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Key Points:

- River impoundments altered longitudinal patterns in the concentration and composition of dissolved organic matter (DOM)
- DOC load was more influenced by river flow, whereas DOM composition was more influenced by river impoundments
- DOM composition was less variable below impoundments then above, and more degraded and terrestrial-like with increased distance downstream

Supporting Information:

- Supporting Information S1

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Impact of seasonality and anthropogenic impoundments on dissolved organic matter dynamics in the Klamath River (Oregon/California, USA)

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Abstract Rivers play a major role in the transport and processing of dissolved organic matter (DOM). Disturbances that impact DOM dynamics, such as river impoundments and flow regulation, have consequences for biogeochemical cycling and aquatic ecosystems. In this study we examined how river impoundments and hydrologic regulation impact DOM quantity and quality by tracking spatial and seasonal patterns of DOM in a large, regulated river (Klamath River, USA). Dissolved organic carbon (DOC) concentrations decreased downstream and longitudinal patterns in DOC load varied by season. Export of DOM (as DOC) was largely driven by river flow, while DOM composition was strongly influenced by impoundments. Seasonal algal blooms in upstream lentic reaches provided a steady source of algal DOM that was processed in downstream reaches. DOM at upstream sites had an average spectral slope ratio (S_R) > 1, indicating algal-derived material, but decreased downstream to an average S_R < 1, more indicative of terrestrial-derived material. The increasingly terrestrial nature of DOM exported from reservoirs likely reflects degraded algal material that becomes increasingly more recalcitrant with distance from upstream source and additional processing. As a result, DOM delivered to free-flowing river reaches below impoundments was less variable in composition. Downstream of impoundments, tributary influences resulted in increasing contributions of terrestrial DOM from the surrounding watershed. Removal of the four lower dams on the Klamath River is scheduled to proceed in the next decade. These results suggest that management should consider the role of impoundments on altering DOM dynamics, particularly in the context of dam removal.

1. Introduction

Dissolved organic matter (DOM) plays a wide variety of roles in aquatic ecosystems [*Battin et al.*, 2008; *Kritzberg et al.*, 2006]. Riverine systems have gained increasingly widespread recognition for their importance in global carbon cycling [*Battin et al.*, 2008; *Raymond et al.*, 2013], and the flux of riverine DOM to receiving coastal ecosystems represents a major source of reduced carbon to these environments [*Hedges et al.*, 1997; *Raymond and Spencer*, 2015]. Naturally, the composition of DOM exported via rivers is of great importance as it determines its biogeochemical role. For example, past studies have linked DOM compositional measurements to ecosystem function through processes such as microbial processing, photodegradation, sorption, complexation, and mineralization [*Cory et al.*, 2014; *Jaffe et al.*, 2008; *Mann et al.*, 2015]. Therefore, drivers of DOM composition are fundamentally important to assess the role of DOM in aquatic environments and its ultimate fate.

Spatial connectivity within a river basin can affect dissolved organic carbon (DOC) concentration and DOM composition [*Baker and Spencer*, 2004; *Massicotte and Frenette*, 2011; *Shen et al.*, 2012]. Anthropogenic impacts, such as river impoundments (i.e., dams), alter spatial connectivity by disconnecting a river from its natural landscape and flow regime (i.e., hydrologic regulation) and can result in a variety of ecological impacts, including alteration of nutrient transport and processing [*Benke*, 1990; *Rosenberg et al.*, 2000]. Impoundments drive the spatial and temporal variation of DOM [*Mash et al.*, 2004; *Duan et al.*, 2007; *Kraus et al.*, 2011]. Reservoirs affect the source and processing of DOM [*Groeger and Kimmel*, 1984; *Hernes et al.*, 2008; *Kemenes et al.*, 2007], including increased degradation of DOM, as well as generation of new DOM via aquatic primary and secondary productivity [*Wehr and Thorp*, 1997; *Bianchi et al.*, 2004; *Mash et al.*, 2004]. In addition, reservoirs on some large, arid rivers have been shown to alter the quantity and composition of carbon in tailwaters and subsequent downstream reaches [*Ulseth and Hall*, 2015]. Because of these factors, DOM dynamics within regulated rivers are likely not representative of conditions found within a free-flowing river and there remains relatively little known about the spatial and temporal dynamics of DOM in large, regulated rivers. This is a particularly pertinent

Figure 1. Map of the Klamath River watershed and sample site locations.

research question as construction of hydropower dams is still increasing [*Winemiller et al.*, 2016], and major questions remain about what dam removal means for aquatic ecosystems [*Poff and Hart*, 2002; *Warrick et al.*, 2015].

The primary objective of this study was to examine how anthropogenic river impoundments and hydrologic regulation affect spatial and temporal patterns in DOC quantity and DOM quality. The study design allowed us to examine if impoundments shifted downstream DOM composition from primarily terrestrial sources to algal sources (i.e., upstream/downstream sampling of dams) and how hydrology (i.e., river discharge) impacts DOM export and composition across seasons. DOM composition was examined using a suite of chromophoric dissolved organic matter (CDOM) parameters that can be linked to molecular weight and aromaticity [*Helms et al.*, 2008; *Spencer et al.*, 2012]. Since several CDOM parameters can be measured in situ at a high temporal resolution [*Spencer et al.*, 2007a, 2007b; *Pellerin et al.*, 2012], a further aim of this study was to assess the utility of different parameters for tracking DOC export and DOM composition in impounded systems. Specifically, this work will help inform restoration activities associated with removal of the four lower dams on Klamath River (Oregon/California, USA) scheduled for the next decade.

2. Methods

2.1. Study Area: The Klamath River

The Klamath River Basin covers approximately 40,632 km^2 of south-central Oregon and northwestern California (Figure 1). The Klamath River emanates from Upper Klamath Lake (surface area ~250 km^2) and flows 402 km to the Pacific Ocean. The watershed is divided into upper (20,875 km^2) and lower (19,757 km^2) basins (Figure 1) having distinct geology, hydrology, and geomorphology. The Klamath River Basin differs from many watersheds in that the greatest relief and topographic complexity occur in the lower basin [*Mount*, 1995]. The upper basin is lower relief and semiarid (average annual precipitation = 330–1650 mm yr^{-1} (Western Regional Climate Center (WRCC); http://www.wrcc.dri.edu/summary/Climsmor.html)), and the majority of hydrologic inputs are derived from groundwater and snowmelt runoff [*Gannett et al.*, 2007]. The lower Klamath Basin, designated as the watershed area below the lowest dam (Iron Gate Dam, river kilometer 360, or "RK360"; Figure 1), is more mountainous than the upper basin and becomes increasingly temperate and wet with distance downstream (average annual precipitation ≥ 2350 mm yr^{-1} (WRCC)).

Table 1. Descriptive Characteristics of the Five Klamath River Reservoirs, Excluding Upper Klamath Lake[a]

	Reservoir				
	Keno	JC Boyle	Copco I	Copco II	Iron Gate
Length (km)	36.21	5.79	7.40	0.48	9.98
Max surface area (km^2)	10.02	1.70	4.05	0.16	3.82
Max depth (m)	5.94	12.71	35.20	8.53	49.56
Total storage capacity (m^3)	2.28×10^7	4.31×10^6	5.78×10^7	9.00×10^4	7.25×10^7
Residence time (days) at 20 $m^3\ s^{-1}$	13	2.5	32	0.5	42
Residence time (days) at 43 $m^3\ s^{-1}$	6	1.2	15	0.03	20
Residence time (days) at 85 $m^3\ s^{-1}$	3	0.6	8	0.01	10

[a]Adapted from *PacifiCorp* [2008a, 2008b].

Upper Klamath Lake (UKL) is a naturally occurring lake, although over the past century a dam located at the lake's outlet has regulated lake water levels. During our study (May 2010 to June 2011) flows out of UKL ranged from 10 $m^3\ s^{-1}$ in winter to 110 $m^3\ s^{-1}$ during spring runoff (U.S. Geological Survey (USGS) station 11507500). Below UKL, there are five additional dams and reservoirs that fragment the 97 km of the upper basin (from here, designated "upper river") into a series of reservoirs and river reaches (Table 1). The upper river reaches of the Klamath River experience seasonal algal blooms (summer and fall) dominated by the nitrogen-fixing cyanobacteria *Aphanizomenon flos-aquae* and are designated hypereutrophic [*Eilers et al.*, 2004; *Jacoby and Kann*, 2007]. Multiple water quality impairments are found throughout the upper river, including organic matter and nutrient enrichment, low dissolved oxygen, high pH, and high water temperatures [*Oregon Department of Environmental Quality*, 2010].

In the lower Klamath River Basin (from here, designated "lower river"), flows are initially controlled by operations at Iron Gate Dam [*National Marine Fisheries Service*, 2010], but downstream in the free-flowing lower river, flows increase and become more variable due to the influence of tributaries and storm events. During our study period releases from Iron Gate Dam ranged from 23 to 161 $m^3\ s^{-1}$ (USGS station 11516530, RK = 306; Figure 1), with accretion downstream contributing to flows of 80 to 2692 $m^3\ s^{-1}$ at the river mouth near Klamath, CA (USGS station 11530500; RK = 6).

2.2. Sample Collection and Processing

Water samples were collected monthly from May 2010 to June 2011 at nine sites over 183 km of the Klamath River from UKL (RK400) to Seiad Valley, CA (RK217) (Figure 1). Sites were selected to capture major longitudinal water quality transformations throughout the study area, including above and below both reservoirs and major tributaries. Due to limited access and the continuity of water (i.e., no intermediate river reaches) between the three lowest reservoirs (Copco I, Copco II, and Iron Gate Reservoirs; total storage ~$13.0 \times 10^7\ m^3$; Table 1), samples were collected above Copco I and below Iron Gate reservoir. For purposes of discussion, four of the nine sampling sites were selected as representative sites of specific river conditions within the project area: the uppermost site below the outlet of UKL (RK400), above Copco Reservoir (RK335), below Iron Gate Reservoir (RK306), and the furthest downstream site at Seiad Valley (RK217) (Figure 1).

At five sampling sites, river discharge was obtained from USGS gauges (Table 1). At the remaining four sites, flows were estimated using the one-dimensional form (i.e., laterally and depth averaged) of the hydrodynamic model, RMA-2 [*King*, 2001]. Flow boundary conditions were established with data from USGS gauges, as well as reservoir storage data provided by PacifiCorp. RMA-2 has been previously calibrated and applied on the Klamath River [*Deas and Orlob*, 1999; *PacifiCorp*, 2005; *Basdekas and Deas*, 2007], and further calibration for this study was not required. Details on the inputs, run specifications, and evaluation of the performance of the RMA-2 hydrodynamic model are given in Table S1 in the supporting information. Error statistics were determined by comparing modeled flows at boundary conditions with observed flows from USGS gauge stations where available.

Water samples were collected as grab samples from the upper 50 cm of a well-mixed water column near the channel midpoint (river depth range of 100–400 cm). Samples were filtered in the field with a prerinsed Whatman GD/X syringe filter (0.45 μm), stored in the dark, and refrigerated at 4°C through the completion of analysis. A YSI 556 sonde (YSI, Yellow Springs, OH, USA) was used to record field measurements of temperature and pH.

Dissolved organic carbon (DOC) measurements were performed using a Dohrmann UV-enhanced persulfate total organic carbon analyzer (Phoenix 8000, Teledyne Tekmar, Mason, Ohio; LOD ~ 0.1 mg/L). Chlorophyll-*a* (Chl *a*) and phaeophytin-*a* (Ph-*a*) were determined by filtering 0.5 to 1 L of well-mixed sample through a GF/F filter. Filters were freeze-dried and extracted with 90% ethanol prior to quantification by fluorometry [*Clesceri et al.*, 1998]. UV-visible absorbance was determined within 72 h of collection with a Shimadzu UV-2501PC spectrophotometer (Shimadzu Scientific Instruments Inc.; Columbia, MD, USA) in a 1 cm quartz cell between the wavelengths of 200–800 nm and then blank-corrected using a reference spectrum of distilled water. Chromophoric dissolved organic matter (CDOM) absorbance data (i.e., a_{350}) are reported as Napierian absorption coefficients $a(\lambda)$ in m^{-1}.

The spectral slope (S) parameter varies with CDOM source and biological and photochemical processes that lead to changes in molecular weight or aromaticity [*Spencer et al.*, 2007a, 2007b; *Helms et al.*, 2008]. Spectral slope values were calculated for wavelength ranges 275–295 nm ($S_{275-295}$) and 350–400 nm ($S_{350-400}$) as previous studies have shown that these wavelength ranges are sensitive to changes in the chemical composition of CDOM and track processes that differentially influence S [*Helms et al.*, 2008]. Calculations of S were subsequently used to determine the spectral slope ratio (S_R) of $S_{275-295}:S_{350-400}$, where lower S_R indicates CDOM of higher molecular weight, increased aromaticity, and greater vascular plant input, and higher S_R indicates CDOM of lower molecular weight, reduced aromaticity, and greater algal contributions or increased biological degradation [*Helms et al.*, 2008].

All statistics were performed using the statistical package Stata [*StataCorp*, 2009]. Site did not have a significant effect on the relationship between DOC concentration and the CDOM optical parameter a_{350}, and so this relationship was evaluated using a general linear regression model. Additional relationships between selected water quality and CDOM parameters were assessed with data from all sites and time periods. Despite transformation, some data lacked linearity and constant variance, and therefore, the data set was assessed using the Spearman's rank correlation coefficient.

2.3. Load Calculations

DOC load calculations were estimated using the software package LoadRunner [*Booth et al.*, 2007], which automates runs of the USGS load estimator program LOADEST [*Runkel et al.*, 2004]. LOADEST uses a time series of paired constituent and discharge data to determine a best fit calibration regression equation using Akaike's information criterion. During model selection, discharge and time were centered to avoid multicollinearity, and because all residuals were normally distributed, the calibrated equation was fit using the adjusted maximum likelihood estimator. The calibration regression equation was then applied to continuous daily discharge records to obtain flux estimates of daily constituent loads (Table S2).

2.4. Designation of Seasonal Time Periods

For purposes of comparisons and discussion, the annual water quality record was reduced to four seasonal periods representing distinct water quality and hydrologic conditions. The four seasonal periods were defined as "bloom," the onset and initial peak of the algal bloom (May–July); "post bloom," the persistence of the bloom through summer following the initial peak and subsequent decline into early fall (August–October); "winter low flow," winter low discharge (November–January); and "winter/spring high flow," high discharge during late winter storms and spring runoff (February–April). Data from selected time periods had small sample size and were nonnormally distributed due to skewed effects of temporal periods of high biological activity. In addition, selected time periods had different sample sizes; therefore, we compared the medians from each time period using the nonparametric Kruskal-Wallis analysis of variance test on ranks [*Kruskal and Wallis*, 1952] and Tukey multiple comparisons to determine time periods that were statistically different for specific water quality parameters. The selected seasonal periods were found to be statistically different ($p < 0.001$) with respect to temperature, discharge, pH, Chl *a*, and DOC. To test the sensitivity for distinguishing the seasonal period assumptions, we modified each time period to include months previous to or following the aforementioned periods. These modifications resulted in nonsignificant differences between bloom and postbloom periods for Chl *a*, and DOC, but not for temperature, discharge, and pH. For winter low-flow and winter/spring high-flow periods, modification resulted in nonsignificant differences in discharge and DOC, but not temperature, Chl *a*, or pH, likely because these seasonal periods experience low biological activity and biogeochemical processing.

Table 2. Site Descriptions, Discharge, Water Quality, and CDOM Data From Sampling Sites on the Klamath River[a,b]

Site Name (river km)	Site Description	Discharge ($m^3 s^{-1}$)	DOC ($mg L^{-1}$)	pH	Chl a ($\mu g L^{-1}$)	Ph-a ($\mu g L^{-1}$)	*a*350 (m^{-1})	$S_{275–295}$ ($10^{-2} nm^{-1}$)	$S_{350–400}$ (nm^{-1})	Sr
RK400	Below Upper Klamath Lake	42.7 ± 24.8 (10.1–109.9)	6.2 ± 1.6 (4.6–9.7)	8.3 ± 0.4 (7.5–8.9)	46.5 ± 78.5 (1.4–274.7)	12.2 ± 22.5 (1.3–78.1)	9.0 ± 3.3 (4.7–16.8)	1.7 ± 0.1 (1.6–1.9)	1.6 ± 0.2 (1.3–1.9)	1.1 ± 0.1 (1.0–1.3)
RK375	Below Keno Reservoir	44.2 ± 27.5 (6.9–119.5)	6.7 ± 1.2 (5.3–8.8)	8.2 ± 0.6 (7.4–9.7)	13.6 ± 11.3 (0.9–38.2)	14.6 ± 33.1 (1.5–124.2)	9.0 ± 1.6 (5.8–10.6)	1.8 ± 0.1 (1.6–1.9)	1.7 ± 0.2 (1.3–2.2)	1.1 ± 0.1 (0.8–1.3)
RK367*	Above JC Boyle Reservoir	36.0 ± 23.8 (9.4–117.6)	6.6 ± 1.1 (5.6–8.8)	7.9 ± 0.5 (6.7–8.7)	10.6 ± 9.11 (1.2–33.1)	11.9 ± 22.2 (2.4–85.5)	9.0 ± 1.9 (5.7–12.0)	1.7 ± 0.1 (1.6–1.9)	1.7 ± 0.3 (1.2–2.2)	1.1 ± 0.2 (0.8–1.3)
RK360	Below JC Boyle Reservoir	43.8 ± 30.4 (9.5–150.9)	5.5 ± 0.8 (4.6–7.2)	7.9 ± 0.6 (6.4–8.6)	9.1 ± 9.6 (0.5–48.3)	7.0 ± 10.3 (1.6–39.3)	7.1 ± 1.6 (4.4–9.8)	1.8 ± 0.1 (1.6–1.9)	1.8 ± 0.2 (1.3–2.3)	1.0 ± 0.1 (0.8–1.2)
RK335*	Above Copco I Reservoir	42.3 ± 25.1 (14.6–114.5)	6.6 ± 0.4 (3.8–5.4)	7.9 ± 0.6 (6.6–8.7)	10.6 ± 13.8 (0.9–19.7)	11.9 ± 10.6 (1.6–6.1)	7.0 ± 1.7 (4.2–9.4)	1.73 ± 0.09 (1.6–2.0)	1.7 ± 0.3 (1.3–2.3)	1.0 ± 0.4 (0.8–1.2)
RK306	Below Iron Gate Reservoir	52.9 ± 32.7 (22.8–161.4)	4.8 ± 0.4 (4.0–5.5)	8.0 ± 0.8 (6.4–8.8)	6.6 ± 14.9 (0.3–37.3)	3.4 ± 10.6 (0.8–14.2)	5.9 ± 1.1 (4.1–8.0)	1.78 ± 0.1 (1.6–2.0)	2.0 ± 0.4 (1.5–2.6)	0.9 ± 0.1 (0.7–1.1)
RK283*	Above Shasta River tributary	59.1 ± 35.6 (25.4–173.9)	4.87 ± 0.59 (4.1–5.7)	7.9 ± 0.8 (5.7–8.7)	7.7 ± 11.7 (0.2–43.2)	5.0 ± 1.5 (1.0–36.6)	6.0 ± 1.0 (4.7–8.0)	1.7 ± 0.1 (1.6–1.9)	1.9 ± 0.3 (1.5–2.3)	0.9 ± 0.1 (0.7–1.1)
RK233*	Above Scott River tributary	71.2 ± 43.4 (27.8–205.3)	4.4 ± 0.6 (3.4–5.4)	8.0 ± 0.8 (5.7–8.7)	4.1 ± 5.8 (19.7–0.3)	2.6 ± 1.4 (1.3–6.1)	5.8 ± 1.1 (4.4–8.0)	1.7 ± 0.1 (1.6–1.9)	2.0 ± 0.3 (1.5–2.4)	0.9 ± 0.1 (0.7–1.1)
RK217	Seiad Valley	102.7 ± 67.1 (29.7–345.5)	3.8 ± 0.7 (1.1–5.0)	8.1 ± 0.8 (7.8–8.6)	2.6 ± 2.6 (0.3–9.6)	3.1 ± 2.6 (0.5–10.3)	4.8 ± 0.7 (4.1–5.9)	1.6 ± 0.1 (1.5–1.8)	1.9 ± 0.3 (1.5–2.3)	0.9 ± 0.1 (0.7–1.2)

[a]Values are mean ± standard deviation; parentheses are minimum and maximum values.
[b]Discharge at sites with an asterisk was obtained using simulated flows from RMA-2.

3. Results

3.1. Hydrology and Water Quality

Hydrologic and water quality conditions exhibited both longitudinal and seasonal trends (Table 2). Discharge magnitude and variability increased downstream and were highly dependent on seasonality. Precipitation during the study period was ~125% of the average (water years 1998–2009, average precipitation = 296 mm at Klamath Falls; http://www.usbr.gov/pn/agrimet) and produced high flows during late winter storm events and snowmelt runoff (February–June 2011). Overall, sites in the upper river exhibited higher temperatures, pH, and concentrations of DOC, Chl *a*, and Ph-*a* than sites in the lower river. The timing of algal blooms was also associated with longitudinal position; bloom development occurred earlier in the summer at more upstream sites. Algal bloom dynamics that most markedly affect water quality in UKL typically peak in June and July, and then abate in September through October [*Eldridge et al.*, 2012; *Wood et al.*, 2006]. Across all sites, the highest concentrations of Chl *a* and Ph-*a* occurred during the bloom period, while the postbloom period exhibited the highest temperatures, highest pH, and lowest DO. Water quality differences between sites were the greatest during the postbloom period, whereas conditions were more homogenous across all sites during winter low-flow and winter/spring high-flow periods (Table 2).

3.2. Spatial and Temporal Patterns in DOC Concentration and Loads

DOC concentrations were generally higher and had greater seasonal variability at sites above dams than below dams, although the most downstream site had lower concentrations but high seasonal variability (Table 2 and Figure 2). There was a significant linear relationship between DOC and the optical measure of a_{350} ($y = 1.27x–0.01$, $r^2 = 0.65$, $p < 0.001$, $n = 115$), and the two parameters exhibited similar longitudinal and seasonal patterns. In contrast to DOC concentrations, which decreased downstream, the annual DOC load (June 2010 to June 2011) increased substantially downstream, from 7.04×10^3 Mg yr^{-1} at RK400 to 1.26×10^4 Mg yr^{-1} at RK217 (Figure 3). However, subannual loads deviated from this pattern and reflected seasonal differences among sites, with notably smaller downstream increases occurring during bloom and postbloom times than other seasons. Seasonal differences were also observed at sites above versus below reservoirs, but the direction of these differences (decreased versus increased load) was site specific. Discharge-weighted mean DOC concentrations indicated that these seasonal differences in DOC loads were driven largely by changes in hydrologic flux. The effect of hydrologic flux on DOC dynamics was especially apparent in the lower river during winter months when lower biological activity and/or higher discharge from tributaries, increased river discharge and DOC load, but reduced DOC concentration (via dilution).

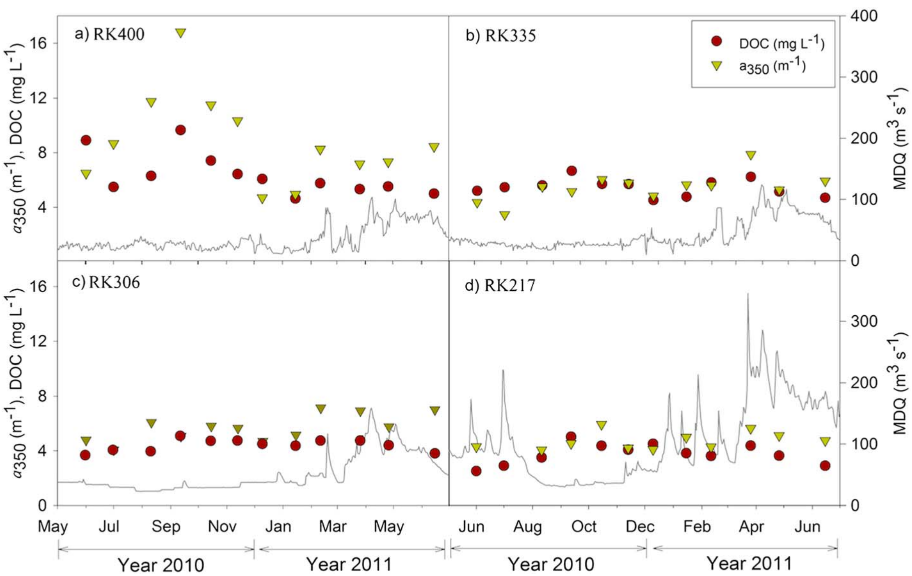

Figure 2. Time series of monthly a_{350}, DOC, and mean daily discharge (MDQ) for representative sites on the Klamath River (a) RK400, (b) RK335, (c) RK306, and (d) RK217.

3.3. Spatial and Temporal Patterns in DOM Composition

DOM composition also varied longitudinally and seasonally (Table 2 and Figure 4). Both $S_{350–400}$ and S_R exhibited longitudinal and seasonal trends; however, $S_{275–295}$ showed little variation over the study period (mean $S_{275–295} = 17.5 \times 10^{-3}$ nm^{-1}, SD $\pm 0.9 \times 10^{-3}$ nm^{-1}, $n = 107$); therefore, observed patterns in S_R were largely driven by changes in $S_{350–400}$ relative to $S_{275–295}$. The most upstream sites had the lowest values of $S_{350–400}$, and these values shifted temporally. Overall, $S_{350–400}$ values increased (i.e., steeper slope) in the downstream

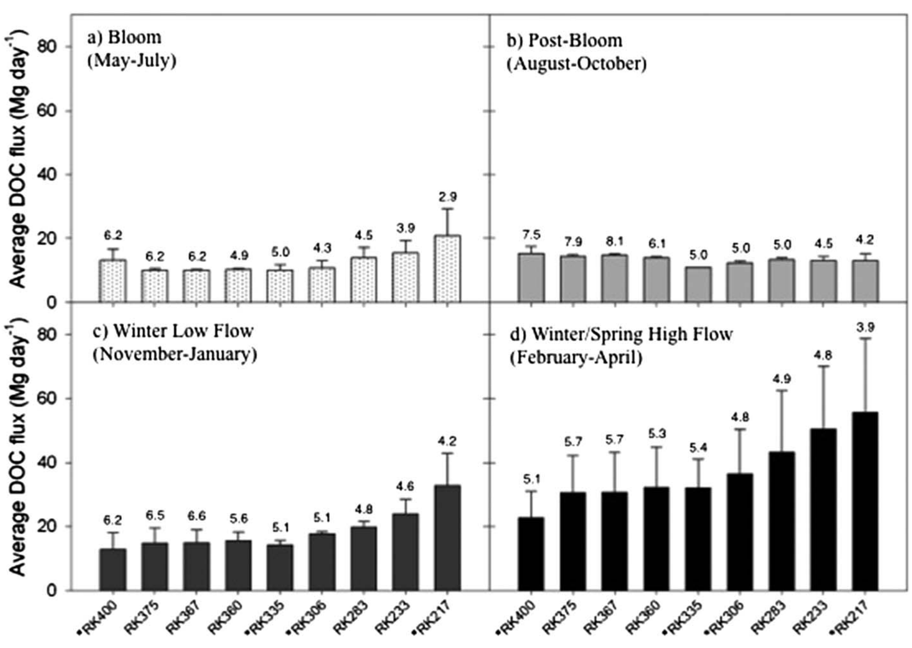

Figure 3. Average (±SD) DOC flux at all sample sites on the Klamath River for the four time periods of our study: (a) Bloom (May–July), (b) post-bloom (August–October), (c) winter low flow (November–January), and (d) winter/spring high flow (February–April). The numbers over bars represent flow-weighted DOC concentration (mg/L) for same time period. The site names marked with an asterisk (*) are selected representative sites used to represent specific river conditions relative to impoundments.

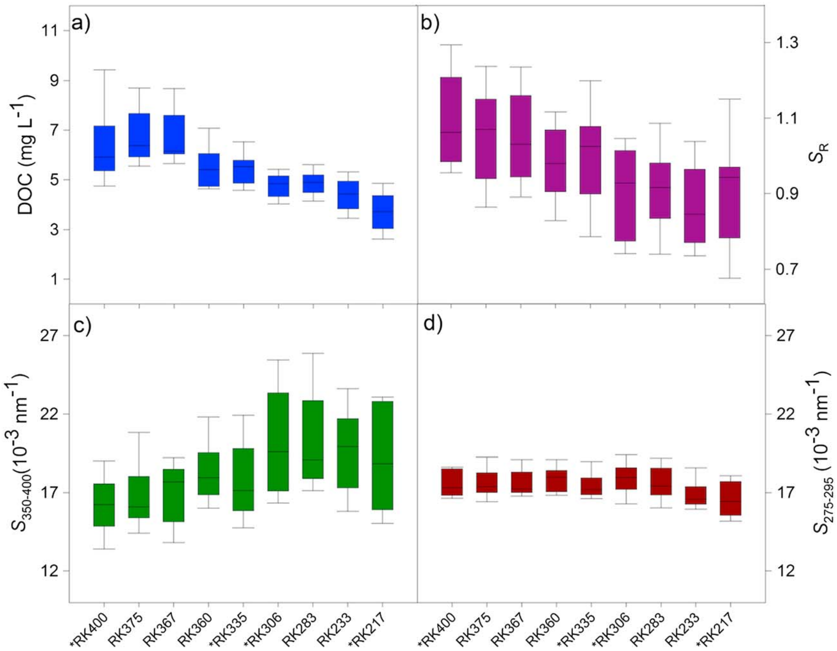

Figure 4. DOC concentration and composition exhibited longitudinal changes within the Klamath River, reflecting upstream to downstream shifts in the source, processing, and delivery of organic material. The box and whisker plots show data for each site from May 2010 to June 2011 for (a) DOC concentration, (b) spectral slope ratio (S_R), (c) $S_{350-400}$, and (d) $S_{275-295}$. The solid black line in the box represents the median, the lower and upper boundaries of the box represent the 25th and 75th percentiles, and the error bars represent the 10th and 90th percentiles. The site names marked with an asterisk (*) are selected representative sites used to represent specific river conditions relative to impoundments.

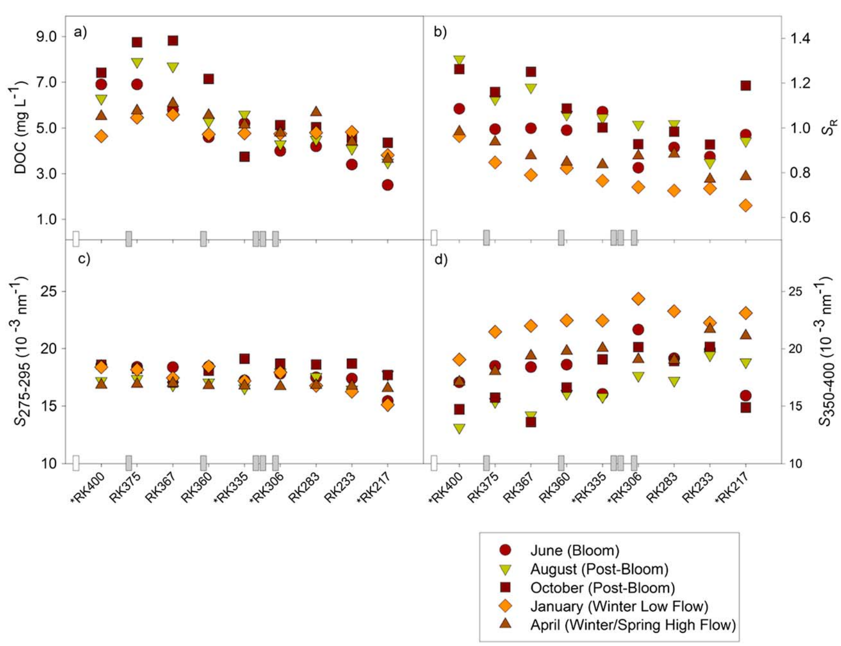

Figure 5. Longitudinal series of downstream changes in (a) DOC, (b) spectral slope ratio (S_R), (c) $S_{275-295}$, and (d) $S_{350-400}$, for 5 months (June, August, October, January, and April) selected to illustrate downstream patterns during the four seasonal time periods established in this study (bloom, post-bloom, winter low flow, and winter/spring high flow). The grey boxes on the *x*-axes represent the locations (relative to sampling sites) of the five impoundments, and the white box represents the location of the outlet of Upper Klamath Lake. The site names marked with an asterisk (*) are selected representative sites used to represent specific river conditions relative to impoundments.

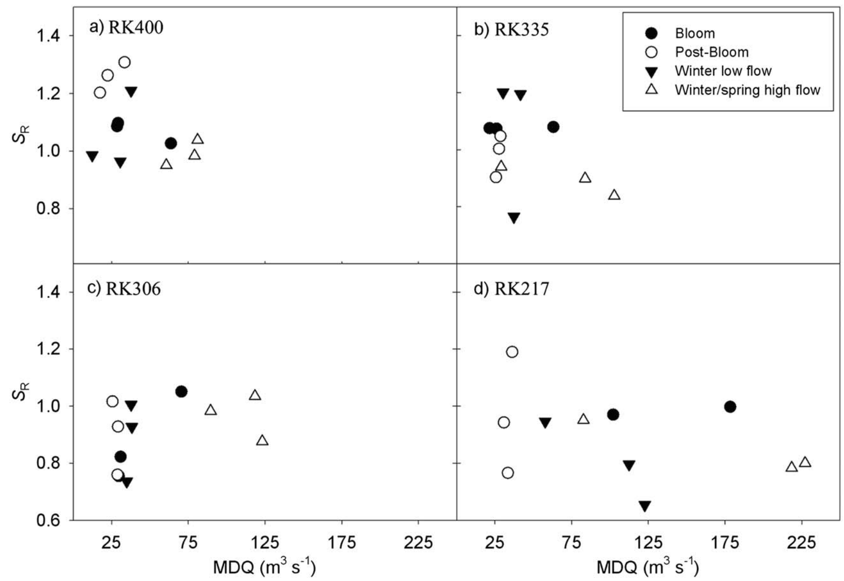

Figure 6. Spectral slope ratio (S_R) versus mean daily flow (MDQ) for four representative sites (a) RK400, (b) RK335, (c) RK306, and (d) RK217, selected to represent specific river conditions relative to impoundments. Downstream patterns in DOM composition appeared to be more influenced by seasonality then by flow, although the relationship appears to vary by site. The symbols represent the seasonal time period during which the data were collected.

direction, indicating shifting molecular weight/aromaticity. Some seasonal differences were observed at all sites; for example, from the bloom to the postbloom period, $S_{350–400}$ decreased at all sites, and similarly, at the onset of winter low flows, $S_{350–400}$ increased to maximum values (Figure 5). Although $S_{350–400}$ differed at sites above versus below reservoirs, there was no consistent directional shift and the direction varied by season and site.

In general, the highest values of S_R occurred at upstream sites and decreased downstream, indicating that CDOM at upstream sites was more representative of autochthonous production and processing (i.e., algal-like and/or degraded) and became increasingly terrestrial-like downstream. Notable exceptions to this trend occurred during the June bloom period, when values remained similar across all upper river sites but decreased dramatically below the lowest reservoir (Figure 5), and during a subset of bloom (June 2010; $S_R = 0.97$) and post-bloom (October 2010: $S_R = 1.19$) months when values at the lowest site (RK217) increased relative to upstream sites. Seasonal trends indicated that values of S_R were the lowest at all sites during winter low flows and highest during the post bloom period. Overall, S_R decreased below reservoirs relative to upstream sites, and although the magnitude of change varied, the pattern was consistent across all seasons.

Comparison of S_R relative to mean daily discharge at selected representative sites further reveals patterns associated with season and flows (Figure 6). Downstream changes in S_R were larger during the post bloom,

Table 3. Spearman's Rank Correlation Coefficients Between CDOM and Water Quality Parameters

	MDQ	DOC	temp	pH	Chl a	Ph a	a_{350}	$S_{275–295}$	$S_{350–400}$	S_R
MDQ	1									
DOC	−0.354[a]	1								
temp	−0.300[b]	0.185	1							
pH	0.215[c]	−0.038	−0.039	1						
Chl a	−0.134	0.410[a]	0.192	0.217[c]	1					
Ph a	0.142	0.430[a]	0.157	0.149	0.781[a]	1				
a_{350}	−0.153	0.805[a]	0.152	0.080	0.567[a]	0.494[a]	1			
$S_{275–295}$	−0.551[a]	0.185	0.113	−0.083	−0.310	0.033	−0.155	1		
$S_{350–400}$	0.056	−0.385[a]	0.004	0.118	−0.168	−0.168	−0.534[a]	0.346[a]	1	
S_R	−0.288[b]	0.549[a]	0.124	−0.121	0.263[b]	0.269[b]	0.670[a]	-	-	1

[a]Correlation statistically significant at the $p \le 0.001$ level.
[b]Correlation statistically significant at $p = 0.01$.
[c]Correlation statistically significant at $p = 0.05$.

when discharge across sites was relatively similar. Conversely, during winter low and winter/spring high flow, S_R did not decrease as appreciably downstream, although differences in discharge between sites were much greater. However, this trend was not consistent between sites above and below the most downstream reservoirs (RK335 versus RK306) where flows were similar in magnitude and relatively synchronous, yet there was significant variation in S_R irrespective of discharge. The greatest variation in flows occurred at the most downstream site (RK217), but variation in S_R appeared to vary by season irrespective of flow, with the possible exception of low S_R values in March and April 2011 that may have been influenced by high spring flows.

Factors negatively correlated with mean daily discharge included DOC, temperature, $S_{275-295}$, and S_R, whereas factors most positively correlated with algal biomass (Chl *a* and Ph-*a*) included DOC, a_{350}, and S_R (Table 3). DOC was also positively correlated with a_{350} and S_R and negatively correlated with $S_{350-400}$.

4. Discussion

The nature of DOC dynamics within the Klamath River is influenced by a combination of factors, including the seasonal effects of algal blooms and hydrologic variability (watershed runoff/leaching), and the longitudinal effects of reservoir production, transport, and processing of algal-derived material. The interaction of these factors and their capacity to alter the transport and processing of carbon and nutrients makes it challenging to predict patterns based on classic models of river function (e.g., River Continuum Concept [*Vannote et al.*, 1980]) or based on previous research in large rivers without impoundments or free flowing headwaters. For example, in riverine systems with lentic headwaters and/or significant impoundments the potential for decoupling between CDOM production and DOC accumulation may result in weaker relationships between CDOM absorbance and DOC [*Larson et al.*, 2007; *Miller*, 2012; *Spencer et al.*, 2012]. However, our study observed a strong relationship between CDOM absorbance values and DOC, suggesting that lentic headwaters and significant impoundment may not be a universal impediment to deriving relationships between CDOM absorbance and DOC or that the Klamath is more dominated by allochthonous CDOM inputs than previously studied impounded systems.

4.1. Seasonal and Longitudinal Effects on DOM

Algal growth, death, and degradation contribute significantly to CDOM in productive ecosystems [*Bianchi et al.*, 2004; *Rochelle-Newall and Fisher*, 2002; *Osburn et al.*, 2011; *Zhang et al.*, 2011]. Algal cells provide a biolabile source of organic matter for microbial degradation [*Petit et al.*, 1999], and this degradation results in a residual fraction of DOM composed of largely stable material [*Hanamachi et al.*, 2008; *Ogawa et al.*, 2001; *Sasaki et al.*, 2005]. In our study, the relationship between indicators of algal production and death (Chl *a*, Ph-*a*) and optical measures of DOM amount and quality (e.g., a_{350}, S_R) suggests that the production and degradation of planktonic algal DOM control the temporal and spatial character of DOM in the upper Klamath River. Production of biolabile algal material in the upper lentic reaches during the bloom period results in subsequent degradation and transport of potentially less biolabile material to downstream reaches. Previous work on other large, arid, and impounded rivers has also shown a decrease in the biolability of DOM below reservoirs [*Ulseth and Hall*, 2015], indicating that reservoirs and tailwaters can have large effects on the composition of energy sources being delivered to downstream reaches.

Downstream decreases in S_R may indicate (1) a relative increase in the contribution of terrestrial DOM, (2) a relative increase in microbial production, and/or (3) the microbial preservation of higher molecular weight DOM at downstream sites [*Helms et al.*, 2008]. During this time, DOC concentrations and loads remained similar or decreased downstream, suggesting that algal DOM produced upstream was rapidly processed with low downstream replacement by additional sources of autochthonous DOM. Microbial processing of algal-derived DOM increases as algal densities increase and algal survivability decreases, such as during the bloom and postbloom periods of our study [*Baines and Pace*, 1991; *del Giorgio and Cole*, 1998]. In addition, the lack of precipitation, low tributary flows, and therefore overall lack of external DOM inputs during the postbloom period further suggest that the decline in S_R was due to a relative increase in degraded algal material, not an increase in terrestrial inputs. The decrease in S_R to a constant level of $S_R < 1$ in the lower river during postbloom months therefore likely reflects the continuous and substantial contribution of microbially degraded algal DOM derived from upstream sources. This observed downstream shift in DOM from algal to more terrestrial in character suggests that DOM dynamics in the lower river may be less influenced by the seasonality of algal blooms and more by seasonal hydrologic patterns that influence river discharge, external watershed inputs, and reservoir residence times. Although it should be noted that at certain times, DOM at the most downstream site did appear to be increasingly algal in character compared to upstream sites, perhaps indicating that benthic production in the free-flowing lower river may have contributed an additional source of DOM.

Due to annual patterns in regional precipitation, hydrology likely has a strong seasonal influence on riverine DOM composition. During the winter and spring months, when biological activity and algal productivity were low and precipitation and runoff/leaching were higher, DOM composition notably shifted. The corresponding downstream increase in DOC load during the wet season suggests that the shift in S_R reflected the increased contribution of terrestrial sources, as DOM is flushed from soils and surface litter layers [*Striegl et al.*, 2005; *Inamdar et al.*, 2006; *Spencer et al.*, 2010]. This was especially prominent in the lower river, where steeper gradients and larger, more numerous tributaries allow for greater inputs from the surrounding watershed.

4.2. Hydrologic Effect of Reservoirs on DOM

The effect of river regulation on constituent fluxes may overshadow watershed processes that would likely have major influence on fluxes within unregulated systems [*Kraus et al.*, 2011; *Miller*, 2012]. For example, previous studies have indicated that highly impounded systems decrease spatial and temporal variability leading to export of relatively stable riverine DOM [*Duan et al.*, 2007; *Miller*, 2012; *Spencer et al.*, 2012]. The impoundments and reservoirs of the Klamath River are utilized principally for hydropower operations, which alter hydrologic residence times and biogeochemical processes and in turn influence seasonal patterns in algal growth and the quantity and quality of the DOM pool. For most of the year, DOM was more algal in character at sites upstream of dams (above reservoirs) than at sites directly downstream of dams (below reservoirs), indicating that reservoirs were contributing to the net degradation or retention of algal material. The magnitude of this effect varied by location of the reservoir in the river system; the change in the characteristics of the DOM bulk pool was greater below reservoirs lower in the system compared with those higher in the watershed. Differences in response may be due to a variety of factors, including difference in the size of the reservoirs (residence time), internal reservoir processes (i.e., stratification, mixing), and upstream processes contributing to cumulative downstream effects [*Kraus et al.*, 2011].

Residence time in Klamath River reservoirs can vary on the order of days to months, depending upon flows and the time of year, and may influence the fate of incoming river water (Table 1) [*PacifiCorp*, 2006]. Residence times may produce a lag in the export of material produced or processed within reservoirs. Reservoir lag time may be one explanation for the character of DOM we observed in the lower river during the bloom and postbloom periods, when longer residence times potentially lead to water leaving the reservoirs that was more representative of DOM that entered earlier in the year. In contrast, during certain times of the year, reservoir stratification may cause incoming river flows to “short circuit” their flow path through the reservoir, reducing or eliminating mixing as warmer, less-dense river flows are shunted through the reservoir above denser waters in the hypolimnion. These processes can result in DOM with very different characteristics at different depths within the water body [*Downing et al.*, 2008; *Bracchini et al.*, 2010]. Therefore, in addition to residence times, the source of the reservoir outflow within the water column (i.e., epilimnion, metalimnion, or hypolimnion release) contributes to the character of DOM released from a reservoir. During the postbloom period, when the reservoirs are frequently stratified, DOM character was more similar at sites above and below the large, downstream reservoirs, and may reflect the previously described “short circuiting” of river water through the epilimnion. Therefore, flow variability within reservoirs may also shift the processing of DOM by delaying or advancing downstream transport.

While reservoirs in arid climates can effectively attenuate allochthonous signals due to replacement by autochthonous sources [*Mash et al.*, 2004; *Miller*, 2012], in general, we observed the opposite effect; DOM entering reservoirs was more algal in character than DOM leaving the reservoirs during the same time period. Although downstream reservoirs can produce large algal blooms [e.g., *Jacoby and Kann*, 2007], during our study they were not a significant source of algal DOM, suggesting that relatively little production of DOM occurred within these reservoirs. However, a more likely alternative is that DOM was produced within the reservoirs but subsequently underwent significant processing, resulting in the net effect of relatively stable export of DOM similar in character to DOM entering the reservoirs during the same time. It is important to note some caveats when interpreting reservoir input/output data. First, the lack of significant algal DOM export from the reservoirs could be due to the timing of sample collection. Since samples were collected monthly, it is the possible periods of peak productivity that were not captured. Second, reservoir residence times vary, and therefore, caution should be used when making direct comparisons for individual time periods between the sites above and below reservoirs. However, despite these considerations, patterns in DOM entering and exiting reservoirs during the same period of time are valid for comparison at distinct time periods and help elucidate overarching trends in upstream-downstream sources, production, degradation, and processing of DOM.

4.3. Implications for Management and Future Research

Impoundments in the Klamath River significantly alter river flow and influence the seasonal and spatial dynamics of DOM. Because export of DOM appears largely driven by discharge, carbon and nutrient loading from regulated reaches may be largely dependent upon management decisions for flow regulation. Therefore, load management needs to be considered in conjunction with seasonal and spatial needs for water delivery. In addition, the location of lentic and lotic environments and their subsequent linkages represents important regions for the production and degradation of autochthonous DOM in large, regulated rivers. These linkages and their relative location within the watershed have downstream implications and should be considered when managing for loads and water quality. Several DOM optical parameters (e.g., a_{350} and S_R) appear suitable as proxies for tracking DOC export and composition in the Klamath River, and in situ sensors could serve as cost-effective tools for the collection of long-term, high-frequency data and monitoring. Removal of the four lower dams on the Klamath River is scheduled to proceed in the next decade and will undoubtedly alter downstream patterns in DOM, including potential shifts in the sources of DOM (i.e., algal production), and the extent of downstream processing of DOM from upstream sources (i.e., leading to export of DOM with more terrestrial character). The extent and magnitude of this alteration will depend on the specific impoundments removed, their location within the watershed, and overall changes in reach-specific hydrology.

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