

# Carbon quality regulates the temperature dependence of aquatic ecosystem respiration

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## Funding information

National Science Foundation, Grant/Award  
Number: EF 1638704, DEB-1754265

## Abstract

1. Ecosystems are responding to broad-scale changes in climate and other factors in complex ways. Two key changes occurring in many inland waterbodies are increasing temperatures and increasing terrestrial dissolved organic matter (tDOM) inputs. Due in part to tDOM inputs, inland waters play an important role in the global carbon cycle, with release of CO<sub>2</sub> from these ecosystems a substantial portion of the combined carbon sinks of terrestrial ecosystems and the oceans.
2. Ecosystem respiration (ER) is an important mechanism regulating CO<sub>2</sub> in aquatic systems, and ER rates are temperature-dependent. However, it is unknown how ER rates will change in the future because ER is sensitive to factors other than temperature, such as the concentration and source of organic matter. Theory posits that ER rates supported by refractory carbon compounds should exhibit a greater temperature dependence than ER rates supported by labile carbon compounds, but empirical tests of this theory are inconclusive.
3. We experimentally manipulated temperature and carbon quality in mesocosms while monitoring dissolved oxygen (DO) with in situ high frequency DO sensors. We used two highly divergent, natural DOM sources and diluted the more refractory source so that dissolved organic carbon concentrations were similar in all mesocosms. We calculated daily ER rates over 27 days in each mesocosm.
4. We found that ER increased more with temperature when tDOM dominated the organic carbon pool. Given widespread increases in temperature and tDOM inputs to aquatic ecosystems, these results highlight important interactions governing how ecosystems may respond to concurrent environmental changes and alter their contributions to the global carbon cycle.

## KEYWORDS

carbon, ecosystem respiration, lakes, metabolism, temperature

## 1 | INTRODUCTION

Recently, atmospheric concentrations of CO<sub>2</sub> crossed the 400 ppm threshold, an increase of 43% over preindustrial times (Battin et al., 2009; NOAA, 2017). Although there is nothing especially important about this number, it is a symbolic threshold that underscores the need to better understand the fate of this excess CO<sub>2</sub> and processes

governing the global carbon cycle more generally. A recent synthesis estimates that as much as 5.1 Pg of terrestrially fixed carbon annually is transferred from terrestrial ecosystems to inland waters (Drake, Raymond, & Spencer, 2017), an upward revision from prior estimates of approximately 2.7 Pg (Biddanda, 2017). Thus, inland waters are a major pool of carbon and a globally relevant flux of CO<sub>2</sub> from the landscape to the atmosphere (Tranvik et al., 2009).

Traditionally, inland waters were viewed as passive transporters of organic carbon received from terrestrial ecosystems to the oceans, with little internal processing occurring en route (Cole, Caraco, Kling, & Kratz, 1994). However, it is now recognised that much of the terrestrial carbon that enters inland waterbodies is processed in situ (Cole et al., 2007; Tranvik et al., 2009). In most inland waterbodies, ecosystem respiration (ER) exceeds gross primary production (GPP), and net ecosystem production (NEP = GPP – ER) is negative, meaning that lakes are usually net metabolic sources of CO<sub>2</sub> to the atmosphere (Cole & Caraco, 2001; Cole et al., 1994; Duarte & Prairie, 2005; Jansson, Bergström, Blomqvist, & Drakare, 2000; Pace & Prairie, 2005; Sobek, Tranvik, & Cole, 2005). On a global scale, the release of CO<sub>2</sub> from inland waters is a substantial portion of the combined terrestrial and oceanic carbon sinks, despite the fact that inland waters comprise less than 4% of global land surface area (Biddanda, 2017; Tranvik et al., 2009). However, estimates of fluxes from terrestrial ecosystems to inland waters, as well as from inland waters to the atmosphere, remain highly uncertain and are in need of further study (Biddanda, 2017; Drake et al., 2017).

The metabolic balance, or ratio between GPP and ER, is an important determinant of whether a given waterbody will be a source or a sink of CO<sub>2</sub> to the atmosphere, and so is of consequence for the global carbon cycle (Yvon-Durocher, Jones, Trimmer, Woodward, & Montoya, 2010). The rates of GPP and ER are both temperature-dependent because they are ultimately biochemical processes controlled by fundamental rules of chemistry and physics (Bosatta & Ågren, 1999). Metabolic theory suggests these rates depend on activation energies determined by certain rate limiting steps (Bosatta & Ågren, 1999; Gillooly, Brown, West, Savage, & Charnov, 2001). Higher activation energies imply a greater temperature dependence. Ultimately, the response to temperature is described by the Boltzmann factor  $e^{-E/kT}$ , where  $T$  is the absolute temperature in Kelvin (K),  $E$  is the activation energy for the process of interest (in eV), and  $k$  is Boltzmann's constant ( $8.62 \times 10^{-5}$  eV/K) (Gillooly et al., 2001). Metabolic theory predicts that the activation energy of ER ( $E_r = 0.65$  eV) exceeds that of GPP ( $E_p = 0.32$  eV), reflecting the higher activation energy of ATP synthesis during cellular respiration than for Rubisco carboxylation during photosynthesis, respectively (Allen, Gillooly, & Brown, 2005; Brown, Gillooly, Allen, Savage, & West, 2004). In many cases, ER is actually constrained by GPP over the long-term because GPP supplies the substrate for ER (Yvon-Durocher et al., 2012). However, aquatic ecosystems receive organic carbon fixed in the terrestrial landscape, so that ER is not necessarily constrained by GPP in these systems (Cole & Caraco, 2001). Thus, as temperatures increase, ER may increase relative to GPP, potentially altering the metabolic balance of aquatic systems and their contributions to the global carbon cycle (Yvon-Durocher et al., 2010).

Complicating this scenario, theory also predicts that  $E_r$  will vary according to the quality of the dissolved organic matter (DOM) substrate available as a carbon source (Bosatta & Ågren, 1999). Simple carbon containing compounds, such as carbohydrates and amino acids, are readily utilised and broken down by organisms (McDonald,

Bishop, Prenzler, & Robards, 2004). In aquatic ecosystems, these compounds are generally autochthonous, meaning they are derived from in situ production by organisms such as phytoplankton. Such labile compounds require relatively less energy to utilise and therefore have a relatively low theoretical  $E_r$  (Bosatta & Ågren, 1999; Jankowski, Schindler, & Lisi, 2014; Ylla, Romani, & Sabater, 2012). Aquatic organic compounds originating from the surrounding catchment, typically from soils and wetlands, are referred to as allochthonous. These materials commonly consist of degraded plant compounds and are generally highly complex (McDonald et al., 2004). Such compounds are frequently high molecular weight materials with a high degree of aromaticity (Helms et al., 2008; Weishaar et al., 2003). These more refractory allochthonous compounds require greater energy input for organisms to break down and utilise and therefore have a relatively high theoretical  $E_r$  (Bosatta & Ågren, 1999; Jankowski et al., 2014; Ylla et al., 2012). In reality, the DOM pool of a lake is a mixture of thousands of different compounds along a gradient from highly labile autochthonous to highly recalcitrant allochthonous carbon (Kellerman, Kothawala, Dittmar, & Tranvik, 2015). However, the DOM pool of a given lake can be characterised by the average quality of the DOM pool. Theory suggests that predicting the metabolic balance of a given lake in response to temperature should require an understanding of the  $E_r$  for the lake given the overall quality of its DOM pool (Bosatta & Ågren, 1999; Yvon-Durocher et al., 2010).

Predicting the metabolic balance of lakes is of considerable interest in light of a predicted increase of up to 4°C in global surface temperatures over the next 80 years (IPCC, 2014). These increased temperatures are expected to increase water temperatures. Recent studies point out that lake temperatures have been increasing over the past several decades (O'Reilly, Sharma, Gray, Hampton, & Read, 2015; Schneider & Hook, 2010; Winslow, Read, Hansen, & Hanson, 2015). Thus, current temperature trends suggest that the metabolic balance of many lakes may already be undergoing changes important to the global carbon cycle. Additionally, inputs of allochthonous organic carbon are increasing in many inland waterbodies due to factors such as recovery from acidification (Monteith et al., 2007), climate change and increasing precipitation (Larsen, Andersen, & Hessen, 2011; Williamson et al., 2015), and land use change (Kritzbeg, 2017). Thus, interactive changes in both temperature and organic carbon concentration and quality may interactively alter the metabolic balance of inland waterbodies (Yvon-Durocher et al., 2010). These increases in temperature and allochthonous organic carbon loading could result in increased release of CO<sub>2</sub>, and thus a positive feedback further stimulating increases in atmospheric CO<sub>2</sub> (Demars et al., 2011). However, the potential for a positive feedback integrates many factors that are difficult to predict in concert.

Despite its importance, it remains unclear how carbon quality will affect the temperature dependence of ER. Many studies have examined the effect of carbon quality on ER in soil systems, with varied results (reviewed in Davidson & Janssens, 2006). Currently, there remains no clear consensus of how carbon quality impacts the temperature dependence of soil respiration (Conant et al., 2011). The

reasons for this include environmental factors that affect substrate availability to enzymes, processes which may in themselves be temperature-sensitive and obscure the inherent temperature sensitivity that is related to molecular structure; modelling approaches that may ignore heterogeneity of the soil organic-C pool that obscures the true activation energy; and experimental durations that are far shorter than the turn-over time of the most refractory portion of the soil organic-C pool (Davidson & Janssens, 2006).

In contrast to soil systems, studies on temperature dependence of ER in aquatic systems are relatively few. Several observational and experimental studies have generally supported the predictions of metabolic theory that  $E_r$  should exceed  $E_p$  in aquatic systems (Demars et al., 2011; Yvon-Durocher et al., 2010, 2012), although Demars et al. (2016) found that  $E_r$  and  $E_p$  were statistically indistinguishable in streams and rivers. Results for the relatively few studies that have examined the impacts of DOM quality on the temperature dependence of ER are inconclusive. In a laboratory setting, Ylla et al. (2012) found that stream biofilms fed a humic carbon source showed an increase in ER only at elevated temperatures, in contrast to a more labile carbon source, showing that temperature had a greater effect on ER for humic carbon sources than labile sources. However, these carbon sources were highly simplified representations of naturally occurring aquatic DOM pools. In contrast, in three Danish streams, no relationship was found between organic matter composition and activation energies (Sand-Jensen, Pedersen, & Søndergaard, 2007). Similarly, Gudas, Sobek, Bastviken, Koehler, and Tranvik (2015) found temperature sensitivities were similar in sediments from an oligotrophic humic (refractory) and a eutrophic (labile) lake. However, Jankowski et al. (2014) found that activation energies in water from 11 streams were highly variable and correlated well with indicators of carbon quality. Although the findings in this study support theoretical predictions, indicators of quality were also highly correlated with DOC concentration. This is common in natural systems where it can be difficult to separate the effects of DOM concentration and quality, because systems dominated by highly refractory DOM also tend to have higher DOM concentrations (Bodmer, Heinz, Pusch, Singer, & Premke, 2016; Rose, Williamson, Kissman, & Saros, 2015).

Here, we experimentally tested whether the temperature dependence of aquatic ER was different when using a more labile autochthonous DOM source than when using a more refractory allochthonous DOM source. We used water from natural sources to capture a realistic mixture of DOM compounds, but diluted the more concentrated allochthonous DOM source to look at the effects of DOM quality independent of DOM concentration. In addition, in contrast to prior studies that measured ER using incubations of water samples in airtight containers, we used continuous, high frequency in situ measurements of DO to calculate daily values of ER. We hypothesised that water from a labile autochthonous DOM source would have a lower temperature dependence of ER than water from a recalcitrant allochthonous DOM source, in accordance with theoretical predictions.

## 2 | METHODS

### 2.1 | Sample collection

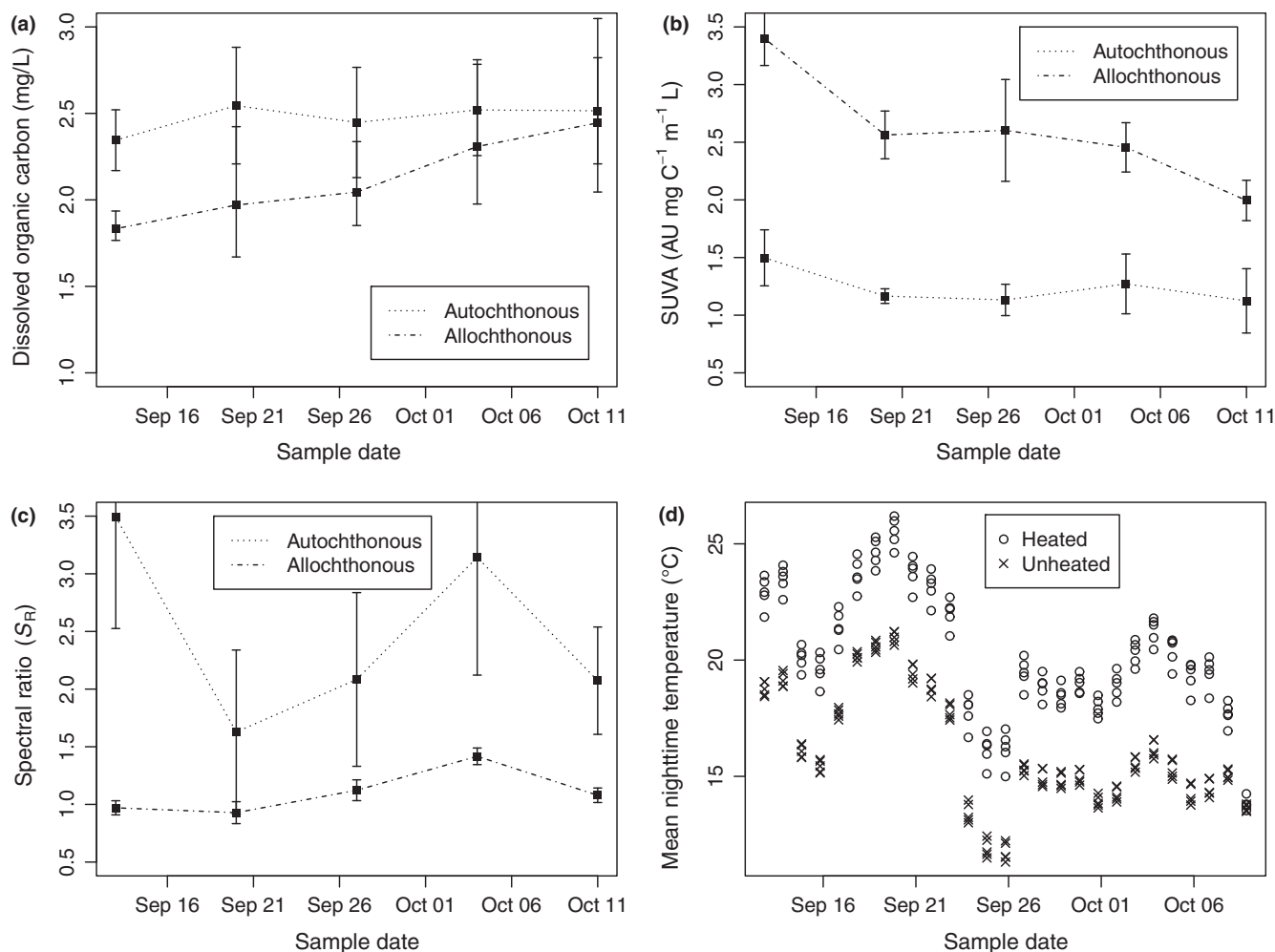
We collected water samples from two locations: one from the deep chlorophyll maximum (DCM, located at a depth of 19 m) of oligotrophic Lake George, NY (43.557854, -73.621418) and another from a nearby wetland bog. These two sources represent extremes in DOM quality. Water from the DCM represented our labile, autochthonous DOM source; the DCM contained the highest concentration of phytoplankton in the water column (based on chlorophyll profiles; data not shown), which likely enriched the DOM pool in this location with labile autochthonous organic carbon. The bog represented our refractory allochthonous DOM source. Our previous samples from this bog indicated it had very high DOC concentrations (approximately 50 mg/L) and was highly chromophoric.

After collection, water from both sources was stored in coolers before the experiment (overnight) and filtered through a 63  $\mu\text{m}$  mesh to strain out debris and remove most zooplankton before putting the source water into mesocosms. This mesh size was selected as it balanced our goal of retaining the phytoplankton community in our experiments, but removing as much of the grazing community as possible to focus on microbial community respiration, which typically dominates total ER in natural systems (del Giorgio & Williams, 2005).

### 2.2 | Experimental set-up

Our experiments contained a two by two factorial design with three replicates, for a total of twelve mesocosms. Treatments included heated versus unheated and autochthonous versus allochthonous treatments. Heated replicates were fitted with an in situ aquarium heater that raised temperatures in the relevant containers 3–5°C above ambient temperature (unheated replicates; Figure 1). Heated treatments were used to characterise the response of ER to DOM source over a broader range in temperature than would have been provided by unheated treatments alone. Our results showed that the DOC concentrations of two autochthonous replicates (one heated and one unheated) increased dramatically after our initial sampling, indicating a likely contamination. Evidence of possible contamination stemmed from the fact that we measured DOC concentrations in these mesocosms of 14.9 and 72.4 mg/L, representing a difference relative to other mesocosms of over 17 and 48 standard deviations, respectively. These mesocosms were adjacent to each other and large visible strands of bacteria were observed suspended in the water. Despite the extremely high DOC concentrations, we observed no greening of the water that would be expected if the high DOC was autochthonously produced. Thus, because of the likely contamination, we dropped these replicates from the experiment.

Each mesocosm contained 17 L of water. For the autochthonous DOM treatments, all water in each mesocosm was derived from the DCM and included all planktonic organisms present in the source



**FIGURE 1** Dissolved organic carbon (DOC) quantity and quality and mean nighttime temperature through the course of the experiment (a) DOC concentration (b) specific UV absorbance (commonly referred to as SUVA) (c) spectral ratio ( $S_R$ ) (d) mean nighttime temperature. Error bars are 95% confidence intervals

water with the exception of large zooplankton (see “Sample collection” above). For the allochthonous DOM treatments, the bog water was diluted to make the DOC concentrations approximately equal between the two DOM source treatments. To do this, we aliquotted 0.533 L of bog water into 16.467 L of DI water. As with the DCM water, this treatment contained all planktonic organisms present in the bog source water with the exception of large zooplankton. We next transferred 250 ml of water between pairs of autochthonous and allochthonous replicates. The purpose of the 250 ml transfer was to ensure that all replicates were seeded with the same microbial organisms at the start of the experiment.

We placed a Precision Measurement Engineering miniDOT sensor (<https://www.pme.com/products/minidot>) into each mesocosm. We programmed the miniDOTs to measure water temperature and dissolved oxygen concentration at a 10-min interval. We then covered all mesocosms with two layers of an optically neutral density filter (window screen) to reduce the incident light level. We did this because the incident light in our experimental treatments would have otherwise been substantially higher than the microbial

organisms would have experienced in their respective natural ecosystems. Based on laboratory optical scans, we estimate that the screen reduced incident light to 32.5% of full intensity.

We ran the experiment from 8 September to 10 October 2016. This length of time was selected to yield a duration that maximised the number of daily ER measurements, yet ensured that DOM quality remained distinct in the two DOM treatments and did not converge while running the experiment. Mesocosms were maintained outdoors on an unshaded lawn adjacent to Lake George, NY, USA. During the course of the experiment, we took 50 ml samples periodically from each container to analyse for DOC concentration and DOM quality metrics (Table 1). Water samples were collected in opaque, acid washed bottles and stored at 4°C upon arrival at the laboratory. At these sampling points, water levels in the mesocosms were monitored for evaporation. If the water level was observed to have dropped in a container, it was replenished with DI water. Water levels were replenished at least one time in seven mesocosms and at most on three occasions (one mesocosm). Added DI volume ranged from 500 ml to 2 L total per mesocosm. In general, the

heated mesocosms needed added DI water, while the unheated mesocosms did not.

### 2.3 | DOM analysis

We measured DOC concentrations using an OI Analytical (College Station, TX) 1010 TOC analyser after filtration through 0.7- $\mu\text{m}$  glass fibre filters. Samples were analysed with the inclusion of a 4-point calibration curve spanning a range of concentrations from 1 to 20 mg/L. All samples were analysed within 48 hr of collection.

We characterised DOM quality using the spectral ratio ( $S_R$ ) and specific UV absorbance (SUVA). The  $S_R$  has been found to be inversely related to the average molecular weight of the DOM pool (Helms et al., 2008), and SUVA is highly correlated with the degree of aromaticity of the DOM pool, an indicator of terrestrial organic matter (Weishaar et al., 2003). To estimate  $S_R$  and SUVA, we first filtered water samples through 0.7- $\mu\text{m}$  glass fibre filters. We then measured dissolved absorbance using a Shimadzu (Kyoto, Japan) UV-2600 spectrophotometer fitted with a 1 cm cuvette over the wavelength range 200–800 nm. A DI blank was run concurrent with samples and was subtracted from the sample values. Prior to calculating absorption metrics, we subtracted the mean value over the wavelength range 700–800 nm.

We calculated SUVA according to the methods of Weishaar et al. (2003). We used raw absorbance measured by the instrument at 254 nm ( $A_{254}$ ) and converted this to a 1 m path length. This value was then divided by DOC concentration of the given sample. SUVA is reported in units of  $\text{AU mg C}^{-1} \text{m}^{-1} \text{L}$ .

To calculate  $S_R$ , we first converted absorbance values to Napierian absorption coefficients using the equation:

$$a = 2.303 A/l \quad (1)$$

Here,  $a$  is the Napierian absorption coefficient ( $\text{m}^{-1}$ ),  $A$  is raw absorbance measured by the instrument, and  $l$  is the path length (m) (Green & Blough, 1994).

**TABLE 1** Water samples were collected from mesocosms on six occasions and analysed for dissolved organic carbon (DOC), specific UV absorbance (SUVA) and the spectral ratio ( $S_R$ ). Values are means within each dissolved organic matter quality type. Two samples were dropped from the deep chlorophyll maximum (DCM) treatment because DOC concentration rapidly increased almost immediately in these samples and are not included in the means

Collection date	Mean DOC (mg/L)		Mean SUVA		Mean $S_R$	
	DCM	Bog	DCM	Bog	DCM	Bog
8/9/2016 (set-up)	1.93	1.55	NA	NA	NA	NA
13/9/2016	2.35	1.83	1.50	3.40	3.49	0.97
20/9/2016	2.55	1.97	1.17	2.56	1.62	0.93
27/9/2016	2.45	2.05	1.13	2.60	2.08	1.12
4/10/2016	2.52	2.31	1.27	2.46	3.14	1.42
11/10/2016 (take down)	2.52	2.45	1.11	1.99	2.07	1.08

To calculate spectral slopes, an exponential decay function of the form:

$$a_\lambda = a_{\lambda_{\text{ref}}} e^{-S(\lambda - \lambda_{\text{ref}})} \quad (2)$$

was fit to the absorbance scans.  $a$  is again the Napierian absorption coefficient,  $\lambda$  represents the wavelength,  $\lambda_{\text{ref}}$  the reference wavelength, and  $S$  is the spectral slope ( $\text{nm}^{-1}$ ) (Helms et al., 2008; Twardowski, Boss, Sullivan, & Donaghay, 2004). We then fit the data to Equation 2 using nonlinear regression starting with coefficients obtained by linear regression done on log-transformed values of  $a$ . Slopes were calculated over the wavelengths from 275 to 295 nm ( $S_{275-295}$ ) and 350 to 400 nm ( $S_{350-400}$ ). We then calculated the dimensionless spectral ratio by dividing  $S_{275-295}$  by  $S_{350-400}$  (Helms et al., 2008). We used R version 3.3.2 (R Core Team, 2016) for all statistical analysis.

### 2.4 | Calculation of respiration rates

We estimated daily values for GPP and ER using the metab function of the LakeMetabolizer package (Winslow et al., 2016) in R (R Core Team, 2016). We used the bookkeeping model, where mean ER rates are computed during the night (i.e., dark hours) and then extrapolated across daylight hours to get daily respiration rates (Cole, Pace, Carpenter, & Kitchell, 2000). In addition to water temperature and DO concentration, the models involved in calculating metabolism estimates require inputs of wind speed and photosynthetically active radiation (PAR). Wind speed was recorded at a gauge located a height of about 1 m above the surface of the mesocosms within 100 m of the experiment. Solar radiation in  $\text{W/m}^2$  was recorded using a pyranometer attached to a buoy in the lake, about 3,000 m from our mesocosms. Solar radiation was converted to PAR ( $\mu\text{mol m}^{-2} \text{s}^{-1}$ ) using the sw.to.par function of the LakeMetabolizer package prior to analysis (Britton & Dodd, 1976; Winslow et al., 2016). For each mesocosm, we dropped the first 4 days of computed R values from our analysis to allow a few days for microbial communities to equilibrate. The final time span of continual ER measurements remaining for statistical analysis was 27 days.

To estimate gas flux, we used the k.cole method to feed the bookkeeping model because it is the most commonly used in lake metabolic studies (Cole & Caraco, 1998). This method of estimating gas flux is based on an empirical study that characterises gas flux primarily as a function of wind speed. However, in our small mesocosms, it is likely that convective mixing played a large role in gas flux. In order to assess how sensitive our results were to a specific gas flux parameterisation, we also calculated our results using three other gas flux models that incorporate the influence of convective mixing; k.macintyre, k.read and k.heiskanen (Heiskanen et al., 2014; MacIntyre et al., 2010; Read et al., 2012). The k.read approach also accounts for lake area under the reasoning that as lake size decreases, the role of convective mixing in gas flux increases while the influence of wind speed decreases.

## 2.5 | Statistical analysis

We analysed the response of respiration to temperature using linear mixed-effects models in the lme4 package (Bates, Maechler, Bolker, & Walker, 2015) in R to account for autocorrelated repeated measurements of ER through time within each mesocosm. We used the natural log of ER as the response. Day of year, temperature and DOC source (autochthonous or allochthonous) were used as predictors in the model, with day of year and temperature centred on the mean values for these variables. Rather than using raw temperature values in °C, we converted temperature to  $1/kT$ , where  $k$  is Boltzmann's constant ( $8.62 \times 10^{-5}$  eV/K) and  $T$  is the absolute temperature in Kelvin (K), following the approach of others (Yvon-Durocher et al., 2010). Using this approach, the slope coefficient for the temperature fixed effect represents the temperature dependence of respiration for the reference DOM source (allochthonous in this case). Because DOM source is a two-level factor in the model, the activation energy for the autochthonous DOM source can be obtained by taking the shift from the reference (allochthonous) DOM source obtained from the coefficient of the temperature  $\times$  DOM interaction term (Bates et al., 2015). Because the book-keeping model extrapolates mean nighttime respiration rates across daytime hours, we used mean nighttime temperature to predict the corresponding daily ER value. We included a random intercept and slope by day of year grouped by mesocosm in the model. We primarily chose this random effects structure to account for the repeated-measures design of the experiment. However, we also used restricted maximum likelihood (REML; Zuur, Ieno, Walker, Saveliev, & Smith, 2009) to verify this model was parsimonious using  $AIC_c$ . We tested for the significance ( $p < 0.05$ ) of fixed effects using likelihood ratio tests (LRT) on full and nested models fit using maximum likelihood. We used  $AIC_c$  on models fit using maximum likelihood to select the final fixed effects structure. Once the final model was selected, parameters for this model were estimated using REML (Zuur et al., 2009).

To plot the fixed effects for temperature and the DOM source by temperature interaction (i.e., the temperature dependence of allochthonous and autochthonous DOM sources, respectively), we used the visreg package in R (Breheny & Burchett, 2017). This package uses the predict method of the model object to plot the fixed effects for the parameter specified, as well as the partial residuals. Partial residuals are meant to represent the effect of the independent variable of interest on the dependent variable after correcting for the effect of other independent variables in the model (Larsen & McCleary, 1972). The fixed effects and partial residuals are given for fixed values of the other explanatory variables and in this case, give predictions at the mean value of other (i.e., day of year) predictors, as these were centred.

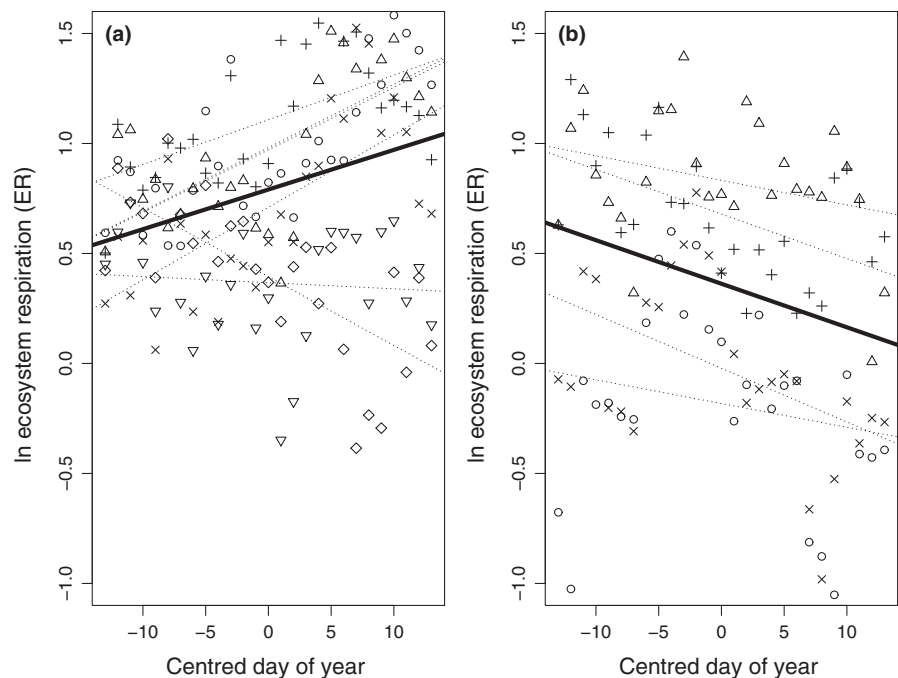
We tested for correlation between GPP and ER estimates using the Pearson product-moment correlation coefficient ( $r$ ) (Quinn & Keough, 2002). We tested for correlation across all pooled estimates of ER and GPP for autochthonous mesocosms, and then all pooled estimates of ER and GPP for allochthonous mesocosms.

## 3 | RESULTS

Our analyses indicated that the DOM quality of the autochthonous and allochthonous treatments was quite different. SUVA values were consistently higher for the allochthonous treatment replicates throughout the course of the experiment, although they declined through time (Table 1; Figure 1), indicating that aromaticity was generally higher in the allochthonous treatments, but became progressively less aromatic and less refractory over time. SUVA values were significantly lower at the end of the experiment for allochthonous treatments ( $t(5) = 6.92$ ,  $p < 0.01$ ) but not autochthonous treatments ( $t(3) = 2.00$ ,  $p = 0.14$ ). Similarly,  $S_R$  values were consistently lower in the allochthonous treatments throughout the experiment, indicating that average molecular weight was also higher in the allochthonous treatments.  $S_R$  values were significantly higher in allochthonous treatments at the end of the experiment than at the start ( $t(5) = -3.54$ ,  $p = 0.02$ ). Mean  $S_R$  values were lower at the end of the experiment for autochthonous treatments, but this difference was not significant ( $t(3) = 2.40$ ,  $p = 0.10$ ).

DOC concentrations were slightly higher in the autochthonous treatments throughout the experiment, having a mean concentration of 2.39 mg/L versus 2.02 mg/L for the allochthonous treatments. However, over the course of the experiment, DOC concentration in the allochthonous treatments steadily increased ( $t(5) = -2.93$ ,  $p = 0.03$ ) so that at the end of the experiment, concentrations were not significantly different in the allochthonous versus autochthonous samples (Figure 1). There was no significant change in DOC concentration in the autochthonous treatments ( $t(3) = -1.31$ ,  $p = 0.28$ ).

Our mixed model analysis retained all two-way interactions in the final model. This indicated that the effect of temperature and DOC source on ER both changed throughout the course of the experiment. In allochthonous samples, ER rates generally increased throughout the course of the experiment, while for autochthonous samples, respiration rates generally decreased (Figure 2). The temperature by DOC source interaction was significant by LRT ( $p = 0.02$ ). This means that the effect of temperature on ER changed depending on DOC source (i.e., the temperature dependence of respiration), supporting the carbon quality temperature hypothesis. In allochthonous samples, the effect of temperature on respiration was positive and was higher than in autochthonous samples (Table 2; Figure 3). The activation energy for allochthonous DOM obtained from the temperature coefficient was 0.21 eV, with confidence intervals ranging from 0.06 to 0.37 eV. The coefficient for autochthonous DOM indicated a slight negative effect of temperature on respiration with an activation energy of  $-0.09$  eV. However, 95% confidence intervals for this parameter were wide and included slopes ranging from  $-0.33$  to 0.15 eV (Table 2). Although the final model had the lowest  $AIC_c$ , a full model that included the three-way interaction was within 2  $AIC_c$  units of this model (Supporting Information Table S1). The three-way interaction was not significant by LRT. For purposes of parsimony and interpretability, we did not include this interaction in our final model.



**FIGURE 2** Plots of ln ecosystem respiration (ER) by day of year (centred) for (a) allochthonous and (b) autochthonous treatments. Within each panel, individual mesocosms are represented by unique plot characters. Heavy solid lines are the fixed effects for day of year for each DOM treatment from the fitted mixed-effects model. Dotted lines are fitted linear regression lines for each individual mesocosm

**TABLE 2** Coefficients of the fixed effects for the final mixed-effects model having all two-way interactions

Model variables	Coefficient	Lower 95% CI	Upper 95% CI
Temperature (1/kT)	-0.211	-0.372	-0.059
DOC (DCM)	-0.428	-0.908	0.051
Day of year	0.018	0.004	0.033
Temp × DOC (DCM)	0.304	0.056	0.542
DOC (DCM) × day of year	-0.038	-0.061	-0.015
Temp × day of year	-0.021	-0.037	-0.006
Intercept	0.791	0.487	1.095

Our analyses using other gas flux models that incorporated convective mixing had mixed results, but generally supported the results described above. Both the *k.read* and *k.heiskanen* gas flux options supported our results obtained above using the *k.cole* flux model. In both cases, the temperature by DOM source interaction was significant and the slope of the relationship was higher for the refractory treatments than for the labile treatments. However, a model using the *k.macintyre* gas flux model did not yield a significant temperature by DOM source interaction.

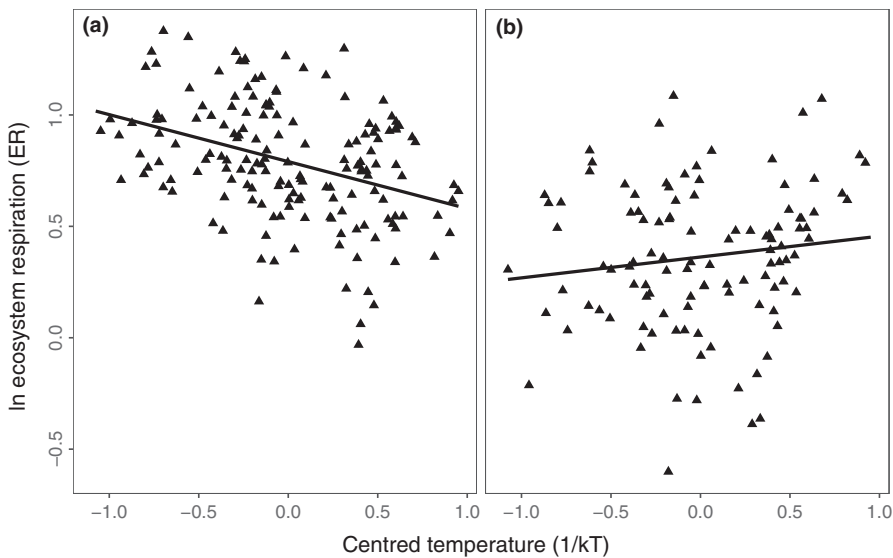
Correlation of GPP with ER in autochthonous treatments was 0.73 and for allochthonous treatments 0.89, indicating that correlation was high in both DOM treatments, but somewhat higher in the allochthonous treatments (Figure 4). We note that estimates of ER did yield some positive values in the autochthonous treatments and GPP resulted in some negative values in both treatments (Figure 4).

## 4 | DISCUSSION

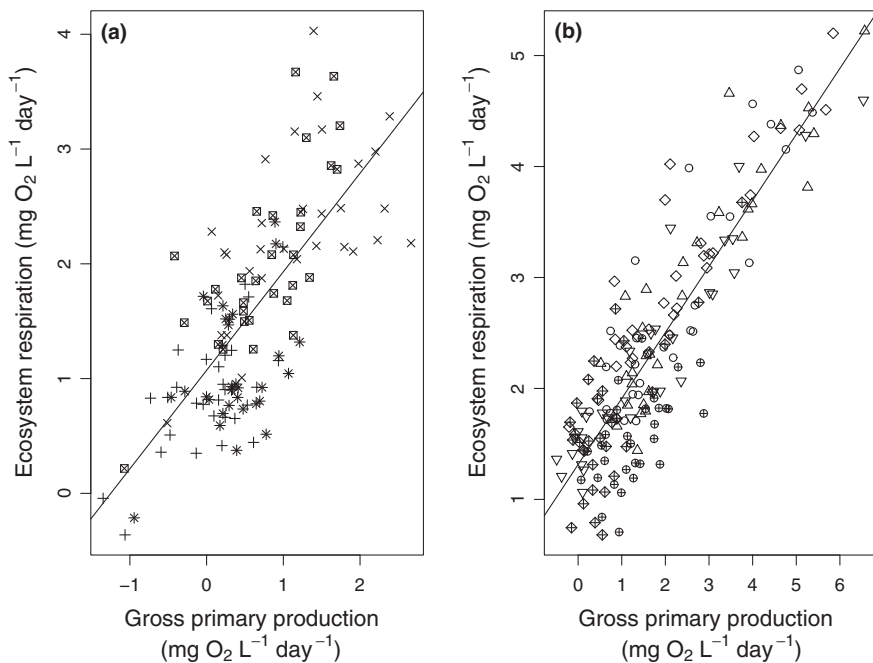
We found that over 27 days of daily respiration measurements, the effect of mean nighttime temperature on daily respiration rates was significantly different between the autochthonous and allochthonous DOM source treatments. ER increased more with temperature in the refractory DOM source treatments, suggesting that the temperature dependence of allochthonous DOM exceeded that of autochthonous DOM. This result supports our hypothesis and the predictions of theory and further implies that ER rates will in fact increase more in lakes having more refractory DOM pools as temperatures increase globally.

Our result for the activation energy of ER for our allochthonous DOM treatment was less than the theoretical value of 0.65 eV. However, it was comparable to values in the range observed in natural systems (Acuña, Wolf, Uehlinger, & Tockner, 2008), especially when considering the wide confidence intervals around point estimates. In contrast, the negative temperature dependence for autochthonous treatments we obtained seems unlikely. However, many positive values are within the confidence intervals, although they are low. In general, we believe that the experimental design of this study is better suited to a comparative analysis of the DOM treatment types than to calculating absolute values of activation energies. This is largely because, while adding ecological realism, estimates of ER made from free water dissolved oxygen measurements can be noisy.

Our results indicate that the effect of DOM source on temperature dependence of ER varied over the duration of our experiment. This result complicated our attempts to calculate absolute activation energies for the allochthonous versus autochthonous treatments and makes interpreting these absolute values difficult due to the



**FIGURE 3** Plots of  $\ln$  ecosystem respiration (ER) by temperature as  $1/kT$  (centred) for (a) allochthonous and (b) autochthonous treatments taken from the fixed effects of the linear mixed-effects model. Plotted points are the partial residuals, representing the effect of the temperature explanatory variable on  $\ln$  ER independent of the effect of the day of year explanatory variable



**FIGURE 4** Plots of ecosystem respiration (ER) by gross primary production (GPP) for (a) autochthonous and (b) allochthonous treatments. Within each panel, individual mesocosms are represented by unique plot characters. Solid lines are fitted linear regression models done on the pooled GPP and ER values within each DOM treatment

confounding effect of sample day. The observation of the changing temperature dependence over time is reflective of actual environmental variability and the ecologically realistic nature of changes in the DOM pool over time in our experiment. It is likely that in situ production of autochthonous DOM is an important factor contributing to the fact that sample day had a significant effect on ER. Our results show that estimates of ER were closely related to GPP (Figure 4), a finding that has been observed in previous field studies (Sadro, Melack, & MacIntyre, 2011; Solomon et al., 2013). Our results also show that the DOM pool of the allochthonous treatment became increasingly autochthonous in nature over time, indicated by a significant decline in SUVA and an increase in  $S_R$  (Figure 1). Furthermore, the increase in DOC concentration in the allochthonous treatment further supports the possibility that in situ production

altered the quality of the DOM pool in this treatment over time. In contrast, the autochthonous DOM pool appeared relatively unchanged over the course of the experiment. It is likely that over the course of the experiment in the allochthonous DOM treatment, the initial allochthonous DOM became depleted and was gradually replaced with more autochthonous DOM, consistent with observations that over longer time scales ER may be constrained by GPP unless it is replenished with new allochthonous inputs (Yvon-Durocher et al., 2012).

Our ecosystem metabolism estimates were initially based on the k.cole method of analysing gas flux. While commonly used in ecosystem metabolism studies, this model does not explicitly account for the effects of convective mixing. Thus, we also estimated metabolic parameters using alternate gas flux models that account for



convective mixing. It is likely that in our small containers, convective mixing played a large role as there were substantial diurnal fluctuations in temperature. Our results were the same using the *k.read* and *k.heiskanen* models but not using the *k.macintyre* model. The *k.macintyre* model is based on prior surface renewal models that account for the effects of surface turbulence due to wind and its influence on wave activity (MacIntyre et al., 2010; Zappa et al., 2007). These effects are not likely to be as relevant to our small containers as to large waterbodies. In contrast, the *k.read* model incorporates waterbody surface area, reducing the influence of wind and increasing the influence of convective mixing as surface area decreases (Read et al., 2012). Based on this, we believe the agreement between the *k.cole* analysis and the *k.read* analysis supports the results of our analysis. However, we do acknowledge some degree of uncertainty in our results if gas exchange differed substantially from the models used here.

Our results indicated that there was no detectable effect of temperature on ER in the autochthonous treatment (Figure 3). Based on the fact that biochemical processes are inherently temperature-sensitive (Davidson & Janssens, 2006), it is likely that rather than no effect, the small temperature dependence of autochthonous organic matter was not detectable in our experiment. Previous work indicates that highly labile organic carbon, such as autochthonous DOM, is rapidly respired regardless of temperature (Ylla et al., 2012). The autochthonous water was obtained from 19 m deep, which was 12°C. While mesocosms experienced a large range in temperature (daily mean range 9.68–26.60°C), we do not think that it negatively impacted our overall results. First, it is unlikely that any influence of the difference in temperature between the deep water sample site and the experiment would persist for multiple weeks because microbial communities can respond to temperature perturbations over the timescale of days (Shade et al., 2011). Second, the mean ER of the heated autochthonous replicates exceeded that of the unheated autochthonous treatments, indicating that the microbial community responded positively to warming within the range of the autochthonous treatment. If the increase in temperature between the environment and the experiment harmed the autochthonous treatment microbial community, we would have expected a greater impact and thus lower ER in the heated autochthonous treatment. Rather, the variability in daily estimates of ecosystem metabolism from free water dissolved oxygen sensors likely contributes a great deal to our uncertainty (Rose et al., 2014). While *in situ* measurements of dissolved oxygen are ecologically realistic compared to bottle incubations, diel curves in dissolved oxygen often are not perfectly sinusoidal and thus estimates of metabolic parameters often contain some uncertainty (Winslow et al., 2016). In addition, it is known that the bookkeeping model we used can produce positive ER results and negative GPP results, which we did observe (Winslow et al., 2016). We chose to leave these values as is rather than alter these data points. While our use of free water dissolved oxygen sensors may have introduced uncertainty into our results, the experimental design permitted a more ecologically realistic setting and our key

finding that our allochthonous treatment exhibited a stronger temperature dependence than the autochthonous treatment holds.

Ecosystem respiration also tended to be somewhat lower on average in the autochthonous treatments than in allochthonous treatments, while GPP was substantially lower in these treatments (Figures 2 and 4). Much of this is likely explained by the previously noted tendency of ER to increase in the allochthonous treatments yet decrease in the autochthonous treatments during the course of the experiment. However, there are other possible explanations for this observation. For example, the autochthonous samples were taken from the pelagic zone in Lake George. Several studies suggest that ER is lower in the pelagic regions of lakes than in littoral areas (Lauster, Hanson, & Kratz, 2006; Sadro et al., 2011; Van de Bogert, Carpenter, Cole, & Pace, 2007) and is partially related to bacterial abundance (Sadro et al., 2011). We have also observed low ER rates in the pelagic region of Lake George (Jane & Rose, unpublished data). Although these differences are usually attributed to the benthic contribution to littoral ER, if other factors that differ in pelagic and littoral habitats affect ER, such as bacterial abundance, this could result in different baseline ER rates in the two treatments. Another possible explanation for the lower ER is that the community taken from the DCM was not adapted to the higher light levels associated with the experimental set-up. However, as noted previously, bacterial communities are able to rapidly respond to changing environmental conditions, and the light levels were cut to about one-third of surface. Finally, if DOM-associated nutrients in the allochthonous treatment were released during decomposition, they may have elevated ER rates as the experiment progressed (Kissman, Williamson, Rose, & Saros, 2017). This could potentially help to explain increasing ER rates through time in these treatments (Figure 2). Regardless of the explanation, the lower ER rates in the autochthonous treatments may partially explain the large uncertainty around estimates of temperature dependence for these treatments (Figure 3) if the result is a low signal-to-noise ratio.

There have been a number of experimental and observational studies in both terrestrial and aquatic ecosystems that have examined how variation in the source and quality of organic matter influences ER rates. The majority of incubation studies on the temperature dependence of ER in soils indicate that decomposition of recalcitrant carbon responds more to temperature than that of more labile carbon (Conant et al., 2011). In contrast, there have been relatively few incubation studies conducted in aquatic systems that examine DOM source or quality influences on temperature dependence, and these studies present conflicting results. Our experiment, which demonstrated that allochthonous carbon sources exhibited a stronger temperature dependence than autochthonous organic carbon is unique in that it measured daily respiration continuously for an extended period, under ecologically realistic conditions, where atmospheric gas exchange could occur and under natural solar radiation.

There are a number of possible reasons the handful of studies in aquatic systems have yielded different results. These studies have been conducted over different time frames, have used varied

methods to quantify carbon quality and have also used multiple methods to measure temperature sensitivity. Ylla et al. (2012), for example, quantified temperature sensitivity using two methods, a Winkler bottle incubation measurement as well as via the activity of enzymes involved in the breakdown of recalcitrant materials. In their experiment, both community respiration and phenol oxidase activity were enhanced at elevated temperatures in recalcitrant treatments only. However, these treatments were extreme examples of labile and recalcitrant DOM. The labile treatment consisted of a disaccharide and a dipeptide, while the recalcitrant treatment consisted of humic compounds isolated from river water. Under natural conditions, the DOM pool is a heterogeneous mixture rather than purely labile or recalcitrant. Gudas et al. (2015) conducted their study on sediment cores. In sediments, the observed activation energy may be affected by resource supply limitation due to diffusion through sediments or across the diffusive boundary layer (Gudas et al., 2015; Jørgensen & Des Marais, 1990) as well as by anoxia within the sediment (Bastviken, Olsson, & Tranvik, 2003; Sobek et al., 2009). In addition, this study measured the temperature dependence of carbon mineralisation, using the rate of dissolved inorganic carbon generation to quantify carbon mineralisation. Sand-Jensen et al. (2007) quantified DOM quality using the ratio of oxygen consumption to TOC. Potentially, this may be a less robust method of quantifying DOM quality than other methods such as C:N ratio (used by Gudas et al., 2015; Jankowski et al., 2014) or specific UV absorbance (used by Ylla et al., 2012 and our study) because factors unrelated to DOM quality can impact respiration rates, including DOM concentration (Hanson, Bade, Carpenter, & Kratz, 2003), bacterial abundance (Sadro et al., 2011) and water temperature (Yvon-Durocher et al., 2010). Additionally, Sand-Jensen et al. (2007) limited their observations to three streams as opposed to the 11 streams studied by Jankowski et al. (2014). The majority of these studies have used dark bottle incubations to measure respiration and to our knowledge, none have used in situ high frequency sensor measurements, as in our current study. It is possible that such incubations in dark containers may limit the supply of carbon to autotrophs and thus may underestimate autotrophic respiration (Acuña et al., 2008).

While conflicting with some previous studies in aquatic ecosystems, our results support the results of the majority of incubation studies and the predictions of theory more generally. Although most incubation studies conducted in soils have arrived at results consistent with theory, there remains disagreement over how to interpret results of studies testing carbon quality effects on temperature dependence of respiration. Much of the ambiguity regarding DOM quality and temperature dependence comes from the fact that experiments may be measuring an apparent temperature sensitivity rather than the intrinsic temperature sensitivity associated with the molecular structure of the DOM compounds (Davidson & Janssens, 2006). There are a variety of potential confounding influences that can make the measured, or apparent, activation energy different from that associated with molecular structure of the DOM source (the intrinsic activation energy). In soils, organic matter may be contained in soil aggregates (Oades, 1988), where

enzymes required for degradation are physically excluded (Sollins, Homann, & Caldwell, 1996), or may be chemically adsorbed onto mineral particles (Oades, 1988). In either case, substrate concentrations at enzymatic reaction sites are decreased, obscuring the intrinsic temperature sensitivity (Davidson & Janssens, 2006; Davidson, Janssens, & Lou, 2006). These and other confounding effects have produced conflicting results in gradient studies and cross-site comparisons conducted in soil systems (Davidson & Janssens, 2006). It is unclear how much these processes apply in aquatic systems, although it is likely that they are relevant to aquatic sediment studies. However, Acuña et al. (2008) found that variations in activation energies from a Swiss river network were partially explained by biofilm thickness, water temperatures in the period immediately preceding sampling and chlorophyll *a* concentrations. Confounding effects may also occur in longer duration studies due to depletion of more labile DOM if primary production is constrained and as incubations progress, leading to increased activation energies (Craine, Fierer, & McLauchlan, 2010). Microbes and phytoplankton may also respond to heating through altered community composition, individual physiological response or via local adaptation to higher temperatures over time (Bradford et al., 2008; Padfield et al., 2017; Schaum et al., 2017; Yvon-Durocher, Schaum, & Trimmer, 2017), altering metabolic responses to temperature and thus observed activation energies. It is impossible for us to rule out entirely that some of these processes may have obscured the intrinsic temperature sensitivities of our DOM treatments.

Nevertheless, our current study is valuable for its use of two widely divergent DOM quality sources that are ecologically realistic, naturally derived, heterogeneous DOM pools. In addition, the experiment reduced potential confounding effects of DOM concentration, as would be found measuring directly within source waterbodies where DOM concentration and quality often covary.

Many lakes are warming globally (O'Reilly et al., 2015; Schneider & Hook, 2010), and in some regions, many lakes are experiencing increasing inputs of allochthonous DOM (SanClements, Oelsner, McKnight, Stoddard, & Nelson, 2012). Our results show that these two regional to global scale processes may be interacting with one another and may be driving widespread changes in the role of inland waters in the global carbon cycle. Because ER increases with temperature and with DOC concentrations, and because allochthonous DOM exhibits a greater temperature dependence, it indicates that many inland waterbodies may be becoming more heterotrophic and thus releasing more CO<sub>2</sub> to the atmosphere over time. However, other feedbacks between warming and DOM may be occurring which may be driving other changes in overall carbon efflux. For example, increases in allochthonous DOM reduce water clarity (Read & Rose, 2013), and water clarity losses can lead to volumetric cooling (Rose, Winslow, Read, & Hansen, 2016). Warming may also alter the flux of DOM through aquatic systems by changing vegetation in the surrounding catchment (Larsen et al., 2011) as well as by altering rates of carbon burial (Gudas et al., 2010). Thus, whether increases in temperature and allochthonous DOM loading will produce greater net heterotrophy depends on the many feedbacks

between these important regional to global scale environmental changes.

## ACKNOWLEDGMENTS

We thank Jeremy Farrell, Charlotte Caldwell, Larry Eichler, Alex Pezuoli, Dave Diehl, Ken Johnston and Sandra Nierzwicki-Bauer at the Darrin Fresh Water Institute for logistical support during the experiment. We thank Dave Winkler and Mark Swinton for assistance with analysing DOC concentrations, Luke Winslow for answering many questions related to respiration calculations and the LakeMetabolizer package, and Taylor Leach for help with statistical analyses. Solar radiation and wind speed data were provided by instrumentation funded through the Jefferson Project at Lake George, which is a collaboration of Rensselaer Polytechnic Institute, IBM, and The FUND for Lake George. Data for this project are maintained in a publicly available repository and can be accessed at: <https://doi.org/10.6073/pasta/ceb96ac6858f54850c2fa474be5ecb09>. This research was supported by US National Science Foundation funding to KCR, Biology directorate grant numbers EF 1638704 and DEB 1754265.

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## SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

**How to cite this article:** Jane SF, Rose KC. Carbon quality regulates the temperature dependence of aquatic ecosystem respiration. *Freshwater Biol.* 2018;63:1407–1419. <https://doi.org/10.1111/fwb.13168>