

## Dissolved organic carbon export and internal cycling in small, headwater lakes

Edward G. Stets,<sup>1</sup> Robert G. Striegl,<sup>1,2</sup> and George R. Aiken<sup>1</sup>

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[1] Carbon (C) cycling in freshwater lakes is intense but poorly integrated into our current understanding of overall C transport from the land to the oceans. We quantified dissolved organic carbon export ( $\text{DOC}_X$ ) and compared it with modeled gross DOC mineralization ( $\text{DOC}_R$ ) to determine whether hydrologic or within-lake processes dominated DOC cycling in a small headwaters watershed in Minnesota, USA. We also used DOC optical properties to gather information about DOC sources. We then compared our results to a data set of approximately 1500 lakes in the Eastern USA (Eastern Lake Survey, ELS, data set) to place our results in context of lakes more broadly. In the open-basin lakes in our watershed ( $n = 5$ ),  $\text{DOC}_X$  ranged from 60 to 183 g C m<sup>-2</sup> lake area yr<sup>-1</sup>, whereas  $\text{DOC}_R$  ranged from 15 to 21 g C m<sup>-2</sup> lake area yr<sup>-1</sup>, emphasizing that lateral DOC fluxes dominated.  $\text{DOC}_X$  calculated in our study watershed clustered near the 75th percentile of open-basin lakes in the ELS data set, suggesting that these results were not unusual. In contrast,  $\text{DOC}_X$  in closed-basin lakes ( $n = 2$ ) was approximately 5 g C m<sup>-2</sup> lake area yr<sup>-1</sup>, whereas  $\text{DOC}_R$  was 37 to 42 g C m<sup>-2</sup> lake area yr<sup>-1</sup>, suggesting that internal C cycling dominated. In the ELS data set, median  $\text{DOC}_X$  was 32 and 12 g C m<sup>-2</sup> yr<sup>-1</sup> in open-basin and closed-basin lakes, respectively. Although not as high as what was observed in our study watershed,  $\text{DOC}_X$  is an important component of lake C flux more generally, particularly in open-basin lakes.

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### 1. Introduction

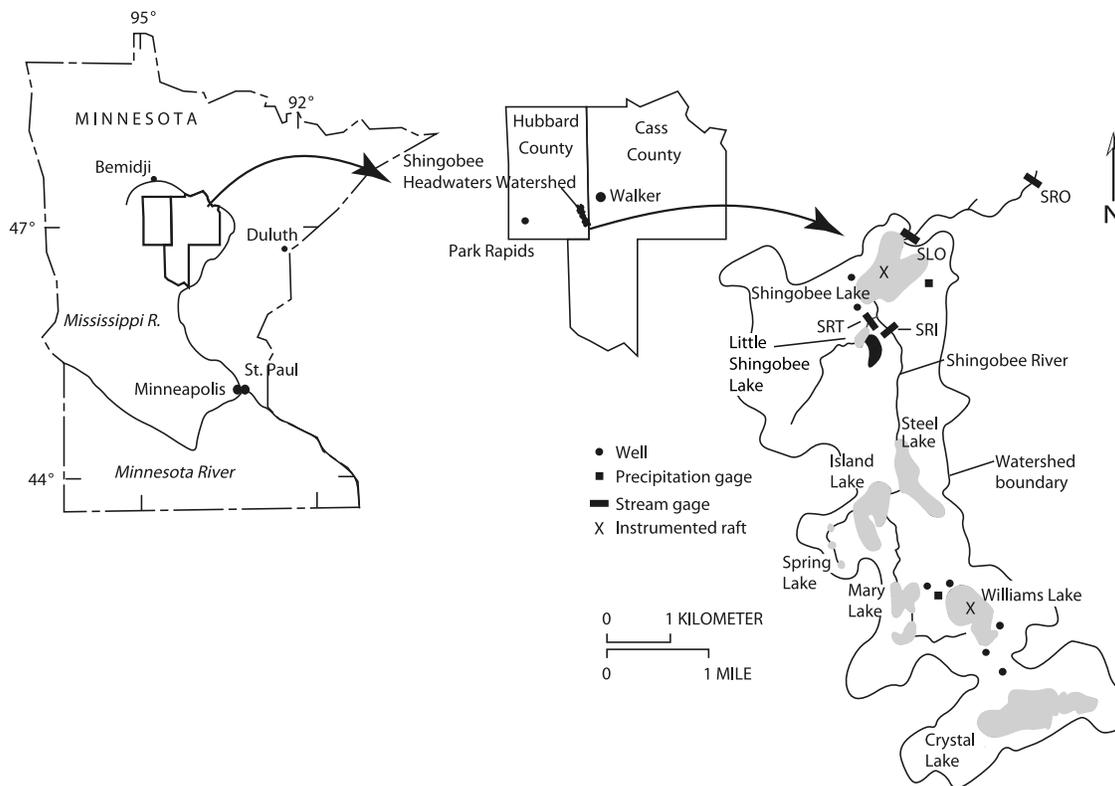
[2] Carbon (C) gas fluxes and sedimentation rates in freshwater aquatic ecosystems commonly exceed those of terrestrial ecosystems on an areal basis because of the intense biogeochemical cycling that occurs in these systems [Dean and Gorham, 1998]. At the broadest scale, C cycling occurring in inland waters can significantly alter the transport of terrestrial C to the ocean [Cole et al., 2007; Stallard, 1998]. Lateral C transport from rivers to the ocean is approximately 1 Gt C yr<sup>-1</sup> [Denman et al., 2007] with nearly equivalent amounts of organic and inorganic C delivered [Cole et al., 2007]. However, C input from terrestrial to inland freshwater ecosystems is greater than 2 Gt C yr<sup>-1</sup> with a substantial amount of C prevented from reaching the oceans because of C gas flux and sedimentation [Tranvik et al., 2009]. These fluxes are quite small in the context of gross global terrestrial-atmosphere-ocean C cycling [Denman et al., 2007]. However, riverine delivery of organic C is significant compared to net production within the ocean, 7.2 Gt C yr<sup>-1</sup> [Hansell, 2002]. And perhaps more

important, the role of freshwater aquatic ecosystems in altering C flux to the oceans is a poorly understood part of the global C cycle.

[3] Lake ecosystems are difficult to understand in the broader context of regional C export because of the variety of lake types and the complexity of the processes occurring within lakes. One salient example of this diversity is lake hydrogeologic setting. Lake basins can be either open, having surface water connections to a regional river system, or closed, lacking a surface water outlet. Closed-basin lakes do not contribute immediately to continental C export because lateral C export, if any occurs, presumably moves into groundwater and aquifers can have residence times of many years. Nevertheless, important C transformations take place in these lakes through the production and mineralization of organic material, sedimentation, and C gas fluxes. Open-basin lakes contribute to C export via their surface water outlet, but internal C cycling is often intense. Importantly, factors controlling the relative magnitude of C export and internal C cycling in lakes are not well understood. For lakes in northern Wisconsin, inorganic carbon (IC) transport typically exceeds net organic carbon (OC) mineralization [Cardille et al., 2007], causing these lakes to act primarily as conduits to the regional river flow system. In contrast, OC mineralization dominates C fluxes in Canadian Shield lakes [Dillon and Molot, 1997]. Hydrologic setting is

<sup>1</sup>U.S. Geological Survey, Boulder, Colorado, USA.

<sup>2</sup>U.S. Geological Survey, Lakewood, Colorado, USA.



**Figure 1.** Shingobee River headwaters watershed showing the location of lakes, Shingobee River, permanent stream gages, and groundwater springs sampled. The permanent stream gages are SRI (Shingobee River inlet to Shingobee Lake), SRT (tributary to Shingobee River downstream of Little Shingobee Lake), SLO (Outlet of Shingobee Lake), and SRO (Shingobee River at the outlet of the watershed).

undoubtedly a primary control on the relative magnitude of these processes [Curtis and Schindler, 1997; Stets *et al.*, 2009; Tranvik *et al.*, 2009]. Detailed hydrologic and biogeochemical data, which are typically unavailable on a large scale, are needed to draw conclusions about the relative magnitude of these processes, so our concept of the role of lakes in regional C export is not well developed.

[4] Here we report on the results of a study designed to compare the magnitude of lake OC export and internal OC processing in a series of headwater lakes located in the Shingobee Headwaters Watershed in Minnesota, USA, and to place these results in the context of a broader survey of approximately 1500 lakes sampled in the Eastern United States [Linthurst *et al.*, 1986]. For the purposes of our study, we focused on dissolved organic carbon (DOC) because it is the major form of OC exported from this watershed [Stets *et al.*, 2009]. For internal processing, we used the gross rate of biological DOC mineralization as an indication of the magnitude of metabolic DOC consumption within the lakes. Other important modifications to the DOC pool can occur through photolysis and biological processing that do not result in complete mineralization. Therefore, we also included analyses of DOC optical properties as a way of gathering information about DOC source and modification in this watershed. We then used the Eastern Lake Survey (ELS) data to evaluate how representative our study lakes were in a broader regional context. We also used this data

set to draw conclusions about the magnitude of DOC export from lakes.

## 2. Methods

### 2.1. Site Description

[5] The Shingobee River Headwaters Watershed is located in north-central Minnesota, USA, and is part of the larger upper Mississippi River watershed, with hydrologic flows generally from south to north (Figure 1). The boundary of the Shingobee River headwaters shown in Figure 1 was drawn on the basis of land surface topography and therefore depicts the surface water watershed, but the groundwater watershed probably extends further [Stets *et al.*, 2010].

[6] Approximately 120 m of sand and silt overlay thick deposits of carbonate-rich glacial till [Winter and Rosenberry, 1997]. Advective groundwater transport occurs throughout the watershed and enters surface water bodies as either diffuse seepage in areas having higher hydraulic conductivities or focused spring water discharge where hydraulic conductivities are lower [Filby *et al.*, 2002]. Crystal and Williams Lakes are closed-basin lakes located in the upper part of the watershed (Figure 1). Hydrologic exchange in these lakes occurs entirely through diffuse groundwater seepage, precipitation, and evaporation. Mary, Island, Steel, and Shingobee Lakes are open-basin lakes connected by the Shingobee River. These lakes are located in sediments

having lower hydraulic conductivity and groundwater flux tends to be focused into visible springs around lake edges. Little Shingobee Lake is a small open-basin lake that receives water from several small streams exiting a nearby fen [Carter *et al.*, 1997]. The outlet of Little Shingobee Lake connects to the main stem of the Shingobee River just upstream of Shingobee Lake (Figure 1). The Shingobee River gains water throughout the watershed from groundwater and surface runoff and exits the watershed below Shingobee Lake with an average discharge of  $0.3\text{--}0.4\text{ m}^3\text{ s}^{-1}$  [Rosenberry *et al.*, 1997]. The presence of carbonate-rich sediments in this watershed causes IC concentrations in surface and groundwater to be very high. As a result, IC fluxes are very large and IC export is much larger than OC export from Shingobee and Williams Lakes [Stets *et al.*, 2009]. We discuss how this relates to overall carbon cycling in section 4.1.

[7] The Shingobee watershed has been the focus of intense hydrologic and biogeochemical studies for more than 30 years [LaBaugh *et al.*, 1995; Winter and Averett, 1997]; groundwater flows, surface water flows, and meteorological conditions are monitored mostly around Shingobee and Williams lakes. In addition, the hydrologic flows, both groundwater and surface water, have been modeled for the entire watershed [Stets *et al.*, 2010]. Figure 1 depicts the locations of permanent streamgaging stations at the outlet of Little Shingobee Lake (Shingobee River Tributary), on the Shingobee River just upstream from this tributary (Shingobee River Inlet, SRI), at the outlet of Shingobee Lake, and where Shingobee River exits the watershed 2 km below Shingobee Lake.

## 2.2. Field Sample Collection

[8] Lake surface water samples were collected biweekly from the surface outlet, for the open-basin lakes, or from the center of the lake, for the closed-basin lakes, during the ice-free season. In winter, water samples were collected monthly by drilling a hole in the ice with a manual ice-auger and sampling water at 0.2 m below the ice using a hand-crank pump fitted with silicone tubing. Groundwater samples were also collected from groundwater springs located near Shingobee Lake in March 2009. Water for DOC analysis was collected by filtering 40 mL of sample water from each lake through a 25 mm Whatman GD/X (pore size,  $0.45\text{ }\mu\text{m}$ ) syringe filter into a precombusted ( $450^\circ\text{C}$  for greater than 4 h) 40 mL amber glass bottle. The filter was initially flushed with 10–15 mL of lake water before collecting water for DOC analysis. After collection, the samples were kept on ice, transported to the laboratory, and analyzed for DOC concentration and ultraviolet light (UV) absorbance, typically within 4 days of sample collection. We also collected samples for chemical fractionation and fluorescence excitation-emission matrices (EEMs) from all seven lakes in July 2007 and the groundwater springs sampled in March 2009.

[9] In 2007, we conducted 14 bottle incubations to determine the biodegradability of the DOC pool in the watershed. This experiment was performed using water from Shingobee and Williams Lakes in April, May, July, and October of 2007. Incubations from Crystal, Mary,

Island, Steel, Little Shingobee lakes and SRI were performed once in July 2007. The incubations followed the methods in the study by Stets and Cotner [2008] and are described in more detail in section 2.5. We used this information to develop our DOC degradation model ( $\text{DOC}_R$ ) and to determine the effect of microbial degradation on DOC optical properties in this watershed. We used  $\text{DOC}_R$  as a way of indicating the magnitude of within-lake DOC production and consumption.

## 2.3. DOC Analyses

[10] DOC concentration was determined via platinum catalyzed persulfate wet oxidation on an O.I. Analytical Model 700 TOC Analyzer. Instrument standard deviation was  $\pm 0.2\text{ mg C L}^{-1}$ . UV absorption was analyzed using a Hewlett-Packard Model 8453 photodiode array spectrophotometer and a 1 cm path length quartz cell. Absorption at  $\lambda = 254\text{ nm}$  divided by DOC concentration is known as specific UV absorption ( $\text{SUVA}_{254}$ ) and gives an “average” molar absorptivity for all the molecules contributing to the DOC in a sample and is assumed to be a measure of DOC aromaticity [Chin *et al.*, 1994; Weishaar *et al.*, 2003].  $\text{SUVA}_{254}$  is reported in units of  $\text{L mg C}^{-1}\text{ m}^{-1}$ , with a standard deviation of  $\pm 0.1\text{ L mg C}^{-1}\text{ m}^{-1}$ .

[11] Several DOC samples were fractionated using Amberlite XAD-8 resin extraction as a way of further characterizing the DOC pools in the various aquatic ecosystems included in this study. The resin preferentially binds hydrophobic organic acids so the DOC passing through the column is composed of hydrophilic and transphilic organic acids. Hydrophobic organic acids can then be eluted from the column following treatment with strong base (NaOH). We analyzed the hydrophobic eluent, which we refer to as hydrophobic organic acids (HPOAs), for DOC concentration and UV absorbance, as described in the previous paragraph.

[12] DOC fluorescence characteristics were measured on a Jobin-Yvon Horiba Fluoromax-3TM. DOC samples were placed in a 1 cm quartz cuvette and excited with light at wavelengths from 240 to 450 nm (5 nm increments), and the resulting fluorescence was measured between 300 and 600 nm (2 nm increments). Fluorescence values were corrected for light absorption occurring within the sample (inner filter effect), Raman scattering, and instrument blank and then the excitation-emission spectra (EEMs) were analyzed by parallel factor analysis (PARAFAC), a modeling technique which classifies EEMs fluorescence patterns based on least squares sum of fluorescence intensities [Stedmon *et al.*, 2003]. We used the model developed by Cory and McKnight [2005], which decomposes the fluorescent landscape into 13 categorical components: 7 quinone-like molecules differing in their degree of oxidation and conjugation (Q1–Q3, SQ1–SQ3, HQ), 2 protein-like molecules (Trp, Tyr), and 4 unknown compounds (C1, C3, C6, C10). Modeled fluorescence intensities (component loadings) were expressed as Raman units ( $\text{nm}^{-1}$ ) [Stedmon *et al.*, 2003].

## 2.4. DOC Export Model

[13] DOC export ( $\text{DOC}_X$ ) was evaluated daily from 1 January to 31 December 2004 as the product of daily interpolated DOC concentration and water export. Annual

$DOC_X$  was calculated as the sum of all daily export values. Water export included groundwater outflow for the closed-basin lakes and stream outlet discharge from the open-basin lakes [Stets *et al.*, 2010]. DOC settling due to flocculation was assumed to be minimal in these lakes. DOC export was expressed as the total annual mass load of DOC divided by lake surface area ( $g\ C\ m^{-2}\ LA\ yr^{-1}$ ).

## 2.5. BDOC and DOC Metabolism Model

[14] BDOC was determined by DOC loss in filtered lake in laboratory incubations lasting 8 months. Water was collected from just below the surface using a peristaltic pump fitted with silicon tubing. Lake water was pumped through an inline Geotech high-capacity capsule filter (0.45  $\mu m$  nominal pore size). The filter was flushed with 1–2 L of lake water and then the filtrate was pumped directly into duplicate precombusted 1 L amber glass bottles. This water was assumed to be free of biologically active particles, so approximately 10 mL of lake surface water filtered through a Whatman 13 mm GF/A glass fiber syringe filter (nominal pore size 1.6  $\mu m$ ), presumed to contain only bacteria, were added to reinoculate with resident lake bacteria. The absence of bacterial grazers can greatly reduce the rate of nutrient (nitrogen and phosphorus) recycling due to bacterial grazing [Hudson and Taylor, 1996]. Therefore, we added inorganic phosphorus and nitrogen (1  $\mu mol\ KH_2PO_4\ L^{-1}$  and 16  $\mu mol\ KNO_3\ L^{-1}$ , final concentration, respectively) at the beginning of each incubation to avoid nutrient limitation. DOC samples were collected 5 to 7 times throughout the incubation, approximately on incubation days 0, 7, 30, 100, and several times thereafter. We also analyzed EEMs at the beginning and ending of the BDOC incubations.

[15] We assumed that the DOC pool was composed of a biodegradable component (BDOC) and a recalcitrant, or nonbiodegradable, component (RDOC) such that

$$DOC = BDOC + RDOC. \quad (1)$$

DOC loss in bottle incubations was assumed to proceed as first-order degradation of the biodegradable pool

$$DOC_t = RDOC + (BDOC \times e^{-kt}), \quad (2)$$

where  $DOC_t$  is the DOC concentration at time  $t$  ( $mg\ L^{-1}$ ), RDOC is the recalcitrant DOC pool ( $mg\ L^{-1}$ ), BDOC is the biodegradable DOC pool ( $mg\ L^{-1}$ ),  $k$  is the degradation constant ( $d^{-1}$ ), and  $t$  is the time of the incubation in days. BDOC and RDOC concentrations were determined by fitting a first-order decay curve to DOC concentrations measured throughout the course of the incubation [Stets and Cotner, 2008].

[16] We used information from the BDOC incubations to develop a DOC metabolism model for the lakes ( $DOC_R$ ). Several features of this metric should be emphasized. First,  $DOC_R$  represents gross DOC mineralization rather than gross ecosystem production or respiration and is therefore conceptually similar to bacterial respiration; second, lakes typically have some gross DOC production as well, so net DOC mineralization is very likely a smaller number than  $DOC_R$  in the vast majority of lakes.

[17] Annual  $DOC_R$  was modeled by summing daily  $DOC_R$  values for the duration of the study (1 January to 31 December 2004). The principal equation used in this model was

$$DOC_R = Z_{mix} \times BDOC \times k_T, \quad (3)$$

where  $DOC_R$  is areal DOC degradation due to bacterial respiration ( $g\ C\ m^{-2}\ d^{-1}$ ),  $Z_{mix}$  is the depth of the surface mixed layer ( $m$ ),  $k_T$  is temperature-corrected  $k$  determined in equation (1), and BDOC was determined as in equation (1) and expressed in  $g\ m^{-3}$ . We assumed that  $k$  was temperature sensitive and incorporated a form of the Arrhenius equation

$$k_T = k \times Q_{10}^{\left[\frac{Temp - 20}{10}\right]} \quad (4)$$

where  $k$  is the average degradation constant determined from laboratory incubations performed at 20°C. Temp is the in situ temperature at the time of  $DOC_R$  evaluation, and  $Q_{10}$  was assumed to be 2.0. There was a linear relation between RDOC and DOC so we used linear regression to calculate RDOC throughout the year in the study lakes. We then solved equation (1) for BDOC and used the result as input into the  $DOC_R$  model (see section 3 for further explanation).  $Z_{mix}$  was determined from 16 temperature-depth profiles collected in Shingobee and Williams lakes throughout 2004. We did not collect temperature-depth profiles in any of the other lakes, but previous work in this watershed suggests that Crystal and Williams Lake have a similar stratification regime while Mary, Island, Steel, and Shingobee lakes have a similar stratification regime (D.O. Rosenberry, written communication, 2008). So, we applied temperature data from Shingobee and Williams to the other lakes appropriately. Temperature-depth profiles in Little Shingobee Lake suggest that maximum epilimnetic thickness is 3 m (C.M. Michmerhuizen and R.G. Striegl, written communication, 2007). Hypolimnetic DOC degradation was assumed to be minimal in this model because hypolimnetic volume was small in these lakes and modeled  $DOC_R$  at hypolimnetic temperatures (<10°C) was small relative to  $DOC_R$  at surface temperatures.

[18] Daily modeled  $DOC_R$  values were summed over the course of the year (2004) to produce an annual estimate ( $g\ C\ m^{-2}\ yr^{-1}$ ). More information on model development and error appear in sections 2.7 and 3. We also considered possible errors in the overall magnitude of  $DOC_R$  in section 4.

[19] We did not quantify photo-oxidation of DOC in these lakes, although in some instances this can be a significant loss term. It is important to distinguish between photo-oxidation, the direct conversion of DOC to  $CO_2$  by sunlight, and photobleaching, the removal of light-absorbing or fluorescent properties of the DOC pool. DOC is more susceptible to photobleaching than photo-oxidation [Moran *et al.*, 2000], and so alteration of DOC optical properties can occur without substantial DOC loss due to photo-oxidation. Granéli *et al.* [1996] estimated that photo-oxidation mineralized 6  $g\ C\ m^{-2}\ yr^{-1}$  in humic lakes in Sweden, with surface volumetric rates of 100–400  $mg\ C\ m^{-3}\ d^{-1}$ . Photo-oxidation rates are likely to be lower in this watershed because the lakes generally have either DOC with low UV

**Table 1.** Relevant Characteristics of the Lakes Included in This Study<sup>a</sup>

Lake	Lake Surface Area (km <sup>2</sup> )	Catchment Area (km <sup>2</sup> ) <sup>b</sup>	Water Export ( $\times 10^6$ m <sup>3</sup> yr <sup>-1</sup> ) <sup>c</sup>	Water Residence Time (yr) <sup>c</sup>	DOC (mg L <sup>-1</sup> )	SUVA <sub>254</sub>	DOC <sub>X</sub> (g C m <sup>-2</sup> yr <sup>-1</sup> )
Crystal	0.77	3.5	0.90	2.50	8.4 ± 0.6	0.9	5
Williams	0.39	5.4	0.51	3.75	7.4 ± 0.3	1.2	6
Mary	0.14	8.3	1.98	0.27	4.6 ± 0.7	2.0	60
Island	0.32	11.6	4.45	0.33	5.0 ± 0.6	2.1	60
Steel	0.25	13.0	5.56	0.33	4.8 ± 0.5	1.9	103
Little Shingobee	0.03	3.9	0.78	0.03	8.3 ± 1.0	2.4	183
Shingobee	0.66	17.7	9.95	0.33	4.8 ± 0.4	1.8	71
Groundwater	n/a	n/a	n/a	n/a	1.9 ± 0.8	2.1	n/a

<sup>a</sup>Catchment area is the surface water catchment directly adjacent to each lake, Water Export is the hydrologic flux of water out of the lakes excluding evaporation. Water residence time is calculated as water export divided lake volume. The mean and standard deviation of dissolved organic carbon (DOC) is presented and the annual average SUVA<sub>254</sub>, defined as absorbance at 254 nm divided by DOC concentration (mg L<sup>-1</sup>). DOC export (DOC<sub>X</sub>) is defined as the annual sum of daily interpolated DOC concentrations multiplied by the daily water export divided by lake surface area.

<sup>b</sup>Calculated as the sum of all upgradient catchments.

<sup>c</sup>Stets *et al.* [2010].

absorbance or short water residence times [Stets *et al.*, 2010, G. R. Aiken, unpublished data, 2004]. Low UV absorbance should minimize the reactivity of DOC to UV photo-oxidation while short water residence time will limit the exposure of the DOC to UV light. Also, a study of photo-oxidation rates in nearby lakes having similar DOC characteristics determined that surface volumetric rates did not exceed 50 mg C m<sup>-3</sup> d<sup>-1</sup> (A. M. Amado, written communication, 2008). Therefore, we excluded DOC photo-oxidation from our DOC<sub>R</sub> estimate. However, we will consider the potential influence of photo-oxidation in section 4.

## 2.6. Eastern Lake Survey (ELS) Database

[20] The ELS was conducted in 1984 by the U.S. Environmental Protection Agency to describe the chemical status of lakes in the eastern United States, particularly with regard to acidification. Therefore, the presence of low-alkalinity, low-pH systems is expected to be overrepresented in this data set compared to lakes in the United States generally [Linthurst *et al.*, 1986]. Nevertheless, the size and scope of this database provides a frame of reference against which to compare the results in the Shingobee headwater watershed. A total of 1797 lacustrine ecosystems were sampled in the northeastern, southeastern, and upper midwestern United States as part of this study. The ELS excluded from analysis water bodies meeting any of the following conditions: surface area <0.04 km<sup>2</sup>, intense anthropogenic disturbance, flowing water (stream), high conductance (>1500  $\mu$ S cm<sup>-1</sup>), bay or estuary, or too shallow to obtain a sample free of debris at 0.5 m depth. Therefore, we did not include Little Shingobee Lake when comparing our results to the ELS results because it has a surface area of 0.03 km<sup>2</sup> (Table 1). For the purposes of our study, we also excluded several other types of water bodies from the ELS data set: those determined to be swamps, reservoirs, or for which lake type was undefined, and those for which lake water residence time (RT) was not defined. All told 1532 lakes from the ELS data set were included in our analysis. Most lakes were sampled once just after fall turnover in the autumn of 1984. A water sample was collected with a Van Dorn bottle from 0.5 or 1.5 m depth, depending upon the depth of the lake, at the deepest part of the lake. Samples were analyzed for

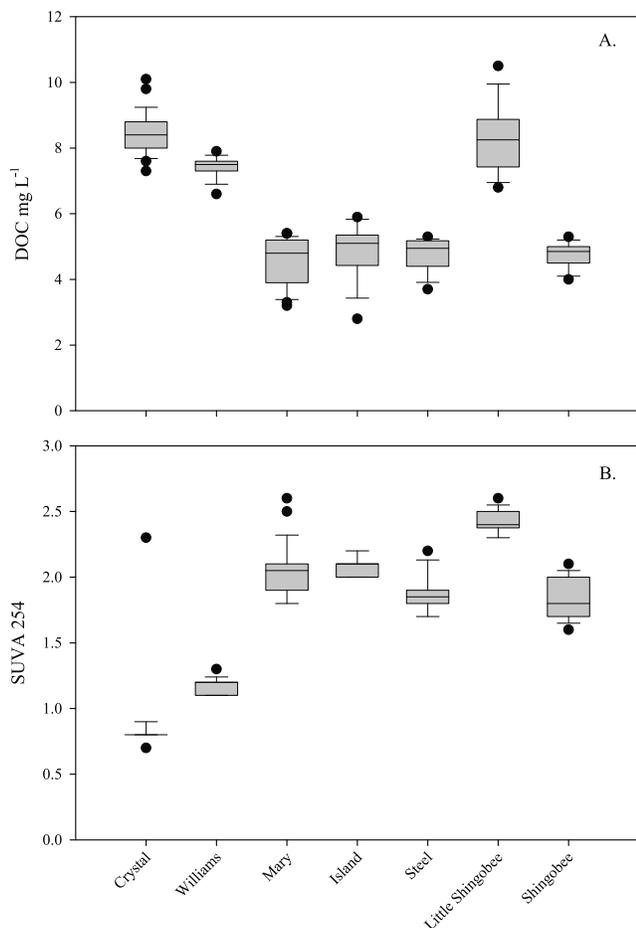
major anions and cations, pH, DOC, and other water quality parameters. The presence of surface water inlets and outlets were determined by visual analysis of maps, whereas lake area ( $A_L$ ) and watershed area were determined by planimetry [Linthurst *et al.*, 1986]. Furthermore, an algorithm was developed that allowed estimation of lake water residence time (RT) [Linthurst *et al.*, 1986]. For the purposes of our study, we used lake hydrologic setting and RT as a means of comparing our study site to other freshwater lakes in the eastern continental United States. We also calculated DOC<sub>X</sub> for the ELS lakes using the following equation:

$$\text{DOC}_X = \frac{\text{DOC} \times V_L}{A_L \times \text{RT}} = \frac{\text{DOC} \times Z_{\text{AVG}}}{\text{RT}}, \quad (5)$$

where DOC is the measured DOC concentration (g m<sup>-3</sup>) of each lake sampled as part of the ELS,  $V_L$  is the calculated lake volume (m<sup>3</sup>),  $A_L$  is expressed in m<sup>2</sup>, and  $Z_{\text{AVG}}$  is average lake depth (m), and RT is expressed in units of years. Linthurst *et al.* [1986] describe the calculations and assumptions used to determine the  $Z_{\text{AVG}}$  and RT of each lake in the ELS. Our chief assumption was DOC concentration was relatively constant in these lakes. This assumption is valid in the Shingobee Headwaters Watershed [Stets *et al.*, 2009], but in other areas, there can be very large intraannual and interannual trends in DOC [Pace and Cole, 2002]. Therefore, these calculations provide a rough estimate of lake hydrologic characteristics, but taken in aggregate, they can convey a sense of DOC<sub>X</sub> in freshwater lakes. In our analyses of the ELS database, we calculated descriptive statistics for all lakes and for lakes categorized by hydrologic setting (open- or closed-basin depending upon the presence of a surface-water outlet).

## 2.7. Statistics and Model Conditions

[21] We developed an estimate of the error associated with modeled DOC<sub>R</sub> by running the model using the best estimated values of BDOC and  $k$  and repeating model runs using the best estimate plus or minus the standard error. BDOC was determined from linear regression (see section 3) so the standard error of prediction ( $\hat{y}$ ) was used. The model was run 9 times (average, high, and low values for BDOC and  $k$ ). The



**Figure 2.** Box plots summarizing annual (a) dissolved organic carbon (DOC) concentration and (b) specific ultraviolet light absorbance at 254 nm. Results are shown for each lake and the groundwater springs sampled. Boxes show median (horizontal line), 25th – 75th percentile (box boundaries), 10th–90th percentile (whiskers), and samples lying outside the 10th and 90th percentiles (black circles).

values presented for  $\text{DOC}_R$  are the average and standard deviation of these nine runs. While this procedure does not provide a true standard deviation, it allows some consideration of the uncertainty involved with modeling  $\text{DOC}_R$ . Analysis of ELS data was performed after log transformation to ensure normality, but untransformed results are presented. All statistical analyses were performed using SAS 9.2 (SAS Institute, Inc., Cary, NC, USA). The  $\text{DOC}_R$  model was run in Berkeley Madonna (Macey & Oster), and PARAFAC was run in MATLAB.

### 3. Results

#### 3.1. DOC Concentration and Export

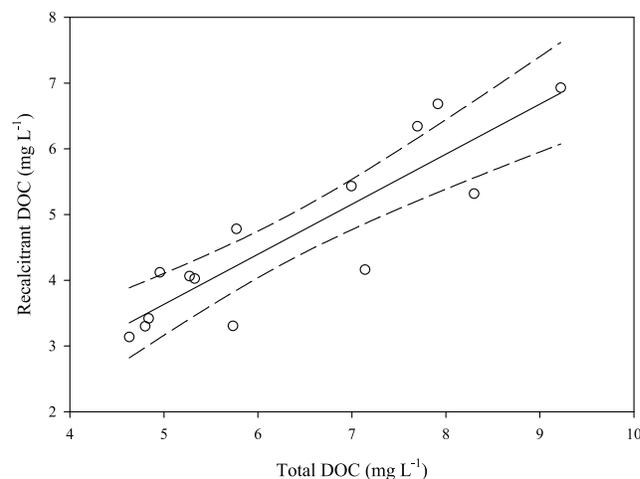
[22] DOC concentrations ranged from approximately 2 to 10  $\text{mg L}^{-1}$  in this watershed. Average groundwater DOC concentrations were  $1.9 \pm 0.8 \text{ mg C L}^{-1}$  with an average  $\text{SUVA}_{254}$  of 2.1 (Table 1). In the closed-basin lakes, mean

DOC concentration was 8.4 and 7.4  $\text{mg C L}^{-1}$  and mean  $\text{SUVA}_{254}$  was 0.9 and 1.2 in Crystal and Williams, respectively (Figure 2 and Table 1). Little Shingobee Lake, the fen lake, had a mean DOC concentration of 8.3  $\text{mg C L}^{-1}$  and a mean  $\text{SUVA}_{254}$  of 2.4 (Figure 2 and Table 1). The other open-basin lakes, Mary, Island, Steel, and Shingobee, had generally lower DOC concentrations with means ranging from 4.6  $\text{mg C L}^{-1}$  in Mary Lake to 5.0  $\text{mg C L}^{-1}$  in Island Lake (Figure 2a and Table 1). Mean  $\text{SUVA}_{254}$  ranged from 2.1 in Island Lake to 1.8 in Shingobee Lake (Figure 2b and Table 1).

[23] The magnitude of  $\text{DOC}_X$ , the hydrologic export of DOC, differed strongly between the open- and closed-basin lakes due to the large differences in hydrologic fluxes. In Crystal and Williams lakes,  $\text{DOC}_X$  was 5 and 6  $\text{g C m}^{-2} \text{ yr}^{-1}$ , respectively (Table 1). In the open-basin lakes,  $\text{DOC}_X$  ranged from 60 (Mary Lake) to 103  $\text{g C m}^{-2} \text{ yr}^{-1}$  (Steel Lake, Table 1).  $\text{DOC}_X$  was highest in the fen lake, 183  $\text{g C m}^{-2} \text{ yr}^{-1}$ , due to the combination of high DOC concentrations and large hydrologic fluxes relative to the size of the lake (Table 1).  $\text{DOC}_X$  was closely correlated with the magnitude of water load, defined as the volume of annual water export divided by lake surface area ( $r = 0.95$ , data not shown). Therefore, the presence of a surface water outlet was a principal organizing feature in the characteristics of DOC export in this watershed.

#### 3.2. BDOC and $\text{DOC}_R$

[24] BDOC concentration ranged from 0.8 to 3.0  $\text{mg C L}^{-1}$ , whereas the degradation rate constant  $k$ , ranged from 0.007 to 0.035  $\text{d}^{-1}$  (Table 2). Average and standard error of  $k$  for all lakes was  $0.016 \pm 0.002 \text{ d}^{-1}$  ( $n = 14$ ), and there were no significant differences between open- and closed-basin lakes (two-tailed  $t$  test,  $P = 0.76$ ,  $t_{13(2)} = 0.31$ ,  $n = 14$ ). There was a significant linear relation between total DOC and  $\text{RDOC}$  (Figure 3 and Table 2). We used this relation to



**Figure 3.** Relation between total dissolved organic carbon (DOC) and recalcitrant dissolved organic carbon ( $\text{RDOC}$ ), determined by laboratory incubations. The regression line displayed is  $\text{RDOC} = -0.17 (\pm 0.74) + (0.76 \pm 0.11) \times \text{DOC}$  ( $R^2 = 0.79$ ,  $P < 0.0001$ ,  $F_{1, 12} = 44.8$ ).

**Table 2.** Summary Statistics of the Biodegradable Dissolved Organic Carbon Incubation Experiments<sup>a</sup>

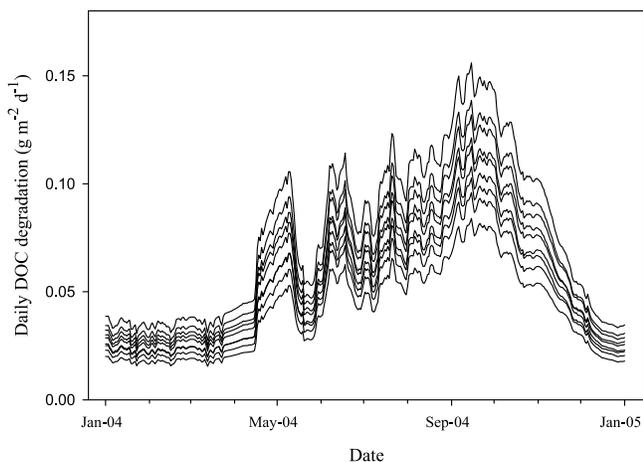
	Statistics
Degradation constant	$k = 0.016 \pm 0.002 \text{ d}^{-1}$ (average and standard deviation), $n = 14$ , maximum $k = 0.035 \text{ d}^{-1}$ , minimum $k = 0.007 \text{ d}^{-1}$
RDOC relation to DOC	$\text{RDOC} = (0.76 \pm 0.11 \times \text{DOC}) - (0.17 \pm 0.74) \text{ mg l}^{-1}$ , $R^2 = 0.79$ , $P < 0.001$ , $F_{0.05(1), 1, 12} = 44.8$
DOC mineralization model	Daily $\text{DOC}_R = k_T Z_{\text{MIX}}(\text{DOC} - [0.76(\text{DOC} - 0.17)]) \text{ g C m}^{-2} \text{ d}^{-1}$ Annual $\text{DOC}_R = \sum \text{Daily DOC}_R$ (annual $\text{DOC}_R$ expressed in $\text{g C m}^{-2} \text{ yr}^{-1}$ )

<sup>a</sup>Includes degradation rate constant ( $k$ ),  $k_T$  is  $k$  corrected for temperature assuming a  $Q_{10}$  of 2.0, recalcitrant dissolved organic carbon (RDOC) relation to total dissolved organic carbon (DOC), and the equations governing the dissolved organic carbon mineralization model ( $\text{DOC}_R$ ).  $Z_{\text{MIX}}$  is the surface mixed-layer depth in meters.

calculate RDOC and therefore BDOC as described in section 2.

[25] Modeled  $\text{DOC}_R$  was lowest in the winter and higher in other parts of the year because of the inclusion of temperature in equation 4 (Figure 4). Within each lake, temperature was a primary control on  $\text{DOC}_R$  and temperature effects were much larger than those associated with the errors in BDOC or  $k$  estimation. Between lakes,  $\text{DOC}_R$  was controlled by DOC concentration and  $Z_{\text{mix}}$ .

[26]  $\text{DOC}_R$  ranged from 15 to 42  $\text{g C m}^{-2} \text{ yr}^{-1}$  with the closed-basin lakes having the highest values (Table 3), owing to the high DOC concentrations. Although Little Shingobee Lake also had high DOC concentrations,  $\text{DOC}_R$  was lower than in the closed-basin lakes because  $Z_{\text{mix}}$  was much shallower (2–3 m) than in the closed-basin lakes (5–10 m).  $\text{DOC}_R$  was larger than  $\text{DOC}_X$  in the closed-basin lakes and the ratio  $\text{DOC}_R/\text{DOC}_X$  ranged from 6.8 to 8.1 (Figure 5). Therefore, within-lake DOC processing domi-

**Figure 4.** Example of dissolved organic carbon mineralization ( $\text{DOC}_R$ ) model results for Shingobee Lake. All nine model runs are displayed for the period 1 January to 31 December 2004. Daily values are shown in  $\text{g C m}^{-2} \text{ d}^{-1}$ .**Table 3.** Modeled Annual Dissolved Organic Carbon Mineralization<sup>a</sup>

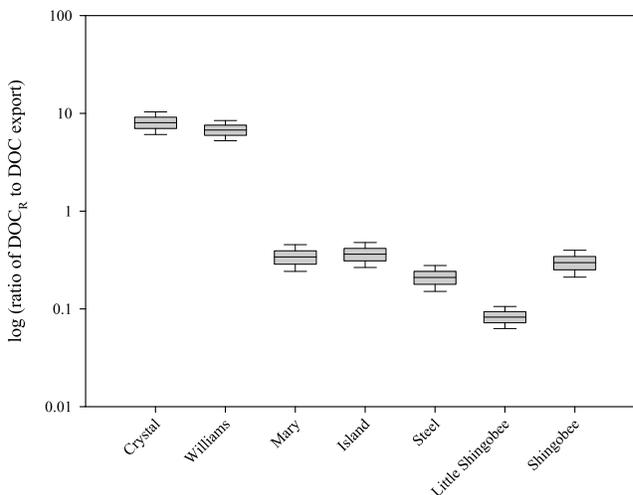
Lake	$\text{DOC}_R (\text{g C m}^{-2} \text{ yr}^{-1})$
Crystal	$42 \pm 7$
Williams	$37 \pm 5$
Mary	$20 \pm 4$
Island	$22 \pm 4$
Steel	$22 \pm 4$
Little Shingobee	$15 \pm 2$
Shingobee	$21 \pm 4$

<sup>a</sup>Expressed as  $\text{g C m}^{-2} \text{ lake area yr}^{-1}$ . The mean and standard deviation of the nine model runs is shown.

nated DOC dynamics in these lakes. In contrast,  $\text{DOC}_R$  was much lower than  $\text{DOC}_X$  in the open-basin lakes with  $\text{DOC}_R/\text{DOC}_X$  ranging from 0.21 to 0.36. In the fen lake, with a hydrologic residence time of approximately 3 weeks (Table 1), the  $\text{DOC}_R/\text{DOC}_X$  ratio was 0.08 (Figure 5). Therefore, hydrologic DOC fluxes dominated DOC cycling in the open-basin and fen lakes. These results underscore the importance of hydrologic setting in determining which processes are most important to DOC cycling in lakes.

### 3.3. DOC Fractionation and Fluorescence Characteristics

[27] The fraction of DOC composed of HPOA, as well as the UV absorbance of this material, differed strongly between lake types. DOC in the fen lake, Little Shingobee, had the highest percentage HPOA, 43%, compared with 34% HPOA in the open-basin lakes and 29% in the closed-basin lakes (Table 4). Similarly, the  $\text{SUVA}_{254}$  of the HPOA was 3.3 in the fen lake, 3.0 in the other open-basin lakes, and 1.6 in the closed-basin lakes (Table 4). These results suggest

**Figure 5.** Ratio of dissolved organic carbon mineralization ( $\text{DOC}_R$ ) to hydrologic dissolved organic carbon export ( $\text{DOC}_X$ ) in this study. The ratio of  $\text{DOC}_R$  to  $\text{DOC}_X$  is shown on a log scale. Boxes show median (horizontal line), 25th–75th percentile (box boundaries), and 10th–90th percentile (whiskers).

**Table 4.** Summary of DOC,  $SUV_A$ , Fulvic Acid Fractionation, and Parallel Factor Analysis for All Lakes in the Present Study

	Closed-Basin Lakes	Open-Basin Lakes	Fen Lake	Groundwater
Fulvic acid characterization				
% HPOA	29	34	43	n/a
$SUV_{A254}$ of HPOA	1.6	3.0	3.3	n/a
Fluorescence properties, PARAFAC				
% C1	6.8	6.9	7.3	6.8
% Q2	19	20	21	21
% C3	7.6	6.0	4.9	6.4
% HQ	14	16	17	17
% SQ1	3.0	3.4	4.0	4.2
% C6	5.7	7.4	7.6	4.3
% SQ2	4.6	4.5	4.9	6.3
% Trp	5.6	2.5	1.1	2.7
% SQ3	2.8	2.3	2.4	4.4
% C10	3.5	3.0	3.3	3.6
% Q1	12	14	14	11
% Q3	10	11	10	10
% Tyr	4.9	4.3	3.1	2.4
%Protein-like (Trp + Tyr)	17	8.7	5.2	5.1
% Photosensitive (SQ1 + SQ2)	6	6.5	8.8	11.0

that the DOC in the fen lake and the open-basin lakes was highly aromatic and originated from the surrounding catchment. The HPOA present in the closed-basin lakes either originated from autochthonous production or had undergone substantial transformation by in-lake processes such as photodegradation or bacterial mineralization.

[28] PARAFAC analysis revealed that total fluorescence was highest in the fen lake,  $6.6 \text{ nm}^{-1}$ , and lowest in the low-DOC groundwater samples, approximately  $0.8 \text{ nm}^{-1}$  (Figure 6a). However, total fluorescence in the higher-DOC groundwater springs reached  $2.8 \text{ nm}^{-1}$ . Total fluorescence ranged from 1.9 to  $2.8 \text{ nm}^{-1}$  in the open-basin lakes, a range similar to that of the groundwater (Figure 6a). Even though the closed-basin lakes had some of the highest DOC concentrations in the watershed, total fluorescence was 1.0 and  $1.2 \text{ nm}^{-1}$  in Crystal and Williams lakes, respectively, among the lowest in the watershed (Figure 6a).

[29] DOC concentration was most strongly correlated with Tryptophan-like (Trp), tyrosine-like (Tyr), and protein-like (Trp+Tyr) fluorescence across all lake types and groundwater in this study ( $r = 0.70, 0.61, \text{ and } 0.75$ , respectively, Figures 6b–6d). The fen lake had the highest fluorescence in each of these components, while low DOC groundwater had the lowest (Figures 6b–6d). Notably, several of the groundwater springs also had high Trp-like fluorescence (Figure 6b). Trp, Tyr, and protein-like fluorescent components were high in the closed-basin lakes despite the low total fluorescence (Figures 6b–6d). As a result, protein-like fluorescence was a large percentage of overall fluorescence in the closed-basin lakes, 17% (Table 4). By contrast, protein-like fluorescence was only approximately 9% of overall fluorescence in the open-basin lakes and approximately 5% in both the fen lake and groundwater (Table 4). An unidentified fluorophore, C6, was also significantly correlated with DOC concentration ( $r = 0.48, P < 0.05$ , not shown); however, none of the other fluorophores from the

PARAFAC model were correlated with DOC. BDOC incubations consumed DOC and protein-like fluorescence in all of the lakes (Figures 6b–6d) suggesting that these fluorophores were susceptible to microbial degradation and therefore maintaining these components in the lakes required continual replenishment.

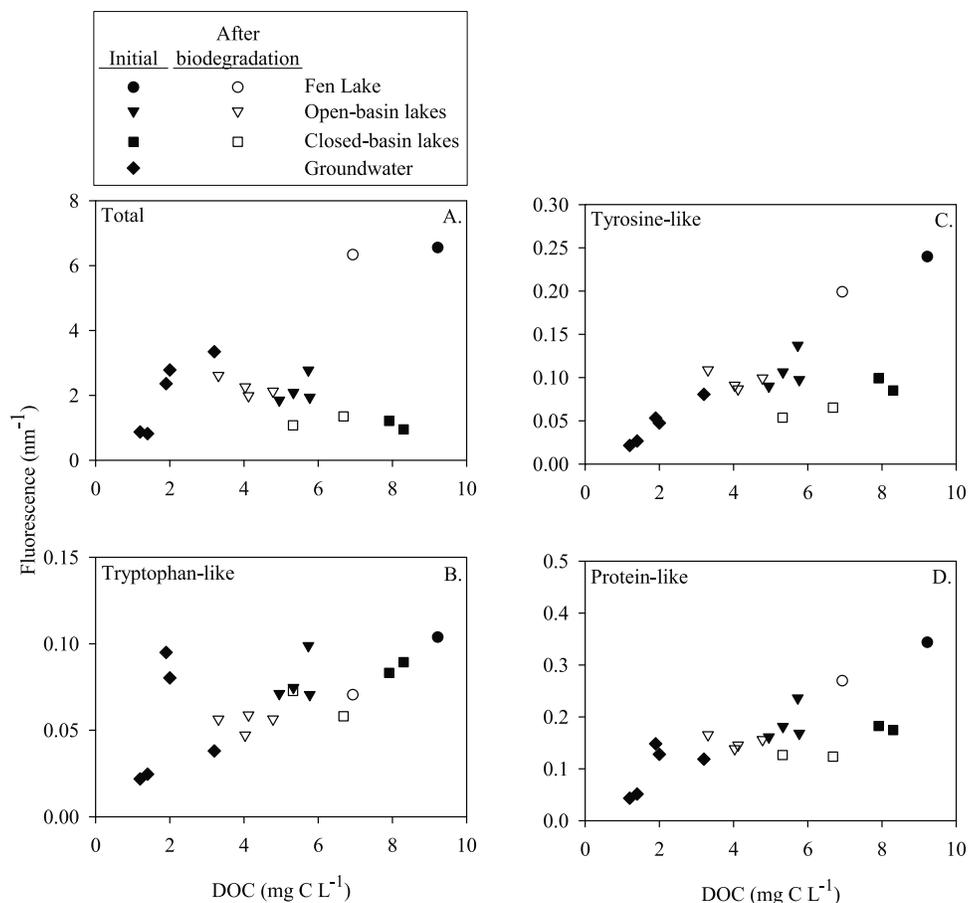
### 3.4. ELS Lakes

[30] Analysis of the ELS lake database placed our results in context of lakes more broadly. For all lakes in the ELS data set ( $n = 1532$ ), mean and median RT were 0.38 and 0.45 years, respectively (Table 5 and Figure 7). For open-basin lakes ( $n = 1038$ ), mean and median RT were 0.27 and 0.30 years, respectively (Table 5 and Figure 7), very similar to the open-basin lakes of the Shingobee Headwaters Watershed (Table 1). On the other hand, the closed-basin lakes in the ELS ( $n = 494$ ) had a mean and median RT of 0.81 and 1.0 years, respectively (Table 5), suggesting that the closed-basin lakes in the Shingobee Headwaters Watershed have unusually long RT (Table 1), close to the 90th percentile of all lakes included in the ELS.

[31] For all lakes in the ELS, the mean and median  $DOC_X$  was 26 and  $23 \text{ g C m}^{-2} \text{ yr}^{-1}$ , whereas for open-basin lakes, the mean and median  $DOC_X$  were 37 and  $32 \text{ g C m}^{-2} \text{ yr}^{-1}$ , respectively (Table 5 and Figure 7).  $DOC_X$  in the open-basin lakes of the Shingobee Headwaters Watershed were close to the 75th percentile of open-basin ELS lakes,  $80 \text{ g C m}^{-2} \text{ yr}^{-1}$  (Table 5 and Figure 7), suggesting that  $DOC_X$  observed in this study was high but not unusual. For closed-basin lakes in the ELS, mean and median  $DOC_X$  were 13 and  $12 \text{ g C m}^{-2} \text{ yr}^{-1}$ , respectively (Table 5 and Figure 7), and  $DOC_X$  for the closed-basin lakes in the Shingobee Headwaters Watershed was near the tenth percentile of these lakes.

## 4. Discussion

[32] C cycling in freshwater aquatic ecosystems is intense with more than half of the C entering aquatic ecosystems from the terrestrial environment undergoing transformation through either mineralization, sedimentation, or C gas efflux [Tranvik *et al.*, 2009]. Our results underscore the importance of lake hydrologic setting in determining the processes that dominate carbon cycling. From the perspective of regional C exports, the open-basin lakes acted primarily to convey DOC from the headwaters to downstream river reaches because  $DOC_R$  was only 0.08 to 0.36 that of lateral fluxes (Figure 5). Analysis of the ELS data set reinforced the importance of  $DOC_X$  in the organic C budget of open-basin lakes more generally (Table 5 and Figure 7). Internal processing dominated DOC fluxes in the closed-basin lakes (Figure 5). However, compared to the ELS data set, these lakes may have had unusually long residence times and a correspondingly low  $DOC_X$  (Table 1 and Table 5). Considering that net DOC mineralization is likely to be much smaller in magnitude than  $DOC_R$ , we conclude that net DOC mineralization is probably a minor component of overall DOC fluxes in the Shingobee Headwaters Watershed and possibly of lakes more broadly.



**Figure 6.** The relation of dissolved organic carbon (DOC) concentration and (a) total fluorescence, (b) tryptophan-like fluorescence, (c) tyrosine-like fluorescence, and (d) protein-like (tryptophan + tyrosine) fluorescence. Symbols indicate whether the samples were fresh or post-biodegradation and whether the samples came from groundwater, closed-basin lakes (Crystal and Williams), open-basin lakes (Mary, Island, Steel, or Shingobee), or the fen lake (Little Shingobee Lake). Fluorescence is expressed in Raman units ( $\text{nm}^{-1}$ ).

[33] DOC optical properties were congruous with the results of the field and laboratory investigations and lent support to our overall conclusions about DOC cycling in this watershed. The similarity of DOC optical properties in groundwater and the four larger open-basin lakes indicates that groundwater is an important source of DOC to them and that within-lake DOC transformations in these lakes are modest compared to hydrologic fluxes (Figure 6 and Table 4). In contrast, the high aromaticity, high overall fluorescence, and high DOC concentration in Little Shingobee Lake all suggest that the allochthonous DOC delivered to it probably originates from organic fen sediments rather than groundwater (Figure 2). Likewise, Carter *et al.* [1997] observed that hydrologic inputs to this lake are primarily from small streams draining the nearby fen. Protein-like fluorescence can arise from either autochthonous production or inputs from organic sediments [Fellman *et al.*, 2008; Stedmon and Markager, 2005b]. Given the presumably high allochthonous DOC load and short water residence time of Little Shingobee Lake (Table 1), we conclude that DOC originating from the fen maintains the high protein-like fluorescence.

Protein-like fluorescence was also relatively high in the open-basin lakes (Figure 6d) and may have arisen from a combination of watershed loading and within-lake production. DOC optical properties have been used to infer the degree of biogeochemical transformation in other aquatic ecosystems [Stedmon and Markager, 2005a; Cory *et al.*, 2007]. And in the present study, coupling the quantification of DOC fluxes with analysis of DOC optical properties proved to be an effective means of gaining insight about DOC sources and transformation throughout the watershed.

#### 4.1. Hydrologic Versus Metabolic DOC Fluxes

[34] Although recent interest in allochthonous DOC has focused on its reactivity and contribution to lake metabolism, DOC mineralization played a minor role in lake metabolism in the Shingobee Headwaters Watershed. In the open-basin lakes, hydrologic DOC fluxes were much larger than metabolic fluxes (Figure 5), suggesting that a low proportion of allochthonous DOC entering the lakes was oxidized. We did not directly quantify how much allochthonous DOC was consumed, but we can arrive at an approxi-

**Table 5.** Mean and Percentile Statistics for Residence Time and Dissolved Organic Carbon Export in the Eastern Lake Survey Data<sup>a</sup>

	n	Mean	Percentiles				
			10th	25th	Median	75th	90th
Residence time (years)							
All Lakes	1532	0.38	0.05	0.14	0.45	1.19	2.37
Open-basin	1038	0.27	0.03	0.10	0.30	0.82	1.78
Closed-basin	494	0.81	0.17	0.39	1.00	1.83	3.10
DOC export (g C m <sup>-2</sup> yr <sup>-1</sup> )							
All Lakes	1532	26	6	10	23	59	160
Open-basin	1038	37	8	14	32	80	218
Closed-basin	494	13	4	6	12	24	53

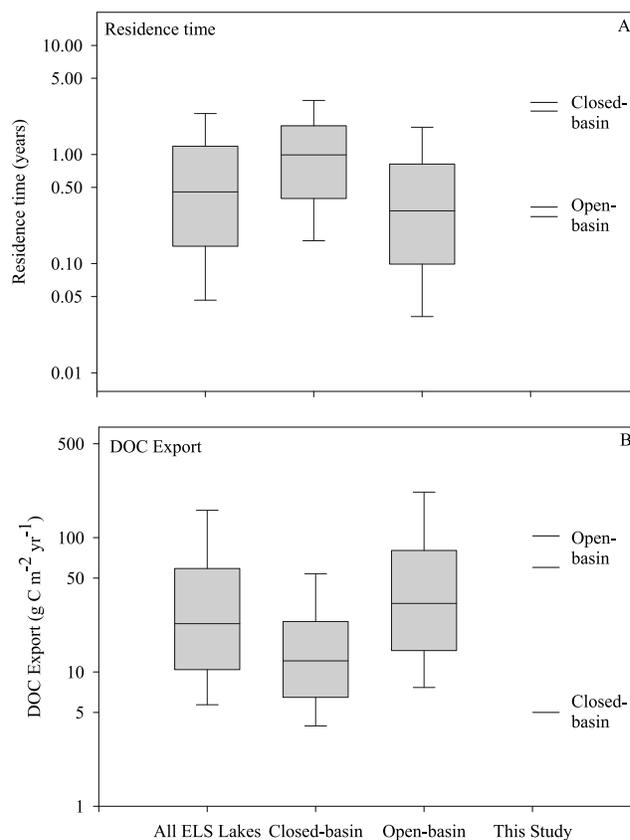
<sup>a</sup>Statistics for all lakes are presented along with statistics for closed-basin lakes (lakes not having a visible surface outlet) and open-basin lakes (lakes having a visible surface-water outlet). The analysis excluded water bodies designated as marshes, reservoirs, or for which a similar designation was not given [see *Linthurst et al.*, 1986]. Residence time and DOC export both had a lognormal distribution in this data set, so the mean value was calculated on natural-log-transformed values.

mation by assuming that there was no net DOC production in the open-basin lakes and that  $\text{DOC}_R$  was sustained entirely by allochthonous DOC. In this hypothetical scenario, allochthonous DOC inputs could be expressed as  $[\text{DOC}_R + \text{DOC}_X]$  and the proportion of allochthonous DOC consumed in the lakes would be  $(\text{DOC}_R/[\text{DOC}_R + \text{DOC}_X])$ , approximately 8%–25%. This is much lower than estimates developed in other lakes, which have been as large as 80% [*Algesten et al.*, 2003; *Dillon and Molot*, 1997; *McCallister and del Giorgio*, 2008]. Other allochthonous OC inputs were not likely to be large. Groundwater OC inputs are important in this watershed [*Stets et al.*, 2009], but because the DOC concentration of groundwater is lower than that of the lakes, groundwater inputs would serve to dilute the DOC pool in the lakes. Airborne OC deposition to lakes typically does not exceed  $2 \text{ g m}^{-2} \text{ yr}^{-1}$  and so would not be a significant source of OC to these lakes [*Gasith and Hasler*, 1976; *Preston et al.*, 2008]. Furthermore, DOC concentrations were nearly constant along the open-basin lake chain (Mary to Shingobee, Figure 2a). If these lakes were strong net sinks for DOC, we could reasonably expect that DOC concentrations to decrease along this hydrologic flow path, an approach used elsewhere to estimate DOC loss in lakes [*Canham et al.*, 2004]. Therefore, these lakes acted primarily as conduits transporting DOC to the regional river system.

[35] Aggregate results for the closed-basin lakes indicate that cycling of autochthonous DOC, rather than consumption of allochthonous DOC, was the dominant process sustaining  $\text{DOC}_R$ . Allochthonous DOC inputs were likely to be low because hydrologic inputs were low (Table 1) and primarily from groundwater having low DOC concentration (Figure 2a). Yet, the closed-basin lakes had some of the highest DOC concentrations in the watershed (Table 1 and Figure 2a). The high percentage of protein-like fluorescence was consistent with prevalence of autochthonous production but could have occurred because of selective photobleaching of the nonprotein-like fluorophores [*Stedmon and Markager*, 2005b]. However, microbial degradation in incubation experiments consumed protein-like fluorophores

(Figures 6b–6d), a finding consistent with several other studies [*Fellman et al.*, 2008; *Wickland et al.*, 2007], indicating that protein-like material needed to be continually replenished. Because allochthonous DOC inputs were likely to be low, autochthonous production was the most likely source of protein-like organic material. Accordingly, the DOC pool in the closed-basin lakes was composed of material having low UV absorbance (Figure 2b), low percentage fulvic acid (Table 4), and relatively high protein-like fluorescence (Figure 6d and Table 4). Taken together, these results suggest that allochthonous DOC consumption in the closed-basin lakes was minimal and that autochthonously produced DOC sustained most of the DOC cycling.

[36] The muted importance of allochthonous DOC to lake metabolism in this watershed is best understood in the context of watershed DOC yield, defined as DOC export divided by surface watershed area. Measured at the outlet of Shingobee Lake, DOC yield for the Shingobee River watershed was  $2.1 \text{ g C m}^{-2} \text{ yr}^{-1}$  (data derived from Table 1).



**Figure 7.** Box plots of the distribution of (a) residence times and (b) calculated DOC export in the Eastern Lake Survey data set. Distributions are shown for all lakes, only closed-basin lakes (i.e., those without a surface water outlet), and only open-basin lakes. We also show the range of observations for open- and closed-basin lakes from the Shingobee Headwaters Watershed. The y axis in both panels is displayed on natural-log scale. Boxes show median (horizontal line), 25th–75th percentile (box boundaries), and 10th–90th percentile (whiskers).

DOC yield is between 1 and 10 g C m<sup>-2</sup> yr<sup>-1</sup> in most watersheds and increases with percentage wetland coverage [Hope et al., 1994]. The relatively low DOC yield in this watershed probably resulted from the importance of low-DOC groundwater to hydrologic fluxes and DOC loading [Stets et al., 2010; Stets et al., 2009]. Generating substantial allochthonous DOC inputs to lakes located in watersheds with low DOC yield requires large hydrologic fluxes. So, lakes with limited hydrologic exchange, such as the closed-basin lakes in this study, do not receive enough allochthonous DOC for it to be an important part of lake metabolism. Conversely, lakes having large allochthonous DOC loads, such as the open-basin lakes in this study, have correspondingly short water-residence times (approximately 0.3 years). The short water residence times may constrain allochthonous DOC mineralization because this material can be fairly recalcitrant and have a slow degradation rate in lakes [Kohler et al., 2002]. For example, the proportion of allochthonous DOC consumed in lakes in Central Ontario, Canada, increased as water residence time increased from 2 to 6 years (data derived from Dillon and Molot [1997]). If allochthonous DOC mineralization can be constrained by water residence times on the order of what was observed in the open-basin lakes of the Shingobee Headwaters Watershed, then this condition may be fairly common because median residence time in open-basin lakes of the ELS data set was also 0.3 years (Table 5 and Figure 7).

[37] It is important to note that watershed IC export is much larger than OC export in the Shingobee Headwaters because of the presence of carbonate-rich sediments. Lateral IC export from Shingobee and Williams lakes were approximately an order of magnitude larger than DOC<sub>X</sub> (782 and 51 g C m<sup>-2</sup> yr<sup>-1</sup>, respectively [Stets et al., 2009]). We did not analyze IC export for the ELS data set and therefore do not have a basis of comparison to lakes more broadly, but most watersheds would probably have an IC-to-OC export ratio much lower than that in the Shingobee Headwaters. Broadly, a reasonable expectation is that OC and IC export are similar because the magnitude of watershed export of these constituents is similar [Hope et al., 1994]. Significant deviations would occur due to the geologic setting of individual watersheds or differential retention or processing of IC versus OC within lakes.

#### 4.2. DOC<sub>R</sub> in Context

[38] Our conclusions regarding the OC cycle in this watershed partly depend upon the accuracy of DOC<sub>R</sub>. Drawing comparisons between this study and other assessments of lake DOC mineralization or bacterial respiration is difficult because annual, depth-integrated estimates of bacterial respiration are rare. However, several studies have modeled or measured seasonal or synoptic bacterial respiration rates in lakes. Calculating DOC<sub>R</sub> for the summer season only (19 May to 26 September 2004) and converting to volumetric units (g C m<sup>-3</sup> d<sup>-1</sup>) by multiplying by epilimnetic depth provides a basis of comparison with other studies. Average volumetric summertime DOC<sub>R</sub> was least in Steel Lake and greatest in Crystal Lake, 0.02 and 0.06 g C m<sup>-3</sup> d<sup>-1</sup>, respectively. Modeled summertime bacterial respiration rate in several small humic lakes in Michigan, USA,

was 0.03–0.12 g C m<sup>-3</sup> d<sup>-1</sup> [Cole et al., 2006; Bade et al., 2007]. Summertime bacterial respiration was 0.003–0.008 g C m<sup>-3</sup> d<sup>-1</sup> in Lake Örsträket, Sweden [Jonsson et al., 2001]. A synoptic survey of lakes in Minnesota, USA, found bacterial respiration rates between 0.005 and 0.07 g C m<sup>-3</sup> d<sup>-1</sup> [Biddanda et al., 2001]. Therefore, our summertime volumetric estimates of DOC<sub>R</sub> fall easily within the ranges of bacterial respiration rates found in other lakes, suggesting that the conclusions drawn from this study are based on ecologically realistic estimates of DOC<sub>R</sub>.

[39] We expect that inclusion of DOC photo-oxidation into our DOC<sub>R</sub> model would not have affected our overall conclusions. Annual photo-oxidation rates in humic lakes in Sweden were estimated to be 6 g C m<sup>-2</sup> yr<sup>-1</sup> [Granéli et al., 1996]. If we add this element to our DOC<sub>R</sub> estimate, then DOC<sub>R</sub> would have ranged from 21 to 48 g C m<sup>-2</sup> yr<sup>-1</sup> and DOC<sub>R</sub>/DOC<sub>X</sub> would have been approximately 8.5 in the closed-basin lakes, 0.4 in the open-basin lakes, and 0.1 in the fen lake (calculations derived from Tables 1 and 3). Therefore, our overall conclusions about the relative magnitude of DOC<sub>R</sub> and DOC<sub>X</sub> in this watershed would stand.

[40] We did not attempt to estimate DOC<sub>R</sub> for the ELS data set and so have very little basis to extrapolate the relative magnitude of DOC<sub>R</sub> and DOC<sub>X</sub> beyond our well-studied watershed. Broadly, we would expect DOC<sub>R</sub> to be higher because temperature is an important part of the DOC<sub>R</sub> and the Shingobee Headwaters Watershed is located in a relatively cold region of the United States. However, the range of published bacterial respiration rates, cited above, suggests that DOC<sub>R</sub> may not be substantially larger than what was calculated in this watershed. In any event, we expect that DOC<sub>X</sub> is a significant component of overall organic C fluxes in lakes.

## 5. Conclusions

[41] DOC export likely exceeds DOC<sub>R</sub> in many lakes. Although C processing within lakes is intense, net DOC mineralization is likely a small portion of the overall C cycle, particularly in open-basin lakes having relatively short water residence times. Hydrologic fluxes, chemical composition, and DOC optical properties all point toward a prevalence of low-DOC groundwater in the aquatic C budget of the Shingobee Headwaters Watershed. It is not clear how common this condition may be, but open-basin lakes having short water residence times, and large DOC<sub>X</sub> are prevalent in the ELS database and suggest that many lakes act primarily as conduits to transport DOC to regional river systems.

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G. R. Aiken and E. G. Stets, U.S. Geological Survey, 3215 Marine Street, Suite E-127, Boulder, CO 80303, USA. (estets@usgs.gov)  
 R. G. Striegl, U.S. Geological Survey, MS 413, Bldg 53, Box 25046, Denver Federal Center, Lakewood, CO 80225, USA.