quantity feature, and one of the \( a_{\text{CDOM}} \) composition proxies \((S_{\text{CDOM}} \text{ or } E_2:E_4; x_2; \text{Table 3})\) to represent the color potency (e.g., quality) feature (e.g., variations in \( a_{\text{CDOM}}(440):\text{DOC} \); Fig. 4e and f). This approach resulted in improved performance in predicting \( a_{\text{CDOM}}(440) \) compared to DOC alone (Fig. 4a) for the individual streams (e.g., Salmon Creek), for all 4 tributaries together, and for the lake (Table 3). Both components, DOC, and each of the
Table 3. Multiple linear regression (\(y = m_1 x_1 + m_2 x_2 + b')\) analyses and performance (\(r^2\) and \(p\) values) for prediction of \(a_{CDOM}\)

<table>
<thead>
<tr>
<th>System</th>
<th>(a_{CDOM})</th>
<th>(y)</th>
<th>(x_1)</th>
<th>(x_2)</th>
<th>(m_1)</th>
<th>(m_2)</th>
<th>(b')</th>
<th>(r^2)</th>
<th>(p)</th>
<th>(\text{total})</th>
<th>(x_1)</th>
<th>(x_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salmon Cr.</td>
<td>(a_{CDOM})</td>
<td>DOC</td>
<td>SCDOM</td>
<td>0.50</td>
<td>-131.06</td>
<td>1.54</td>
<td>0.98</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(a_{CDOM})</td>
<td>DOC</td>
<td>E2:E4</td>
<td>0.48</td>
<td>-0.23</td>
<td>0.45</td>
<td>0.98</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>=0.009</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Four tributaries</td>
<td>(a_{CDOM})</td>
<td>DOC</td>
<td>SCDOM</td>
<td>0.41</td>
<td>-199.04</td>
<td>3.16</td>
<td>0.85</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(a_{CDOM})</td>
<td>DOC</td>
<td>E2:E4</td>
<td>0.39</td>
<td>-0.34</td>
<td>1.43</td>
<td>0.87</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cayuga L.</td>
<td>(a_{CDOM})</td>
<td>DOC</td>
<td>SCDOM</td>
<td>0.10</td>
<td>-24.73</td>
<td>0.44</td>
<td>0.49</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(a_{CDOM})</td>
<td>DOC</td>
<td>E2:E4</td>
<td>0.05</td>
<td>-0.02</td>
<td>0.40</td>
<td>0.70</td>
<td>&lt;0.001</td>
<td>&lt;0.019</td>
<td>&lt;0.001</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(a_{CDOM}\) composition proxies, were significant in each of the multiple regression relationships (Table 3). Performance was similar for the \(S_{CDOM}\) versus \(E_2:E_4\) models for the tributaries (\(r^2 = 0.85\) and 0.87, respectively), but \(E_2:E_4\) performed better than \(S_{CDOM}\) (\(r^2 = 0.70\) vs. \(r^2 = 0.47\)) as the second component in explaining the in-lake variance of \(a_{CDOM}\). These results support a 2-component representation of \(a_{CDOM}\), which accommodates the effects of both quantity (e.g., DOC concentration) and quality (composition). The composition component was more important in the lake, where the DOC concentration component was relatively small, than in the tributaries, where the DOC concentration component was relatively large. The model coefficient values for the individual components differed greatly between the lake and the tributaries (Table 3), consistent with the differences in the slopes of the single component analyses (Fig. 4a, e, and f).

The indicated loss pathways for the tributary loads of \(a_{CDOM}\) and DOC over the study period, estimated through the approximate budget analysis, differed substantially (Table 4). The estimated in-lake losses of \(a_{CDOM}\) (~80%) were much greater than for DOC (~20%). The estimated fraction of \(a_{CDOM}\) exported (~20%) was about 3-fold smaller than for DOC. A noteworthy fraction of the DOC load (~20%) was manifested as an increase in DOC in the upper waters, whereas there was no estimated net change in \(a_{CDOM}\) over the study period in those lake layers.

**Discussion**

**Lake conditions, patterns, and relationships**

The important contribution of \(a_{CDOM}\) to \(a\) in the blue wavelengths observed for Cayuga Lake (Fig. 2c) has been a recurring feature for lakes in north temperate climates (Binding et al. 2008, Perkins et al. 2009, 2010, 2013). In the 11 Finger Lakes of New York, \(a_{CDOM}\) (440) represented from 48 to 68% of \(a\) (440) (Perkins et al. 2009). In Onondaga Lake, New York, \(a_{CDOM}\) (440) accounted for 45–60% of \(a\) (440) over a 5-year period during which the lake’s trophic state changed from highly eutrophic to upper mesotrophy (Perkins et al. 2010). The average contribution of \(a_{CDOM}\) (440) in the Laurentian Great Lakes ranged from ~50% (Lake Erie) to ~75% (Lake Superior; Perkins et al. 2013). The contribution of \(a_{CDOM}\) (440) to \(a\) (440) ranged from 40 to 75% for 11 sites in Lake Champlain (O’Donnell et al. 2013).

The dominant role of \(a\) in regulating \(k_1\), (Fig. 3a) prevails widely (Davies-Colley et al. 2003, Perkins et al. 2009, 2010). Accordingly, \(a_{CDOM}\) is an important driver of light penetration, having ecological implications associated with primary production, photochemical reactions, habitat, and the stratification regime (Wetzel 2001). The temporal variability of particulate absorbing constituents, particularly phytoplankton (Perkins et al. 2014), has received greater attention; however, the variability of \(a_{CDOM}\) (440) documented here for pelagic sites in Cayuga Lake (Fig. 2b; cv ~20%), Onondaga Lake (cv ~20%; Perkins et al. 2010), and Lake Ontario (cv ~20%; Perkins et al. 2013) indicates that this component is subject to noteworthy variation in lakes. This contributes to the overall variability in \(a\) and related apparent optical properties (AOPs; Fig. 3b) and limits the representativeness of single survey characterizations.

The shortcomings of DOC and \(a_{CDOM}\) as metrics of each other in Cayuga Lake (Fig. 2e and 4a) apparently prevail in many lakes (Binding et al. 2008, Effler et al. 2010, Perkins et al. 2010, 2013). The \(a_{CDOM}\) per unit DOC, represented here by the \(a_{CDOM}\) (440):DOC ratio, is subject to substantial differences between systems and temporal variations (e.g., Fig. 2e) within individual systems (Morris and Hargreaves 1997). Accordingly, DOC is not a reliable
estimator of \( a_{\text{CDOM}} \) in the absence of direct measurements of this absorbing component, and it is greatly limited as an OAC to be targeted for retrieval by remote sensing (e.g., Shuchman et al. 2013). DOC, however, is well predicted by paired absorbance measurements at 270 and 350 nm (Carter et al. 2012).

The dependencies of lake \( a_{\text{CDOM}} \) levels on the composition proxies of \( S_{\text{CDOM}} \) (Fig. 4b) and \( E_2\):\( E_4 \) (Fig. 4c) indicate that changes in aspects of composition contributed to variations in \( a_{\text{CDOM}} \). The adoption of \( E_2\):\( E_4 \) here instead of \( E_2\):\( E_3 \) (De Haan and De Boer 1987, Peuravuori and Pihlaja 1997) was due to the limitation in the wavelengths covered by our spectrophotometric (400–700 nm) scans; however, analysis of more complete scans for other systems (Onondaga Lake, \( n = 20 \); and Lake Michigan, \( n = 15 \)) indicates that these ratios are highly correlated (\( r = 0.96 \)), and that \( E_2\):\( E_4 \) values can be adjusted to estimate \( E_2\):\( E_3 \) (\( = 0.45E_2\):\( E_4 \) + 0.04; \( p < 0.0001 \)). The negative dependencies of \( a_{\text{CDOM}} \) on these composition proxies indicate that increases in \( a_{\text{CDOM}} \) were linked to greater molecular size, aromaticity, and contributions by humic versus fulvic acids (De Haan and De Boer 1987, Carder et al. 1989, Helms et al. 2008, Minor and Stephens 2008). The lack of a relationship with \( \text{SUVA}_{254} \) (Fig. 4d) suggests this widely used composition proxy for aromaticity of the DOC pool (e.g., Blough and Green 1995, Minor and Stephens 2008) does not provide a valuable metric for its colored component in Cayuga Lake. The extent to which this is a broadly representative finding deserves further attention.

This study seems to be the first demonstration of the dependence of \( a_{\text{CDOM}} \) dynamics in a lacustrine system on both an amount, or quantity, driver (DOC) and the effects of composition, or quality (\( S_{\text{CDOM}} \) or \( E_2\):\( E_4 \); Table 3), represented here in a 2-component linear least-squares regression format:

\[
 a_{\text{CDOM}}(440) = m_1 \cdot (\text{DOC}) + m_2 \cdot (E_2\):\( E_4 \) + \( b \),
\]

where \( m_1 \), \( m_2 \), and \( b \) are regression coefficients. Accordingly, the magnitude of \( a_{\text{CDOM}} \) is represented as a summation of quantity and quality (e.g., potency) terms. Although there are not well-defined mechanistic justifications to represent these effects as simple summations, the performance compared to single-driver relationships (Table 3, Fig. 4a–c) is impressive. The ratio \( E_2\):\( E_4 \) supported better overall model performance (Table 3), probably because of the larger signature provided by the \( a_{\text{CDOM}}(254) \) measurements compared to the visible wavelength measurements. The indicated interplay between quantity and quality characteristics of the colored components of the DOM pool argue against describing \( a_{\text{CDOM}} \) as the colored fraction of DOC.

### Table 4. Loss pathways for external inputs of \( a_{\text{CDOM}} \) and DOC from budget calculations.

<table>
<thead>
<tr>
<th>Loss Pathway</th>
<th>( a_{\text{CDOM}} ) (%)</th>
<th>DOC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>export</td>
<td>19.0</td>
<td>57.4</td>
</tr>
<tr>
<td>( \Delta ) lake content</td>
<td>0</td>
<td>23.8</td>
</tr>
<tr>
<td>in-lake losses</td>
<td>81.0</td>
<td>18.8</td>
</tr>
</tbody>
</table>

Table 4. Loss pathways for external inputs of \( a_{\text{CDOM}} \) and DOC from budget calculations.

Fig. 8. Comparison of observations for 4 streams (3 entering the south end of the lake: Fall Creek [Fall], Six Mile Creek [6M], and Cayuga Inlet [Inlet]), and 3 lake sites, for the April–October interval of 2013, as box and whisker plots (points: 5 and 95 percentile; bars: 10 and 90 percentiles; box limits: 25 and 75 percentiles; line within box is median; x is flow-weighted value for tributaries): (a) \( a_{\text{CDOM}}(440) \), (b) DOC, (c) \( a_{\text{CDOM}}(440) \):DOC, (d) \( \text{SUVA}_{254} \), (e) \( S_{\text{CDOM}} \), and (f) \( E_2\):\( E_4 \). cv values in % appear above boxes.
language that implies a strictly mass contribution relationship. Moreover, our parameterization of this interplay (equation 4) established a level of interconsistency for the observed temporal variations for several of the monitored metrics relative to their relationships with \( a_{\text{CDOM}}(440) \) patterns. These do not emerge from simple inspection of these dynamics (e.g., Fig. 2d, e, g, and h).

### Stream conditions, patterns, and flow relationships

Shifts in the flow path of water entering streams and rivers during runoff events from lower mineral horizons, which prevails during base-flow, to upper soil and litter horizons during flood events occur widely (Frank et al. 2000, Hood et al. 2005, Fellman et al. 2009, Wiegner et al. 2009, Spencer et al. 2010). This change in flow path origin apparently imparted the signatures of DOC and \( a_{\text{CDOM}} \) amount and composition for each of the 4 streams of this study (Fig. 5–7). These signatures of runoff events included (1) several-fold increases in DOC concentrations, (2) even greater increases in \( a_{\text{CDOM}} \) levels, and (3) major changes in composition proxies indicative of higher molecular weights (De Haan and De Boer 1987, Peuravuori and Pihlaja 1997), increased aromaticity (Weishaar et al. 2003), and greater contributions of humic acids relative to fulvic acids (Carder et al. 1989).

Our observations are qualitatively consistent with those reported for other lotic systems. Increases in DOC during runoff events have been reported widely (Inamdar et al. 2006, Fellman et al. 2009, Raymond and Saiers 2010, Yang et al. 2013). Increases in \( a_{\text{CDOM}} \) have been reported less often, and visible wavelengths have not been targeted (Spencer et al. 2009, 2010, Asmala et al. 2012, Yang et al. 2013). Our SUVA\(_{254}\) observations were generally in the range of those reported elsewhere (Hood et al. 2005, Fellman et al. 2009, Spencer et al. 2010), except for the much higher values reported for the North Jiulong River, China (Yang et al. 2013). Increases in SUVA\(_{254}\) during runoff events, as observed for the 4 streams of this study (Fig. 6e and 7d), were also reported by Fellman et al. (2009), Spencer et al. (2010), and Yang et al. (2013). The ratio \( E_{2}E_{4} \) (and here \( E_{2}E_{3} \)) has apparently not been tracked by others during runoff events; instead the spectral slope ratio (Helms et al. 2008) has been applied. Decreases in the spectral slope ratio during events have been reported (Spencer et al. 2010, Yang et al. 2013). Our decreases in \( E_{2}E_{4} \) reported here (Fig. 6g and 7f) are qualitatively consistent with those observations; similar responses for the slope ratio and \( E_{2}E_{3} \) have been observed (Helms et al. 2008).

Development of quantitative dependencies of these attributes on flow rates has lagged the qualitative descriptions of responses to runoff events. DOC has received the greatest attention to date (Inamdar et al. 2006, Raymond and Saiers 2010). The dependence of DOC on Q was well represented by power-law relationships, such as adopted here, in the development of DOC loads (export) from 30 small forested watersheds in the eastern United States (Raymond and Saiers 2010). Such parameterizations are widely used to develop stream and river loading estimates for a broad range of constituents (Vogel et al. 2003). The event-based sampling and analysis conducted here enabled representative loading estimates for DOC and \( a_{\text{CDOM}} \), which each demonstrated the disproportionate contributions of runoff events (~70 and 75% of the total, respectively), similar to that reported for DOC (86%) by Raymond and Saiers (2010). To our knowledge, loading estimates of \( a_{\text{CDOM}}(440) \) have not been reported previously, and neither have the dependencies of \( a_{\text{CDOM}}(440) \) (Fig. 7a), \( a_{\text{CDOM}}(440):\text{DOC} \) (Fig. 7c), SUVA\(_{254} \) (Fig. 7d), \( S_{\text{CDOM}} \) (Fig. 7e), and \( E_{2}E_{4} \) (Fig. 7f) on Q in the power-law format. In addition to providing a quantitative context for such Q dependencies (Table 2), these relationships served to support the calculations of flow-weighted average conditions for each of the tributaries (Fig. 8), which enhance comparisons to the lake and among the streams.

In the context of the individual streams, there were cases of noteworthy differences in the relationships and in the performance of the simple Q-based power-law expressions (Table 2). Other drivers may have contributed to the observed dynamics, such as temperature, antecedent dry weather intervals, and land use activities. Such an array of factors likely contributed to the observed differences in the signatures of the individual events. In the context of the goals of this paper (linking lacustrine \( a_{\text{CDOM}} \) patterns to terrestrial inputs), the signals of amount, timing, and composition of \( a_{\text{CDOM}} \) delivered by the 4 streams to this lake have unifying (Fig. 4, 7, and 8) rather than divergent characteristics. Moreover, these unifying features provided support for the extrapolation of the loading estimates to the ungauged portion of the watershed.

### Linking lacustrine patterns and stream inputs

The substantially higher levels of \( a_{\text{CDOM}} \) (Fig. 8a) and DOC (Fig. 8b) in the tributaries compared to the lake establish allochthonous inputs as important sources of these constituents and suggest the operation of loss processes within the lake. These differences are magnified during runoff events when most of the \( a_{\text{CDOM}} \) is delivered. The lower degree of temporal variations in the lake compared to the streams is broadly representative of the modulating effects of lentic systems for lotic system inputs (Chapra 1997). The differences in the composition...
proxies indicate that lake $a_{\text{CDOM}}$ has lower contributions of CDOM to the DOC pool (Fig. 8c), reduced aromaticity (Weishaar et al. 2003; Fig. 8d), decreased molecular size of CDOM (De Haan and De Boer 1987, Peuravuori and Pihlaja 1997; Fig. 8f), and decreased amounts of humic versus fulvic acids (Carter et al. 1989) relative to the stream inputs. In-lake losses of $a_{\text{CDOM}}$ and DOC (Table 4) and the indicated composition transformations of $a_{\text{CDOM}}$ are consistent with the effects of the operation of photo-chemical (photobleaching) and interactive microbial degradation processes (Moran et al. 2000, Ma and Green 2004, Helms et al. 2008). Minor and Stephens (2008) reported lower DOC and SUVA_{254} and higher E_{2}E_{4} in western Lake Superior relative to local tributaries.

Features of the budget analysis results (Table 4) are generally consistent with the above, but it is important to consider their limitations that lead the authors to describe these as first approximations. These limitations include: (1) incomplete coverage of the entire watershed; (2) representation of outflow conditions by the mid-lake (site 5) observations; (3) an incomplete hydrologic budget; (4) no representation of internal sources; and (5) the acknowledgment that, while these budget calculations remain effective to assess approximate changes in $a_{\text{CDOM}}$, this component is not a constituent concentration, but rather an optical measure. Some observations mitigate these limitations, however, including: (1) the similar general characteristics of the monitored streams (Fig. 7, Table 2); (2) the similarity of DOC concentrations for other tributaries resolved from additional, but temporally limited, monitoring (Upstate Freshwater Institute, 2013, unpubl. data); (3) the uniformity of $k_{s}$ (i.e., $a$; Fig. 3a) observations extending from site 5 to the outlet at the northern end, supporting the use of mid-lake observations to represent outflow conditions (Upstate Freshwater Institute, 2013, unpubl. data); (4) the approximate equivalence of direct precipitation inputs with evaporative losses for lakes in the region (Effler 1996); (5) the success in modeling long-term trends for a conservative substance for the lake based on gauged flows for only part of the watershed (Effler et al. 1989); and (6) the successful inclusion of other optical metrics (e.g., turbidity, not a concentration) in lake mass balance type analyses (Gelda et al. 2013). Given the uncertainties, we emphasize the differences in general magnitudes between $a_{\text{CDOM}}$ and DOC rather than their individual values (Table 4). The lack of a net change in $a_{\text{CDOM}}$ (Fig. 2b) and the estimated substantial (80%) in-lake loss of the tributary load over the study period (Table 4) are consistent with the operation of an effective loss process such as photobleaching (Helms et al. 2008). Given that the CDOM component is subject to photobleaching, and assuming that other source and sink processes are in balance within the upper waters of the lake, the in-lake loss of DOC (–20%) would correspond to the CDOM fraction of the DOC load. The gain in DOC content (–20%) in the upper waters of the lake over the study interval likely corresponds to non-CDOM components of the DOC load. Lake systems can be considered closed in character compared to marine waters and thus more amenable to budget calculations and testing of mechanistic models, contingent on robust monitoring and integration of process studies to independently quantify source and sink processes (Chapra 1997).

The configuration of the tributaries, with such a large fraction of the inflow entering a small area (Fig. 1), together with the large differences between these inputs and the lake (Fig. 8), particularly during runoff events, support expectations for local transition signatures at the southern end of Cayuga Lake, intermediate to those of the streams and pelagic areas. Such transition signatures were resolved for the near-shore site 2 for $a_{\text{CDOM}}$ and certain composition proxies (Fig. 2). These local signatures, however, were generally only modest and short-lived for at least 3 reasons: (1) the photochemical transformations proceed rapidly (Ma and Green 2004); (2) the long retention time (10 y) of the lake (i.e., exposure to photobleaching); and (3) the high level of mixing that prevails in that portion of the lake (Effler et al. 2010). Seiche activity, promoted by the shape of the lake and its orientation (axis along the prevailing wind direction), contributes to the elevated local mixing that brings pelagic photobleached water onto the shelf (site 2) to mix with the tributary inputs. More pronounced and spatially extensive gradients can be expected where the advective components of mixing are more prominent, such as reservoirs (also shorter residence times; Effler et al. 1998) and estuaries (Kostoglidis et al. 2005, Helms et al. 2008).

The signatures of the allochthonous inputs were manifested throughout the well-mixed upper waters of the pelagic zone, albeit more subtly, through the temporal variations in $a_{\text{CDOM}}$ (440) (Fig. 2b), $a_{\text{CDOM}}$ (440):DOC (Fig. 2e), $S_{\text{CDOM}}$ (Fig. 2g), and $E_{2}E_{4}$ (Fig. 2h). Neither the amount of variation nor the details of its temporal structure should be expected to be recurring because these features reflect the magnitude and timing of runoff events that have stochastic characteristics. However, the general character of these signatures, consistent with the effects of photobleaching on terrestrial inputs, is expected to be recurring for this lake and many other lacustrine systems. Stubbins et al. (2010) has described the photoreactivity of DOM according to 3 pools: (1) photo-labile, (2) photo-produced, and (3) photo-resistant. The CDOM of the photo-labile pool received from the watershed is essentially eliminated in its conversion to photo-produced constituents (Stubbins et al. 2010); however, there is a fraction, the photo-resistant pool, which is generally
unaffected and likely contributes importantly to the levels of CDOM measured in this and other lakes. The progression of these transformations and their effect on $\alpha_{\text{CDOM}}$ seem to be well represented in this lake by the $\alpha_{\text{CDOM}}$ composition proxies.

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