Remote Sensing of Environment 156 (2015) 395–402

Contents lists available at ScienceDirect

Remote Sensing of Environment

journal homepage: www.elsevier.com/locate/rse

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

Erin L. Hestir [a,b,*], Vittorio Brando [a,c], Glenn Campbell [d], Arnold Dekker [a], Tim Malthus [a]

[a] Division of Land and Water, Commonwealth Scientific and Industrial Research Organization (CSIRO), Canberra, ACT, Australia
[b] Department of Marine, Earth and Atmospheric Sciences, North Carolina State University, Raleigh, NC, USA
[c] Italian National Research Council (CNR) - Institute for Electromagnetic Sensing of the Environment (IREA), Milan, Italy
[d] School of Civil Engineering & Surveying, University of Southern Queensland, Toowoomba, Australia

ARTICLE INFO

Article history:
Received 20 May 2014
Received in revised form 16 September 2014
Accepted 20 September 2014
Available online xxxx

Keywords:
Reservoirs
Lakes
Dissolved organic carbon
CDOM
Landsat
Sentinel-2
Water quality

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.

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 ($a_{CDOM}(\lambda)$) is often summarized with two parameters, amplitude and shape, described with a quasi-exponential decrease in absorptivity with increasing wavelength (Roesler et al., 1989):

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

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

* Corresponding author at: 2800 Faucette Drive, Jordan Hall, North Carolina State University, Raleigh, NC 27695, USA.
E-mail address: elhestir@ncsu.edu (E.L. Hestir).

http://dx.doi.org/10.1016/j.rse.2014.09.022
0034-4257/

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