Verh. Internat. Verein. Limnol.
2009, vol. **30**, Part **7**, p. 1117–1120, Stuttgart, July 2009

Variability in the optical properties of colored dissolved organic matter in Missouri reservoirs

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Introduction

Dissolved organic carbon (DOC) plays multiple roles in aquatic ecosystems, from physical to chemical to biological (Williamson et al. 1999). Consistent with these varied functions, DOC comprises a heterogeneous mixture of many compounds derived from processes within lakes and influent streams (autochthonous carbon) or from surrounding terrestrial environments (allochthonous carbon). The latter includes colored dissolved organic matter (CDOM), largely composed of humic compounds that strongly absorb solar radiation within the water column. This absorption is greatest for ultraviolet radiation (UVR; 280–400 nm) but also extends into the photosynthetically available radiation (PAR; 400–750 nm) waveband, particularly over the range 400–500 nm. This blue region of PAR is also the waveband where phytoplankton absorption of light is most intense (Markager & Vincent 2000), making CDOM a potentially important control on underwater photosynthesis (Retamal et al. 2008). The optical characteristics of CDOM in turbid lake waters, however, have been little explored.

In Missouri, USA, most standing waters are impoundments constructed for hydropower, flood control, recreation, and water supply (Jones et al. 2008). The trophic condition of these waters varies, but most are eutrophic. Many also contain high concentrations of suspended inorganic sediments derived from the erosion of agricultural soils (Jones et al. 2004, Jones et al. 2008). As a result, the underwater light field of these lakes is influenced by algal and nonalgal particulates (Knowlton & Jones 2000); however, the role of CDOM has not been assessed.

The primary objective of this study was to evaluate the importance of CDOM relative to other optically active substances in underwater PAR attenuation in Missouri reservoirs. As a secondary objective, we also sought to characterize the absorption properties of CDOM across the state.

Key words: CDOM, DOC, light, Missouri, reservoirs, turbid lakes

Materials and methods

Nine reservoirs that represented the range of limnological conditions of Missouri reservoirs were sampled near their retaining dams to characterize the apparent and inherent optical properties (AOPs and IOPs, respectively) and limnological conditions. Each site was visited 4 times during May–August 2002 (n = 36). Secchi depth (Z_{SD}; 20 cm disk) and the vertical diffuse attenuation of PAR were measured with a Li-Cor LI-1000 data logger with spherical submersible quantum sensor and a deck-mounted reference cell. The vertical diffuse attenuation coefficient of PAR (K_d) was calculated as the slope obtained by regression analysis of the natural logarithm of percent incident PAR as a function of depth (Knowlton & Jones 2000). Surface water was collected and kept on ice until processing within 12 h of collection. Samples were analyzed for total phosphorus (TP), total nitrogen (TN), total chlorophyll (Chl), nonalgal seston (NAS), and DOC in the laboratory (Jones et al. 2008, Knowlton & Jones 2000, and references therein). The absorption coefficient at 440 nm (a_{440}) was also measured as an indicator of CDOM (Cuthbert & del Giorgio 1992); detailed methods for the absorption analyses are given below. Multiple linear regression analyses were conducted to determine the relationship between K_d and optically active substances: CDOM, Chl, and NAS.

Sixty eight reservoirs, including the 9 reservoirs described above, were sampled to characterize CDOM. Each site was visited 2–4 times during summer 2002, resulting in 250 samples. The spectral absorption coefficient (a_λ) for the lake water after filtration through a 0.2-µm nitrocellulose membrane filter was measured every 10 nm from 250 to 400 nm, every 25 nm from 400 to 650 nm, and every 50 nm from 650 to 900 nm in a Spectronic Genesys 2 spectrophotometer with a 10 cm cuvette blanked on deionized water. Measurements of a_{440} were also made. The exponential slope parameter (S) was derived from the slope of the regression of the natural logarithm of a_λ against wavelength for the range 300 to 440 nm (Bricaud et al. 1981, Davies-Colley & Vant 1987).

0368-0770/09/1117 $ 1.00

Results

The 9 reservoirs in which AOPs were measured spanned a wide range of limnological conditions (Table 1), with TP varying by a factor of 40, Chl values ranging over 2 orders of magnitude, and K_d ranging from 0.24 to 7.46 m^{-1}. The mean value of the product of K_d and Z_{SD} of the reservoirs (1.27) was consistent with the worldwide mean value for turbid waterbodies (1.30) presented by KOENINGS & EDMUNDSON (1991).

Forward stepwise multiple regression analysis showed that K_d was significantly dependent on all 3 optically active substances (CDOM, Chl, and NAS):

$$K_d = 0.094\ \text{CDOM} + 0.030\ \text{Chl} + 0.077\ \text{NAS} + 0.245$$
$(r^2 = 0.99, p < 0.01)$

The partial r^2 values for NAS and Chl were 0.82 and 0.17, respectively. The variable CDOM was also significant in the model ($p = 0.04$); however, its contribution was minimal, with a partial r^2 value of only 0.002.

For the 68 reservoirs, a_{440} ranged from 0.16 to 6.59 m^{-1}, and DOC varied by a factor of 5 (Table 1). The relationship between a_{440} and DOC was wedge-shaped, with absorption exhibiting a wide range at high DOC concentrations ($r^2 = 0.15$, $p < 0.01$; Fig. 1). The ratio of a_{440}/DOC (DOC-specific absorption) ranged from 0.03 to 0.97 m^2/g (mean 0.23 m^2/g).

The exponential slope parameter, S, ranged from 0.0148 to 0.0262 nm^{-1} and was not significantly related to DOC ($p = 0.66$). However, a_{440} and a_{440}/DOC showed a clear nonlinear negative relationship with S (Fig. 2 a and b). Variables a_{440}/DOC and S were correlated in opposite ways to NAS and Chl. The NAS was positively related to a_{440}/DOC ($r = 0.58$, $p < 0.01$; Fig. 3a) and negatively related to S ($r = -0.43$, $p < 0.01$; Fig. 3c). Chlorophyll was related negatively to a_{440}/DOC ($r = -0.15$, $p = 0.02$; Fig. 3b) and positively to S ($r = 0.18$, $p < 0.01$; Fig. 3d).

Table 1. Summary of limnological and optical conditions of sampled reservoirs.

Variables	Mean	Range
9 reservoirs with AOP measurements (n = 36, except for NAS where n = 34)		
TP (µg/L)	43	4–168
TN (mg/L)	0.68	0.23–2.02
DOC (mg/L)	4.4	2.1–8.0
CDOM (m^{-1})	1.04	0.16–3.66
Chl (µg/L)	18.5	0.6–102.5
NAS (mg/L)	11.8	0.7–89.3
K_d (m^{-1})	1.75	0.24–7.46
Z_{SD} (m)	1.4	0.1–4.9
All 68 reservoirs (n = 250)		
a_{440} (m^{-1})	1.28	0.16–6.59
DOC (mg/L)	5.52	1.92–10.78
a_{440}/DOC (m^2/g)	0.23	0.03–0.97
S (nm^{-1})	0.0192	0.0148–0.0262

Discussion

These observations underscore the broad range of optical conditions that occur in Missouri reservoirs. Secchi depth ranged from 0.1 to 4.9 m and euphotic zone depth (calculated from K_d values as 1 % of surface irradiance) ranged from 0.6 to 19.2 m. Our results are consistent with the view that optical variability is an important limnological control on the structure and function of these reservoir ecosystems (KNOWLTON & JONES 2000).

The AOP measurements (Secchi depth and K_d) in our study show the influence of wide variations in optically active substances within and among the reservoirs. Algal and nonalgal particulates varied by a factor of 100, and CDOM varied by a factor of 20. The regression analysis showed that the variation in K_d was primarily determined by nonalgal suspended particles (82 % of variation in K_d), with algal particles also contributing substantially (17 %); CDOM, however, played a much lesser role (<1 %).

Although CDOM contributed little to overall variation in AOPs, its optical properties ranged widely. Most reservoirs (84 %) had low a_{440} values (<2.0 m^{-1}); however, there was 40-fold variation statewide, a range comparable to those of other mid-latitude North American lakes (ELSER 1987, CUTHBERT & DEL GIORGIO 1992, MORRIS et al. 1995). The DOC accounted for only 15 % of this variation (Fig. 1), indicating considerable heterogeneity in the com-

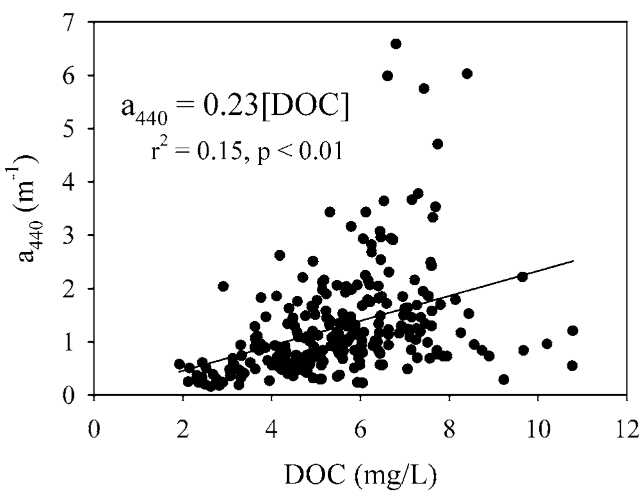

Fig. 1. Relationship between the absorption coefficient at 440 nm (a_{440}) and dissolved organic carbon (DOC) with a fitted linear model.

position of dissolved organic matter in Missouri reservoirs. Relationships of CDOM-DOC can be used to estimate CDOM (e.g., Pienitz & Vincent 2000) and to predict UVR attenuation (e.g., Scully & Lean 1994, Morris et al. 1995) from DOC concentration, if the composition of DOC is relatively uniform. Our data suggest that such estimates for Missouri reservoirs would be very imprecise.

The nonlinear relationship between S and a_{440} (Fig. 2a) is similar in shape to that observed (Stedmon & Markager 2001) and modeled (Stedmon & Markager 2003) for oceanic waters. This relationship also underscores the heterogeneity of DOC composition in Missouri reservoirs. Values of S showed an even stronger nonlinear relationship with a_{440}/DOC (Fig. 2b), which would better represent the variation in the DOC composition and its influence on optical properties. Variations in a_{440}/DOC and S are likely due to different sources of organic matter. The NAS, which is indicative of allochthonous inputs of soil and associated organic substances, was correlated with the more intensely colored DOC (high a_{440}/DOC; Fig. 3a) with a flatter UV-absorbance spectrum (low S; Fig. 3c). Chlorophyll, an indication of autochthonous production, was associated with less intensively colored materials with a steeper absorbance spectrum (low a_{440}/DOC and high S; Fig. 3b and 3d). These indicators explained only a small part of the variation, however, implying that DOC was not compositionally uniform even within the autochthonous and allochthonous categories, and that other factors such as photobleaching and biological degradation also likely influenced the optical properties of dissolved organic matter in these reservoirs. Further research is needed to determine the composition of DOC pools from these sources and to identify other sources of variation.

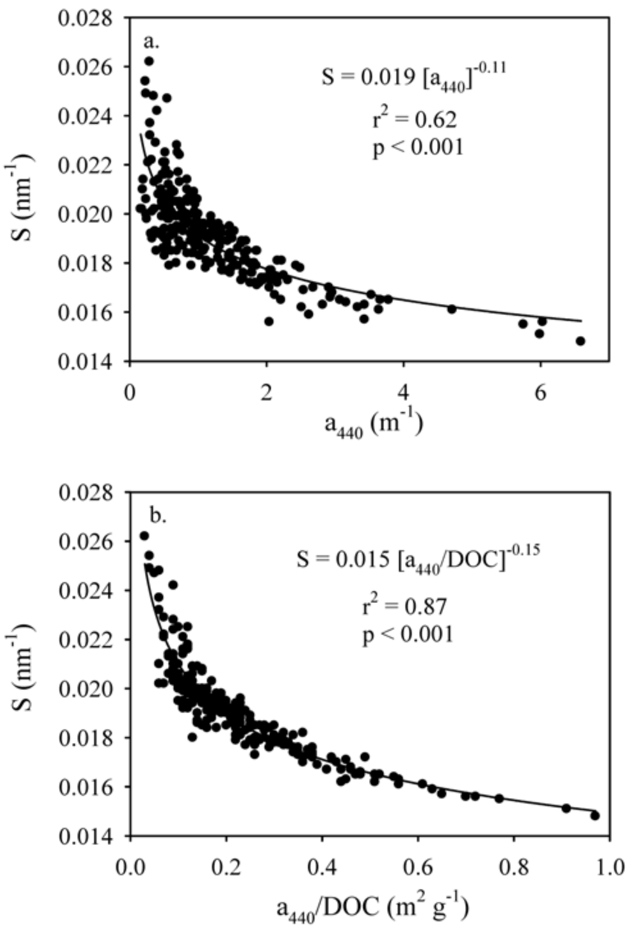

Fig. 2. Relationship of the exponential slope parameter (S) to (a) the absorption coefficient at 440 nm (a_{440}) and (b) DOC-specific absorption at 440 nm (a_{440}/DOC), with fitted power models.

Missouri reservoirs show a strikingly wide range of optical conditions that are mainly controlled by algal and nonalgal suspended particles. Although CDOM plays little role in the overall attenuation of PAR, our statewide sampling showed wide variation in the inherent optical properties of CDOM, which has implications for optical models analyzing relationships among DOC, CDOM, and UVR attenuation. Further study is needed to evaluate the source of this variation.

Acknowledgements

This study was supported by the Missouri Department of Natural Resources. DOC analyses were conducted at Columbia Environmental Research Center, US Geological Survey, MO, USA. We would like to thank D.V. Obrecht and students at MU for their laboratory and field assistance.

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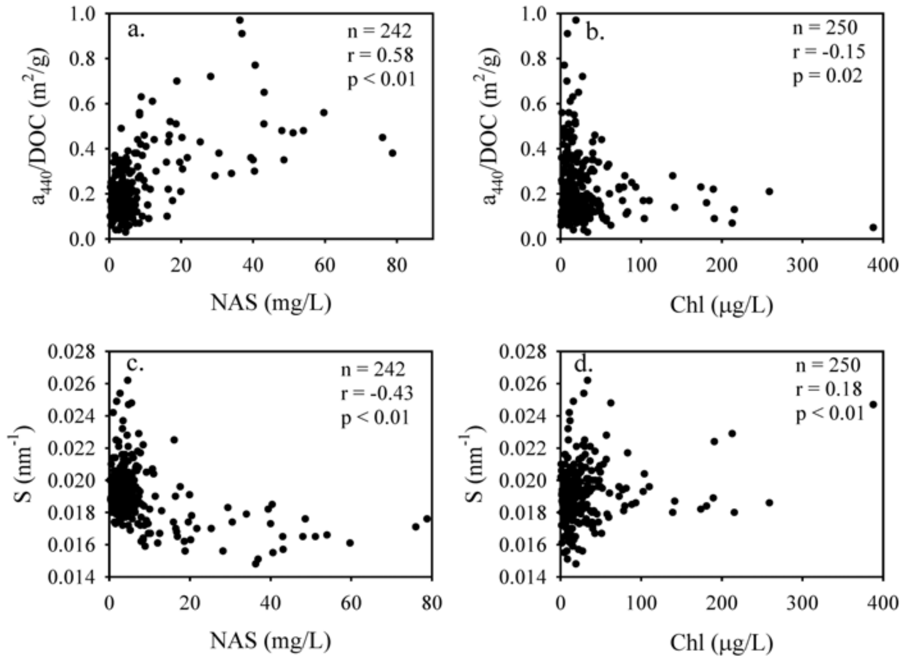

Fig. 3. Relationship of the DOC-specific absorption at 440 nm (a_{440}/DOC) to (a) nonalgal seston (NAS) and (b) chlorophyll (Chl), and that of the exponential slope parameter (S) to (c) NAS and (d) Chl in the reservoirs.

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