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The relationship between dissolved organic matter absorption and dissolved organic carbon in reservoirs along a temperate to tropical gradient

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ABSTRACT

Recent and upcoming launches of new satellite sensors will provide the spatial, spectral and radiometric resolution to globally assess freshwater chromophoric dissolved organic matter (CDOM), and thus estimate dissolved organic carbon (DOC) concentration. However, estimating DOC from optical remote sensing requires a robust relationship between CDOM and DOC. This is particularly problematic for reservoirs because they have variable dissolved organic matter composition that complicates the CDOM–DOC relationship. We investigated six manmade reservoirs along a temperate to tropical gradient that represent a range of reservoir types and watershed conditions to determine whether a linear relation between CDOM and DOC could be established. We measured CDOM absorption and DOC concentration during the wet and dry seasons in the six reservoirs.

We found the CDOM absorption coefficient and CDOM spectral slope were uncorrelated due to exogenous DOC inputs from multiple sources. Alone, the absorption coefficient of CDOM was a poor predictor of DOC concentration. Including both CDOM absorption coefficient and spectral slope in a multiple regression accounted for both composition and concentration, significantly improving the regression r^2. By using both CDOM absorption coefficient and spectral slope, we identify a framework for a potential solution to overcome the influence of dissolved organic matter source and transformation history on the CDOM–DOC relationship. We conclude that local variability, seasonality and optical complexity should be considered in remote sensing based approaches for global freshwater DOC estimation.

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1. Introduction

Lakes, manmade reservoirs and other inland waters play a major role in the global carbon (C) cycle (Tranvik et al., 2009). Reservoir construction is increasing globally, and the role of manmade reservoirs in C transformations is growing in importance (Williamson, 2009). Dissolved organic matter (DOM) is the major pathway for carbon transfer from terrestrial to aquatic systems (Jaffé et al., 2008; Wetzel, 1992). DOM is the underlying driver of lake ecosystem metabolism and trophic status (Williamson, Morris, Pace, & Olson, 1999) and plays a significant role in other ecosystem processes such as controlling nutrient and heavy metal bioavailability and mobility (Porcal, Koprivnjak, Molot, & Dillon, 2009; Williamson et al., 1999). Additionally, DOM in manmade reservoirs can interfere with drinking water disinfection and may cause harmful disinfection byproducts (Downing, Bergamaschi, Evans, & Boss, 2008).

DOM is often characterized analytically by estimating the dissolved organic carbon (DOC) concentration, or by estimating the chromophoric dissolved organic matter (CDOM). CDOM is the fraction of DOM that is optically significant, and can be measured using absorption (e.g., Roesler, Perry, & Carder, 1989) or fluorescence spectrometry (e.g., Newson, Baker, & Mounsey, 2001; Rochelle-Newall, Hulot, Janeau, & Merroune, 2013). The spectral properties of CDOM absorption are determined by both the amount and composition of DOM. The absorptivitiy of CDOM at a wavelength λ ($a_{\mathrm{CDOM}}(\lambda)$) is often summarized with two parameters, amplitude and shape, described with a quasi-exponential decrease in absorptivity with increasing wavelength (Roesler et al., 1989):

$$a_{\mathrm{CDOM}}(\lambda) = a_{\mathrm{CDOM}}(\lambda_0)e^{-S(\lambda-\lambda_0)} \quad (1)$$

where $a_{\mathrm{CDOM}}(\lambda_0)$ is the absorption (m^{-1}) at a given wavelength, and S is the exponential constant. The magnitude of the absorption coefficient

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of CDOM at a given wavelength $a_{CDOM}(\lambda_0)$, is commonly used to indicate the amount of CDOM in the water (Boss & Zaneveld, 2003; Twardowski, Boss, Sullivan, & Donaghay, 2004), and can be used as a proxy for CDOM concentration. As a measure of the spectral shape of CDOM absorption, spectral slope (S) can be used as an indicator of the composition and processes acting on DOM. CDOM spectral slope (S) has been shown to be related with DOM molecular weight, and is affected by photodegradation (Helms et al., 2008). Smaller S values (up to ~0.008 m^{-1}) indicate lower short wavelength absorption and stronger absorption at longer wavelengths, typical of higher molecular weight humic material, and larger S values (up to ~0.037 m^{-1}) often indicate lower molecular weights and more fulvic substances. In coastal waters, these values are often used to distinguish terrigenous DOM sources from oceanic/autochthonous ones (Downing et al., 2008; Green & Blough, 1994; Stedmon & Markager, 2001, 2003).

Absorption spectrometry provides a direct link to optical remote sensing methods that can facilitate global C assessments (Siegel, Maritorena, Nelson, Hansell, & Lorenzi-Kayser, 2002). Increasingly, studies report (e.g., Spencer et al., 2009), or recommend (e.g., Tranvik et al., 2009) using CDOM absorption to estimate DOC, highlighting the potential utility of satellite remote sensing for large scale DOC assessments. With the recent and upcoming launches of new satellite sensors that have the spatial resolution and spectral channels to measure CDOM in lakes and reservoirs (e.g., Landsat 8 and Sentinel-2), interest is growing in using remote sensing for large scale DOC assessments. Satellite remote sensing has been used to obtain large-scale regional assessments of coastal (Mannino, Russ, & Hooker, 2008) and lake (Kutser et al., 2005) DOC by using regression models between $a_{CDOM}(\lambda_0)$, which is estimable from optical satellite sensors, and DOC concentration. However, this approach requires a correlation between DOC concentration and $a_{CDOM}(\lambda_0)$, which will work when the chromophoric fraction of DOM represents most of the DOC pool, and when that chromophoric fraction has a relatively homogenous molecular weight and composition.

In order to make large scale or global assessments of lake and reservoir DOC from satellite remote sensing, robust relationships between $a_{CDOM}(\lambda_0)$ and DOC concentration are required. Using $a_{CDOM}(\lambda_0)$ to estimate DOC concentration depends on the assumption that the chromophoric fraction of DOM represents the most of the DOC pool, essentially when $a_{CDOM}(\lambda_0)$ and spectral slope are coupled. However, this assumption is violated when the source of the OM comes from autochthonous production or wastewater effluent (a significant consideration for urban reservoirs) where DOM has relatively low color intensity per unit DOC (Brezonik, Olmanson, Finlay, & Bauer, 2014), or when pools of natural DOM undergo transformations such as photo and bacterial degradation. Often these transformations act preferentially on DOM from different sources (e.g., allochthonous versus autochthonous DOM *sensu* Boyd & Osburn, 2004), resulting in a decoupling of $a_{CDOM}(\lambda_0)$ and S.

Many studies reporting $a_{CDOM}(\lambda_0)$ and DOC concentration relationships are performed in coastal waters (Fichot & Benner, 2011; Fichot et al., 2013), though there is a limited but growing literature for inland systems (Kutser et al., 2005; Spencer, Butler, & Aiken, 2012; Ylöstalo, Kallio, & Seppälä, 2014; Zhang, Qin, Zhu, Zhang, & Yang, 2007). Yet all of these relationships are reported for temperate and boreal systems, and with some exception (e.g., Morris et al., 1995), most studies are in the Northern Hemisphere. Moderate to strong $a_{CDOM}(\lambda_0)$–DOC relationships have been shown for boreal (Kutser et al., 2005; Ylöstalo et al., 2014), mid-latitude (Brezonik et al., 2014; Morris et al., 1995), small mountain temperate (Laurion, Ventura, Catalan, Psenner, & Sommaruga, 2000; Zhang et al., 2007) and large subtropical lakes (Zhang et al., 2007), as well as for mid-latitude and small temperate coastal (Yacobi, Alberts, Takacs, & McElvaine, 2003) rivers. Spencer et al. (2012) reported moderate to strong relationships for 19 of 30 major North American river systems. Notably, in all of these studies the regression models and the coefficients of determination varied for each study and by region. Brezonik et al. (2014) highlighted a similar variability in both other published and unpublished CDOM–DOC regressions.

Recent evidence suggests large scale DOC estimation from CDOM absorption will not work in the open ocean (Nelson & Siegel, 2013), dammed rivers or the St. Lawrence River (Spencer et al., 2012), which is supplied by the North American Great Lakes, or water bodies subject to heavy impacts from human activities (Brezonik et al., 2014), where no or weak correlation has been observed between $a_{CDOM}(\lambda_0)$ and DOC concentration. Because of their distinctive hydrodynamic characteristics, reservoirs may be particularly problematic for developing robust CDOM–DOC relationships. Depending on runoff, precipitation and dam operations, reservoirs can function as stratified lakes, well-mixed lakes, or rivers. More typically, they behave as intermediate waterbodies, displaying both river and lake-like characteristics. The variable hydrodynamics created by dams can cause spatial and temporal switches between allochthonous to autochthonous production (Friedl & Wüest, 2002). Thus, using $a_{CDOM}(\lambda_0)$ for DOC concentration estimation may not be extensible to reservoirs, where the sources of DOM vary, and processes acting on the DOM are likely to change depending on the watershed, morphology, and hydro-limnology of the reservoir.

To evaluate the potential for using optical methods to assess DOC concentration in reservoirs, we investigated six reservoirs along a temperate to tropical gradient that represent a range of reservoir types and watershed conditions to determine whether a linear relationship could be established to estimate DOC concentration from $a_{CDOM}(\lambda_0)$. We then tested the hypothesis that including S as an indicator of DOM composition would improve the regression between $a_{CDOM}(\lambda_0)$ and DOC concentration.

2. Sampling & methods

2.1. Site descriptions

We sampled six reservoirs in Eastern Australia, spanning climatic regimes from alpine to tropical, across a latitudinal range of almost 16 degrees to represent a large range of hydro-limnological conditions (Table 1). The reservoirs are: a deep alpine hydroelectric lake (Blowering Reservoir, "BL"); a temperate major headwater storage (Lake Hume, "HU"); a semi-arid, small, shallow vegetated weir subject to cyanobacterial blooms (Lake Cargelligo "CA"); a large humid subtropical reservoir whose watershed receives nearly 1000 mm or rainfall per year (Lake Wivenhoe, "WI"); a dry tropical dammed river with notably high sediment load and one of the most variable annual flows measured in Australia (Fairbairn Dam, "FA"); and a reservoir with an exceptionally large watershed that spans tropical rainforest and savannah in the north, and dry-tropical and semi-arid savannah in the south (Burdekin Falls Dam, "BF").

2.2. Sampling methods & analysis

We sampled each reservoir twice, once during the Austral spring and once in the summer to cover both wet and dry seasons for each reservoir: Sep–Nov 2012 (temperate wet season, subtropical/tropical dry season) and Feb–Mar 2013 (temperate dry season, subtropical/tropical wet season).

At each reservoir, we visited 5–10 stations spatially distributed across the reservoir. We revisited the same stations during each sampling period. At each station, a discrete sample of surface water was collected for subsequent laboratory analysis. Total suspended solids (TSS), CDOM, and DOC samples were handled and analyzed following the protocols described by (Clementson, Parslow, Turnbull, McKenzie, & Rathbone, 2001). DOC concentrations were determined using the non-purgeable organic carbon method with a Shimadzu TOC-$V_{CSH/CSN}$. The spectral range over which CDOM spectral slope is fitted influences the resulting value (Babin et al., 2003; Carder & Steward, 1989; Loiselle et al., 2009; Twardowski et al., 2004). Therefore, we calculated

Table 1
Site characteristics and measurement summaries.

Site name	Reservoir name	Description	Lat (S)	Lon (E)	Max depth (m)	Surface area (km^2)	Storage capacity (ML x10^6)	Water-shed area (km^2)	Mean precip. (mm/yr)	N[a]	TSS (mg/L)[b]	DOC (mg/L)[b]
BF	Burdekin Falls	Dry tropics, portion of watershed in wet tropics. Irrigation, urban supply.	20.627	147.045	40	220	1.86	114,240	600	20	9.24 (8.88)	4.65 (0.87)
FA	Fairbairn	Dry tropics. Irrigation, coal washing and groundwater recharge.	23.685	148.028	32	150	1.30	16,317	600	20	13.77 (1.98)	4.08 (0.66)
WI	Wivenhoe	Humid subtropical. Flood control, hydro-power and urban supply.	27.297	152.538	44	109.4	2.60	7020	1000	12	7.74 (6.95)	5.06 (0.39)
CA	Cargelligo	Semi-arid grassland. Diversion weir/inflow wetland.	33.285	146.402	5	15	0.004	86,554[c]	400	17	88.41 (58.90)	10.81 (3.98)
BL	Blowering	Cool temperate/alpine. Hydro-power, irrigation and recreation.	35.466	148.261	91	44	1.63	1606	1700	18	0.99 (0.49)	1.69 (0.12)
HU	Hume	Warm temperate. Hydro-power, irrigation, river regulation and recreation.	36.119	147.039	40	202	3.04	15,540	700	18	2.96 (1.58)	2.97 (0.25)

[a] Number of sample stations.
[b] Mean (standard deviation) of our observations.
[c] Watershed area for all of the Lachlan River.

spectral slope for both 350–680 nm ($S_{350–680}$), the range used by Brando, Dekker, Park, and Schroeder (2012), Clementson et al. (2001) and Schroeder et al. (2012), and for 350–440 nm ($S_{350–400}$), the range used by Helms et al. (2008) and Spencer et al. (2012). We chose these two ranges because they are readily comparable to the literature and contain the spectral regions most relevant to remote sensing applications. Fig. 1 summarizes the ranges of CDOM and DOC values sampled.

We tested whether $a_{CDOM}(\lambda_0)$ and S are coupled by calculating Kendall's tau, a non-parametric rank correlation coefficient (Helsel & Hirsch, 1992) because not all sites met parametric assumptions for correlation analysis. We then calculated univariate linear regressions between DOC concentration and each $a_{CDOM}(\lambda_0)$ wavelength between 350 nm and 680 nm (1 nm bandwidth). We then included both $a_{CDOM}(\lambda)$ and S as predictor variables of DOC concentration in multiple linear regression. We tested for significant differences between the multiple regression and the univariate regression using analysis of variance (ANOVA) F-tests. All analyses were performed using the R statistical software (R Development Core Team, 2013).

For brevity, we display all univariate regression results between DOC concentration and each $a_{CDOM}(\lambda_0)$ in Fig. 3, but limit the discussion of

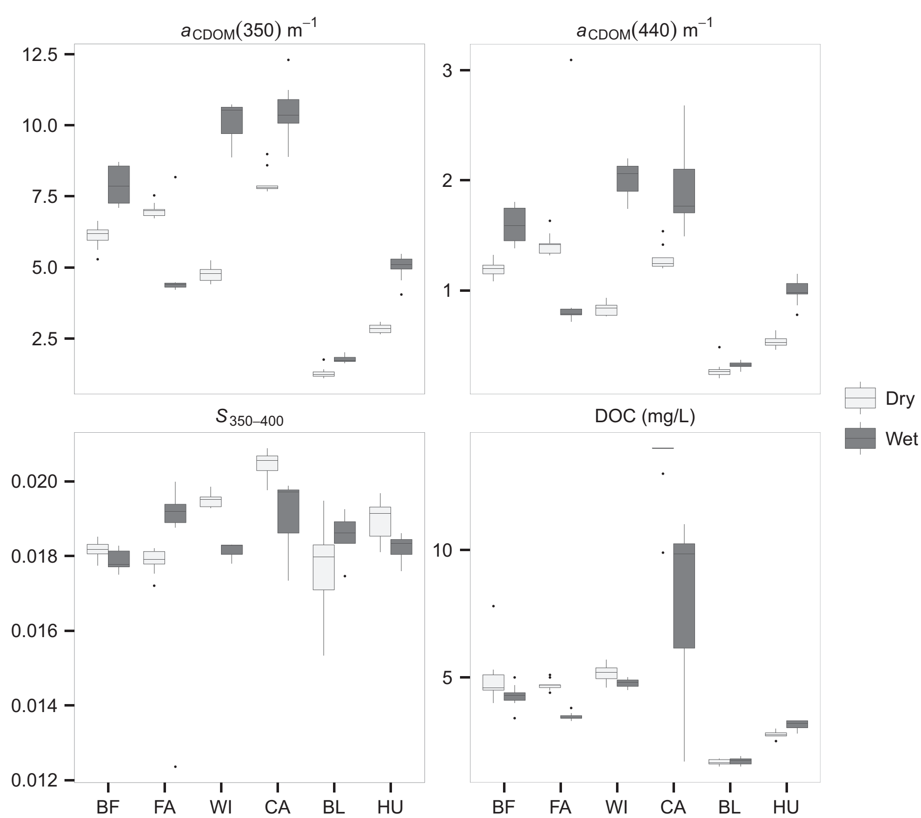

Fig. 1. Boxplot of the range of values measured for the CDOM absorption coefficient at 350 nm (top left) and 440 nm (top right), CDOM spectral slope (bottom left), and DOC concentration (bottom right) during each field campaign (dry season on left, wet season on right). For each season, the box bounds the interquartile range (IQR; 25–75 percentile), the horizontal line inside the box indicates the median, and the whiskers are 1.5*IQR. Outliers are shown as points. See Table 1 for site abbreviations.

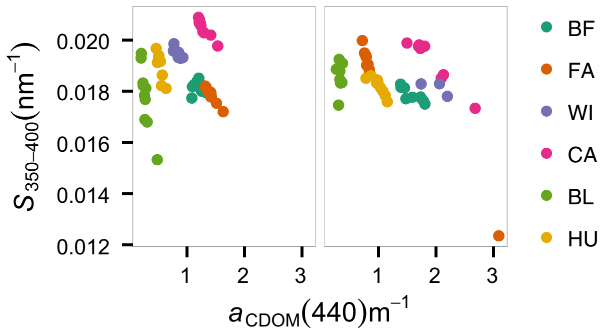

Fig. 2. CDOM absorption coefficient at 440 nm ($a_{CDOM}(440)$) versus spectral slope ($S_{350-400}$) plotted for the six reservoirs for the wet (right) and dry (left) seasons.

our of all results to the two λ_0 that best address our question of applicability to large scale remote sensing assessments, 350 and 440 nm: $a_{CDOM}(350)$ and $a_{CDOM}(440)$. Thus below, we report on the results for $a_{CDOM}(350)$, $a_{CDOM}(440)$, $S_{350-400}$, and $S_{350-680}$.

3. Results & discussion

3.1. $a_{CDOM}(\lambda_0)$ and S are decoupled in Australian reservoirs

Our study shows evidence for locally variable DOM sources and transformation processes. Over all sites and seasons there is no strong relationship between $a_{CDOM}(\lambda_0)$ and S; $a_{CDOM}(350)$ and $a_{CDOM}(440)$ are not correlated with $S_{350-680}$ or $S_{350-400}$ (Kendall's $\tau = 0.01$–0.15; Fig. 2). Similarly, if we divide the datasets across the wet and dry seasons, there is no strong correlation (wet $\tau = -0.27$–0.32; dry $\tau = -0.08$–0.23). A possible explanation for the lack of a correlation is that there are multiple sources of exogenous DOC inputs affecting the composition of the DOM pool (Stedmon & Markager, 2001) at the broad continental and seasonal scales. There are also clear site-specific differences in the $a_{CDOM}(\lambda_0)$ and S relationship (Fig. 2). Negative correlations were moderate to high at CA ($\tau = 0.34$–0.91), FA ($\tau = 0.73$–0.95) HU ($\tau = 0.48$–0.71), and WI ($\tau = 0.64$–0.75), and low at BF ($\tau = 0.03$–0.53) and BL ($\tau = 0.03$–0.20). Differently from other freshwater studies in boreal lakes, a subtropical lake and temperate coastal rivers (Yacobi et al., 2003; Ylöstalo et al., 2014; Zhang et al., 2007), $a_{CDOM}(\lambda_0)$ and S are decoupled in reservoirs at the continental scale.

In coastal studies, an inverse relationship between $a_{CDOM}(\lambda_0)$ and S is often reported and used to identify transformation and mixing processes on the DOM pool such as degradation of autochthonous DOC or conservative mixing between terrigenous and autochthonous DOC (Stedmon & Markager, 2001, 2003). The range of slopes measured in our study ($S_{350-400} = 0.012$–0.021 nm^{-1}; $S_{350-680} = 0.008$–0.20 nm^{-1}, Fig. 1) is limited relative to coastal studies (0.008–0.037 nm^{-1}), but is consistent with ranges observed in other inland studies (Spencer et al., 2009; Spencer et al., 2012; Zhang et al., 2007).

At the reservoir with the weakest $a_{CDOM}(\lambda_0)$–S correlation, the alpine reservoir BL, the seasonal responses of DOC concentration and S were also decoupled (Fig. 1): there was no significant difference in DOC concentration at BL (Wilcoxon, $p = 0.49$) despite a significant seasonal difference in S (Wilcoxon, $p = 0.002$–0.02; Fig. 1). This is probably

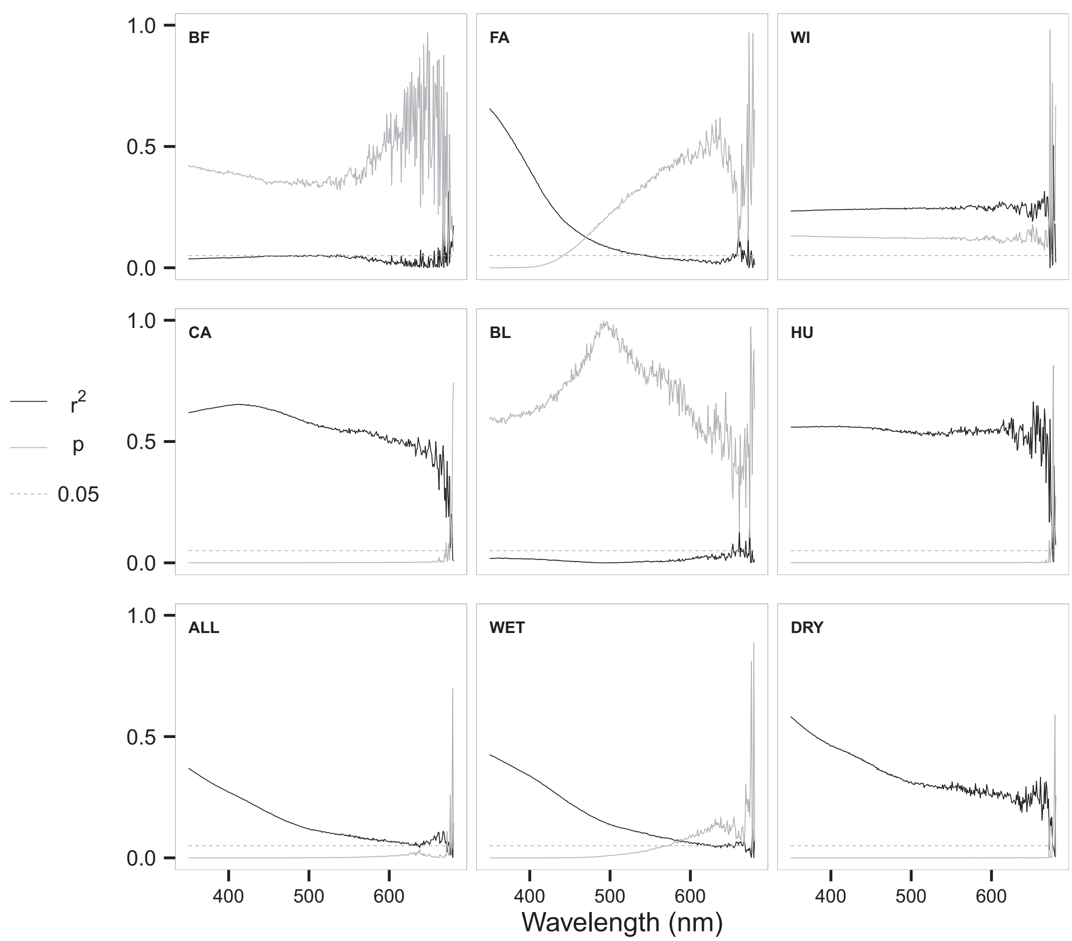

Fig. 3. Linear regression for estimating DOC from CDOM absorption ($a_{CDOM}(\lambda_0)$) model statistics (r^2 in black, p-value in gray) plotted by wavelength for each reservoir, for all reservoirs combined, and for the wet and dry seasons. The dashed horizontal gray line indicates $p = 0.05$.

Table 2
Coefficient of determination (r^2) and the probability value (p) of the regression model DOC prediction following the model: DOC = βCDOM + α, where CDOM is $a_{CDOM}(350)$, $a_{CDOM}(440)$.

	$a_{CDOM}(350)$		$a_{CDOM}(440)$	
	r^2	p	r^2	p
ALL	0.37	<0.01	0.18	<0.01
BF	0.04*	0.42	0.05*	0.36
FA	0.66	<0.01	0.17	0.07
WI	0.23*	0.13	0.24*	0.12
CA	0.62*	<0.01	0.65*	<0.01
BL	0.02	0.60	0.02	0.62
HU	0.56	<0.01	0.56	<0.01
WET	0.43	<0.01	0.24	<0.01
DRY	0.58**	<0.01	0.37	<0.01

* indicates slope (β) is < 0.
** indicates intercept (α) is < 0.

due to photo-degradation of the BL DOM pool in the dry season (summer) when the reservoir was likely stratified. With the exception of BL, the strong local patterns we observed are probably due to the varying contributions of allochthonous organic matter in each reservoir because of the distinct characteristics of their different watersheds. While mixing and transformation processes within the lakes may be contributing to some of the local patterns, our overall ability to detect it from our observations is swamped by the local variability or perhaps the general noise from measurement error or *S* calculation error (Loiselle et al., 2009).

Because the spectral properties of CDOM are determined by both the amount and composition of DOM, normalizing $a_{CDOM}(\lambda)$ by the carbon mass per volume concentration ($a_{CDOM}^*(\lambda) = a_{CDOM}(\lambda)/[DOC]$) may provide a more direct link with *S*. Anderson and Stedmon (2007) observed a relationship between $a_{CDOM}^*(375)$ and $S_{350–400}$ in arctic lakes, and Ylöstalo et al. (2014) reported a strong relationship between $a_{CDOM}^*(350)$ and $S_{275–295}$ in boreal lakes. Ylöstalo et al. (2014) noted their observations were similar to the relationship observed by Fichot and Benner (2011) in a coastal environment. However, Fichot and Benner (2011) reported no significant relationship for $S_{350–400}$, and Ylöstalo et al. (2014) did not report on $S_{350–400}$. We found no relationship between $a_{CDOM}^*(\lambda)$ and $S_{350–400}$ in this study, providing further indication that $a_{CDOM}(\lambda_0)$ and *S* are decoupled in Australian reservoir systems.

3.2. $a_{CDOM}(\lambda_0)$ alone is a poor predictor of DOC concentration

Univariate linear regressions using $a_{CDOM}(\lambda_0)$ as a predictor variable for DOC concentration were highly variable between reservoirs and seasons (Fig. 3). The r^2 of the $a_{CDOM}(\lambda_0)$ regressions decreased with increasing wavelength (λ), consistent with previously reported freshwater observations (Spencer et al., 2012; Zhang et al., 2007; Fig. 3). Table 2 reports the regression statistics for the regressions using $a_{CDOM}(350)$ and $a_{CDOM}(440)$. The regression models using $a_{CDOM}(350)$ had slopes ranging from −2.12 to 0.73 and for $a_{CDOM}(440)$ slope values ranged −7.81 to 5.40. The regression models using $a_{CDOM}(350)$ had intercepts ranging from - 0.79 to 30.25 and for $a_{CDOM}(440)$ intercept values ranged 0.33-23.19. Contrary to many other studies, the regression slope values for both $a_{CDOM}(350)$ and $a_{CDOM}(440)$ were negative for BF, WI and CA.

Regressions using $a_{CDOM}(350)$ or $a_{CDOM}(440)$ as predictor variables for DOC were statistically significant at only three of the six reservoirs (CA, FA, and HU; Table 2) and even these had only modest coefficients of determination (r^2 = 0.56–0.66). Of the significant sites, FA and HU had a positive correlation, while CA had a negative correlation.

When the data for all the sites were combined and then subset into wet and dry seasons, regressions using $a_{CDOM}(350)$ or $a_{CDOM}(440)$ as predictor variables for DOC concentration became significant and the r^2 moderately increased (wet: 0.24 for $a_{CDOM}(350)$ and 0.43 for $a_{CDOM}(440)$; dry: 0.37 for $a_{CDOM}(350)$ and 0.58 for $a_{CDOM}(440)$). Fig. 4 shows the scatterplot of $a_{CDOM}(440)$ and DOC for the wet and dry seasons.

The variability between seasons is expected for reservoirs: these systems can function as stratified lakes, well-mixed lakes, or rivers depending on precipitation and dam operations. The dry season regression using $a_{CDOM}(350)$ as a predictor has a negative intercept, which indicates a limitation of using $a_{CDOM}(\lambda)$ at shorter wavelengths; low $a_{CDOM}(350)$ values may not reliably predict DOC concentration.

Because of site and seasonal variability, overall (all sites and seasons) univariate regressions using $a_{CDOM}(\lambda_0)$ are only a weak predictor of DOC concentration (r^2 = 0.18–0.37; Table 2). Because CA is so different relative to the other reservoirs (small, shallow and turbid; Table 1), when removed from the dataset, the overall r^2 for the regressions using $a_{CDOM}(\lambda_0)$ as the predictor variable increased to 0.45–0.61. Despite this improvement, the coefficients of determination in this study are lower than correlations previously reported across a range of freshwater sites: boreal lakes (r^2 = 0.77–0.97; Kutser et al., 2005; Ylöstalo et al., 2014), midlatitude lakes (r^2 = 0.72–0.93; Brezonik et al., 2014; Morris et al., 1995), mountain lakes (r^2 = 0.58; Laurion et al., 2000), subtropical shallow lakes (r^2 = 0.58; Zhang et al., 2007 and references therein), a large temperate shallow lake (r^2 = 0.73–0.77; Zhang et al., 2007 and references therein), small temperate coastal rivers (r^2 = 0.91–0.92; Yacobi et al., 2003), and major North American rivers (r^2 = 0.18–0.99; Spencer et al., 2012).

3.3. Regressions using both $a_{CDOM}(\lambda_0)$ and S are better predictors of DOC concentration

When both $a_{CDOM}(\lambda_0)$ and *S* are included as predictor variables in a multiple linear regression, there are statistically significant improvements to the adjusted coefficient of determination (*adj.* R^2). This implies that there may be a way to account for the various influences affecting DOM optical complexity and how it represents the DOC pool. There were significant improvements in the regressions that included data from all lakes, the regressions using data only from FA, and regressions using only wet and only dry season data (Table 3).

The regressions with the greatest improvements were those using $a_{CDOM}(440)$ and $S_{350–400}$ as predictor variables. The multiple regressions using data from all sites and all seasons improved the most, followed by the multiple regressions using data only from the wet season. In these cases, the multiple regressions predicted DOC concentration more successfully because $a_{CDOM}(\lambda_0)$ and *S* were not coupled. Each predictor variable was able to provide additional information that led to a better prediction of the response variable (DOC concentration). Because the predictor variables were uncorrelated, we can interpret the improvement as being due to the inclusion of new information (in this case, spectral shape and amplitude).

Multiple exogenous DOM sources are probably the most important factor controlling the estimation of DOC concentration in reservoirs.

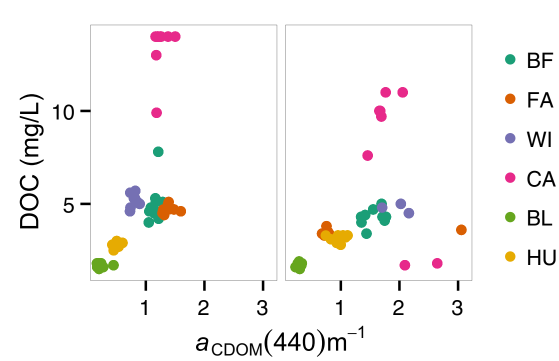

Fig. 4. CDOM absorption coefficient at 440 nm ($a_{CDOM}(440)$) plotted against DOC concentration for the wet (right) and dry (left) seasons.

Table 3
Multiple regression adjusted coefficient of determination (*adj.* R^2), multiple model probability value (p), and probability value from ANOVA F-test ($_{ANOVA}p$) between multiple $a_{CDOM}(\lambda_0) + S$ and univariate $a_{CDOM}(\lambda_0)$–DOC regressions indicating whether there is a significant difference between the models.

	$a_{CDOM}(350) + S_{350\text{-}680}$						$a_{CDOM}(440) + S_{350\text{-}680}$					
	adj. R2	p	β $a_{CDOM}(\lambda 0)$	β *S*	α	ANOVA p	*adj.* R2	p	β $a_{CDOM}(\lambda 0)$	β *S*	α	ANOVA p
ALL	0.46	0.00	0.66	655.98	-9.77	0.00	0.38	0.00	2.72	926.32	-	0.00
BFD	-0.03	0.43	-0.14	430.23	-1.50	0.40	-0.03	0.37	-0.67	388.76	-0.88	0.45
BLO	-0.11	0.61	0.06	-2.01	1.63	0.88	-0.11	0.63	0.24	2.15	1.58	0.86
CAR	0.57	0.00	-1.99	231.77	25.00	0.74	0.63	0.00	-9.72	-800.80	40.45	0.33
FAI	0.90	0.00	0.53	216.64	-2.56	0.00	0.77	0.00	2.62	674.39	-	0.00
HUM	0.50	0.00	0.17	19.74	1.96	0.80	0.51	0.00	0.84	58.91	1.35	0.48
WIV	0.04	0.16	-0.09	-66.58	6.78	0.87	0.06	0.15	-0.48	-119.25	7.68	0.78
WET	0.51	0.00	0.56	472.71	-7.25	0.00	0.46	0.00	2.67	795.16	-	0.00
DRY	0.61	0.00	1.02	577.85	-9.29	0.02	0.49	0.00	4.00	966.68	-	0.00

	$a_{CDOM}(350) + S_{350\text{-}400}$						$a_{CDOM}(440) + S_{350\text{-}400}$					
	adj. R2	p	β $a_{CDOM}(\lambda 0)$	β *S*	α	ANOVA p	*adj.* R2	p	β $a_{CDOM}(\lambda 0)$	β *S*	α	ANOVA p
ALL	0.61	0.00	0.70	-	-	0.00	0.60	0.00	3.47	-	-	0.00
BFD	-0.02	0.42	0.01	-908.26	-	0.33	-0.02	0.36	0.03	-911.01	-	0.39
BLO	-0.11	0.61	0.05	-3.54	1.55	0.90	-0.10	0.63	0.35	-16.09	1.29	0.64
CAR	0.59	0.00	-1.23	-	-8.32	0.41	0.61	0.00	-11.55	1682.57	62.53	0.64
FAI	0.90	0.00	0.64	-321.62	-5.52	0.00	0.58	0.01	4.79	-	-	0.00
HUM	0.51	0.00	0.15	45.09	3.21	0.70	0.50	0.00	0.76	-3.26	2.31	0.98
WIV	0.05	0.16	-0.03	-160.66	2.19	0.83	0.05	0.15	-0.28	-48.86	4.46	0.95
WET	0.54	0.00	0.57	-785.44	-	0.00	0.54	0.00	2.93	-	-	0.00
DRY	0.78	0.00	0.97	-	-	0.00	0.73	0.00	4.77	-	-	0.00

This is supported by the improvements of the multiple regressions, which capture both spectral amplitude and shape and use the full optical information of $a_{CDOM}(\lambda)$ measurements. Yacobi et al. (2003) explained the spectral dependence between $a_{CDOM}(\lambda_0)$ and *S* observed in coastal rivers as a dependence on DOC molecular size distribution, where additive exogenous inputs determined CDOM optical characteristics. It is likely that the reason $a_{CDOM}(\lambda_0)$ and *S* are decoupled in this study is because there are multiple different sources and potentially some transformation of the DOM. Including both $a_{CDOM}(\lambda_0)$ and *S* improved the regressions, indicating that there may be potential solutions for overcoming the problem of decoupled $a_{CDOM}(\lambda_0)$ and *S* for a more generalized solution. However, this solution may not necessarily be as simple as the linear addition presented in this study. More data are needed to test different forms of the regression and the generalizability across conditions.

3.4. Optical complexity & local variability should be considered for global approaches to DOC estimation

Recently, Ylöstalo et al. (2014) reported a clear, non-linear relationship between *S* and $a_{CDOM}(\lambda_0)$ in Finnish boreal lakes, noting that this pattern is consistent with other observations made in the Baltic Sea (Kowalczuk, Stoń-Egiert, Cooper, Whitehead, & Durako, 2005; Kowalczuk, Stedmon, & Markager, 2006), and is related to conservative mixing of different end-members of DOM composition (Stedmon & Markager, 2003). They speculated that the occurrences of a similar relationship among the separate lakes made in their study may indicate a more general coupling of *S* and $a_{CDOM}(\lambda_0)$. Differently from Ylöstalo et al. (2014) and the studies they cite, we found that *S* and $a_{CDOM}(\lambda_0)$ are generally decoupled in Australian reservoirs; there was no overall relationship between *S* and $a_{CDOM}(\lambda_0)$.

We found reservoirs to have optically complex CDOM. Optical complexity in this study is illustrated by the poor overall and highly localized *S* and $a_{CDOM}(\lambda_0)$ correlations (Fig. 2). Our results lead us to conclude that Ylöstalo et al.'s (2014) speculation on a general coupling of *S* and $a_{CDOM}(\lambda_0)$ does not extend to Australian reservoirs. Because both source and transformation processes affect $a_{CDOM}(\lambda)$, the optical complexity of DOM in reservoir environments makes using $a_{CDOM}(\lambda_0)$ alone for DOC estimation in reservoirs with varied DOM sources problematic. While our results indicate that DOC estimates are improved by incorporating additional spectral information that better characterizes optical complexity, we question whether a generalizable approach for large reservoir DOC estimation from satellite remote sensing can be accomplished using the framework of studies such as Kutser et al. (2005) or Mannino et al. (2008).

The results from our study contrast with other freshwater studies that report relatively successful regressions using $a_{CDOM}(\lambda_0)$ as a predictor for DOC concentration. However, other studies in Northern latitudes have also shown non constant CDOM–DOC relationships (Brezonik et al., 2014 and references therein). Brezonik et al. (2014) report r^2 values ranging from 0.72–0.925 for lakes and rivers in Minnesota and Wisconsin (DOC ranged 2.66–27.64 mg/L), with values varying based on seasonal flow. Zhang et al. (2007) introduced a large geographic distribution of data by calculating regressions on data reported in several earlier studies. They found an overall $r^2 = 0.58$ for 26 mountain lakes in Austria, Italy, and Spain (DOC ranged 0.21–3.5 mg/L), and an overall $r^2 = 0.73$ for 64 lakes in Alaska, Colorado, the Northeastern U.S. and Argentina (DOC ranged 0.24–23.5 mg/L). Our study included samples from a much larger geographic distribution and under a wider range of environmental conditions than many of the previously reported results, and is one of the few to describe Southern hemisphere conditions. While it is possible that our relatively poor regression results are due to the variable range of conditions, it is also likely that the intermediate nature of reservoirs and the optical complexity are responsible for the poor predictive capability of $a_{CDOM}(\lambda_0)$ for DOC concentration.

Another potential cause of the limited success of the regressions is the sample size and range of DOC and CDOM in this study. Although we sampled a representative range of reservoirs and their conditions for robust regression model development, the sample size is still limited relative to the variance, which challenges successful regression. Further, while the range of DOC concentrations we sampled (1.5–15 mg/L) was larger than the ranges sampled in many previous studies (Del Castillo, Coble, Morell, López, & Corredor, 1999; Kutser et al., 2005; Laurion et al., 2000), we did not capture very high DOC concentrations such as those sampled in the southeastern United States coastal plain (>40 mg/L e.g., Spencer et al., 2012; Yacobi et al., 2003). Similarly, the range in CDOM absorption we observed in Australian reservoirs (Fig. 1) is larger or comparable to measurements in European mountain lakes (Laurion et al., 2000), the Yangtze River (Zhang, Qin, Zhang, Zhu, & Chen, 2005), and Lake Taihu in China (Zhang et al., 2007). However, other studies have observed much greater CDOM absorption ranges. Ylöstalo et al. (2014) reported $a_{CDOM}(442)$ values from 0.43–14.53 m^{-1} in boreal lakes and Brezonik et al. (2014) reported $a_{CDOM}(440)$ values from 0.6–25.1 m^{-1} in Minnesota and Wisconsin water bodies in North America. We did however sample a larger range of latitudes and climatic conditions (Table 1) relative to most freshwater studies (Kutser et al., 2005; Laurion et al., 2000; Yacobi et al., 2003; Ylöstalo et al., 2014; Zhang et al., 2005), though only captured the Eastern portion of the continent. Increasing sample size and expanding the range of DOC concentrations and CDOM absorption could potentially improve the overall predictive power of $a_{CDOM}(\lambda_0) + S$ regressions for reservoir DOC concentrations. Testing other forms of an $a_{CDOM}(\lambda_0)$ and S function, such as multiplicative or polynomial expressions may also improve predictions, but should be performed on a larger dataset.

We used simple linear regressions in this study in order to best compare our results to other reports. Better regression results could be accomplished by non-linear fitting methods, yet the fundamental problem of variable site and study-specific regression equations remains (Brezonik et al., 2014). Nevertheless, more sophisticated, non-linear, non-parametric modeling techniques could be more appropriate to describing CDOM-DOC relationships. Further, more sophisticated techniques or large amounts of training data may be necessary for success across widely varying regional and hydrodynamic domains.

Local variability should be accounted for when developing predictive models for large-scale satellite remote sensing-based DOC estimations. For example, we observed that while the overall trend is for increasing r^2 with decreasing $a_{CDOM}(\lambda_0)$ wavelengths, there is inter-site variability between the optimum wavelength for maximizing the coefficient of determination for the regressions using $a_{CDOM}(\lambda_0)$ (Fig. 3). Most satellite sensors have limited bands in the spectral range used in our study and generally reported in the literature, and the bands center on just one or a few wavelengths (e.g., Landsat8 centers on 440 nm, Sentinel-2 centers on 440 nm, OLCI centers on 412 and 442 nm). A regression model established for one reservoir using a satellite-specific wavelength may not be successfully transferred to another water body. This is because poor radiometric sensitivity significantly affects CDOM estimation from reflectance in high CDOM waters (Kutser, 2012). Further, it is still undetermined whether band position and bandwidth will affect CDOM detection from remote sensing reflectance, although simulations by Brezonik et al. (2014) suggest that while band position may be important, bandwidth may not since CDOM has a broad exponential increase in absorbance with decreasing wavelengths. The results from this study suggest that the potential variability of optimal band positions based on site characteristics pose a major challenge to the large-scale remote sensing of reservoir DOC from satellite remote sensing. However, this could be partially overcome with satellite-borne high fidelity, high spectral resolution sensors that could provide many narrow band measurements across the visible region for optimal wavelength selection.

4. Conclusions

Large scale DOC estimation for reservoirs from satellite remote sensing is likely to be complicated by variability in hydrologic function and watershed characteristics that drive variability in DOM source and composition. Including both the magnitude and spectral shape of CDOM absorption accounts for CDOM optical complexity from various sources and transformation history, and improves DOC concentration estimation for Australian reservoirs. Due to its simplicity and approachability, univariate linear regression is the most popular approach to using optical methods for DOC estimation. However, univariate analyses are not appropriate when there are confounding factors such as the variability of CDOM source and composition. We are encouraged that results using remote sensing-relevant wavelength regions (350–600 nm) are significant predictors for DOC, if only moderately so. We urge careful consideration of local variability and optical complexity when developing regional or global remote sensing approaches for estimating DOC concentration.

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