Large CO₂ effluxes at night and during synoptic weather events significantly contribute to CO₂ emissions from a reservoir

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Abstract

CO₂ emissions from inland waters are commonly determined by indirect methods that are based on the product of a gas transfer coefficient and the concentration gradient at the air water interface (e.g., wind-based gas transfer models). The measurements of concentration gradient are typically collected during the day in fair weather throughout the course of a year. Direct measurements of eddy covariance CO₂ fluxes from a large inland water body (Ross Barnett reservoir, Mississippi, USA) show that CO₂ effluxes at night are approximately 70% greater than those during the day. At longer time scales, frequent synoptic weather events associated with extratropical cyclones induce CO₂ flux pulses, resulting in further increase in annual CO₂ effluxes by 16%. Therefore, CO₂ emission rates from this reservoir, if these diel and synoptic processes are under-sampled, are likely to be underestimated by approximately 40%. Our results also indicate that the CO₂ emission rates from global inland waters reported in the literature, when based on indirect methods, are likely underestimated. Field samplings and indirect modeling frameworks that estimate CO₂ emissions should account for both daytime–nighttime efflux difference and enhanced emissions during synoptic weather events. The analysis here can guide carbon emission sampling to improve regional carbon estimates.

1. Introduction

The significance of inland waters to regional and global carbon cycles is rarely disputed (Cole et al. 2007, Battin et al. 2009, Raymond et al. 2013). The total CO₂ and CH₄ emissions from inland waters are estimated at 2.1 Pg C yr⁻¹ and 0.65 Pg C yr⁻¹, respectively (Cole et al. 2007, Bastviken et al. 2011, Raymond et al. 2013). CO₂ emissions from inland waters are a consequence of the super-saturation of CO₂ in the surface water, as quantified by CO₂ concentration in the surface water (hereafter pCO₂) (Cole et al. 1994, Sobek et al. 2005). Such super-saturation is primarily due to respiration of allochthonous organic carbon and transport to aquatic systems of dissolved CO₂ by surface runoff and ground water flows (Kling et al. 1991, Cole et al. 2007). CO₂ emission rates are conventionally estimated by indirect methods (e.g., wind-based gas transfer models and the surface renewal model) that rely on pCO₂ and a gas transfer coefficient (hereafter indirect methods) (Cole et al. 1994, 2010).

Therefore, one major focus has been on ways that biotic and abiotic processes affect pCO₂ and thus CO₂ emissions. Recent studies found that lake CO₂ fluxes, directly measured by eddy covariance, can be weakly or entirely uncorrelated with water pCO₂ at short time scales (Aberg et al. 2010), suggesting that physical processes within the water column mediate CO₂ emissions. Another major focus has been on reducing the uncertainty in quantifying the gas transfer coefficient (e.g., Cole et al. 2010, MacIntyre et al. 2010, Raymond et al. 2013). Widely used models of the gas exchange coefficient are parameterized with empirical relations that depend upon mean wind speed (Cole et al. 2010).
Rates of CO₂ transfer across the water-atmosphere interface may also be governed by physical processes other than wind speed in the low to intermediate wind speed regimes (e.g., Eugster et al. 2003, McGillis et al. 2004, Zappa et al. 2004, Jeffery et al. 2007, MacIntyre et al. 2010, Rutgersson and Smedman 2010, Rutgersson et al. 2011). Since different processes co-regulate CO₂ exchange across the water-air interface, it is expected that these processes exert varying levels of controls on different time scales, leading to temporal variations in CO₂ emission rates.

Temporally discrete field samplings of pCO₂ and atmospheric CO₂ concentrations for estimating CO₂ emission rates are usually conducted during daytime when fair weather conditions predominate, and these emission rates are then temporally up-scaled to obtain annual emission rates (Cole et al. 2007, Raymond et al. 2013). This temporally discrete sampling strategy, widely used in quantifying gas transfer across the water-atmosphere interface, does not account for nighttime–daytime emission differences and emissions during periods between samplings. The time-continuous eddy covariance method and the temporally up-scaled wind-based gas transfer method result in substantial discrepancies in annual CO₂ emission estimates (Jonsson et al. 2008, Huotari et al. 2011), raising questions about the currently reported CO₂ emission rates from global inland waters (Raymond et al. 2013). Resolving this issue by identifying the sources of uncertainties and understanding underlying mechanisms is necessary for reducing uncertainties in the contribution of carbon emissions from global inland waters to regional and global carbon budgets and the response of inland waters to climate change (Cole et al. 2007, Battin et al. 2009, Tranvik et al. 2009, Raymond et al. 2013).

Here, half-hourly eddy covariance data of CO₂ fluxes and other microclimate variables over a 1-year period in 2008 over a large reservoir in Mississippi are analyzed and presented. Our objectives are to characterize variations in CO₂ fluxes across the water-atmosphere interface on diurnal and seasonal time scales, and demonstrate the significance of such diurnal variations and sub-seasonal events in CO₂ effluxes when upscaling to annual CO₂ emission estimates.

2. Site, instruments, and methods

The Ross Barnett Reservoir is located in central Mississippi (32°26’N, 90°02’W), USA, and has a surface area of about 134 km² and water depths varying from 4 to 8 m. The construction of the reservoir was completed in 1963. The main purpose of the reservoir is to provide a permanent water source to supply drinking water for the Mississippi capital city of Jackson. Water is monitored and controlled from an electrical/mechanical spillway and gate system in its southern shore by releasing water into the Pearl River. The reservoir is ice-free year round. A 5 m tower (Climatronics Corp.) was constructed over a stationary wooden platform in the south center of the reservoir, with the mean water depth around the tower of about 5 m and the distance from the tower to the shore ranging from 2 km to more than 14 km (Liu et al. 2009, 2011, 2012, Zhang and Liu 2013, 2014). An eddy covariance system at a height of 4 m above the water surface was installed to measure CO₂ fluxes. The system consisted of a three-dimensional sonic anemometer (model CSAT3, Campbell Scientific, Inc.) and an open path CO₂/H₂O infrared gas analyzer (IRGA; Model LI-7500, LI-COR, Inc.). Three-dimensional wind velocity components and sonic virtual temperature from the sonic anemometer and densities of carbon dioxide and water vapor from the IRGA were recorded by a datalogger (model CR5000, Campbell Scientific, Inc.) at a frequency of 10 Hz.

Other microclimate variables were also measured as 30 min averages with 1 s readings, including net radiation (Rn) at 1.2 m (model Q-7.1, Radiation and Energy Balance Systems, Campbell Scientific, Inc.), air temperature (T_a) and relative humidity (RH) (model HMP45C, Vaisala, Inc.) at 1.9, 3.0, 4.0, and 5.5 m, wind speeds (U) and wind direction (WD) (model 03001, RM Young, Inc.) at 5.5 m. The water skin temperature (T_s) was measured by an infrared temperature sensor (model IRR-P, Apogee, Inc.). Vapor pressure on the water surface (e_w) was calculated as the saturation vapor pressure at the infrared-determined T_s. Water temperatures at eight depths of 0.10, 0.25, 0.5, 1.0, 1.5, 2.5, 3.5, and 4.5 m below the water surface were measured at 1 min interval and then integrated into 30 min mean values by eight water temperature probes (model 107-L, Campbell Scientific, Inc.), all tied to a buoy. The 107-L sensors have Steinhardt-Hart equation errors of less than ±0.01 °C. We did an internal correction on the sensors, which had accuracy of order 0.2 °C, based on the assumption that nocturnal mixing would cause uniform temperatures near midnight. Instrument drift led to residual errors on the order of 0.1 °C. Half-hourly precipitation totals were measured using an automated tipping-bucket rain gauge (model TE525, Texas Instruments, Inc.). All instruments were powered by six deep-cycle marine batteries that were charged by two solar panels (model SP65, 65 Watt Solar Panel, Campbell Scientific, Inc.).

The post-field data processing program was developed following FLUXNET’s standard procedures and has been used in previous studies (Liu et al. 2009, 2011, 2012, Zhang and Liu 2013, 2014) (see supplementary materials: note S1). After quality control and quality assurance (QA/QC), the 30 min time-series eddy covariance CO₂ flux in 2008 is shown in supplementary figure S1.
3. Results and discussion

3.1. Diurnal variations in CO2 efflux and their influence on CO2 emissions

Monthly and annually averaged diurnal variations of CO2 fluxes showed overall larger CO2 effluxes at night than during the day, with the daily maxima in the early mornings and the minima in the late afternoons (figure 1, supplementary figure S3). The mean CO2 effluxes during the nighttime (0.39 μmol m⁻² s⁻¹) over the 1-year period of 2008 were approximately 70% larger than those during the daytime (defined as the 12 h period from 08:00 to 20:00 LT) (0.23 μmol m⁻² s⁻¹) at a 95% significance level, resulting in the annual daily mean (i.e., 24 h average) efflux of 0.31 μmol m⁻² s⁻¹. Therefore, the daytime mean efflux was 26% smaller than the daily mean efflux on an annual basis. Field samplings of aquatic pCO2 for estimating CO2 emissions are commonly conducted during the daytime when eddy covariance CO2 efflux measurements report lower values than at night. This sampling bias in timing inherent in reported fluxes from indirect methods here underestimates the annual daily mean efflux by 26%, as compared with the time-integrated eddy covariance measurements. It should be noted that this bias is strictly due to the choice of sampling times of aquatic pCO2 when estimating CO2 emission rates and is not related to any particular formulation of gas transfer or measurement uncertainty in aquatic pCO2.

A variety of biotic and abiotic controls contributed to the greater gas emissions at night than during the day. In the reservoir, the mean pH, dissolved oxygen, and oxygen saturation were 8.0, 7 mg L⁻¹, and 91%, respectively (Wersal et al. 2006). Chlorophyll-α varied from 5 to 15 μgL⁻¹ chl-α in the summer months (May, June, and July) (Wersal et al. 2006, Sobolev et al. 2009). It was observed that the upper water layer from 0–0.5 m was supersaturated with oxygen of 105%–144%; whereas the deeper water layer was undersaturated with oxygen decreasing to 30% (Wersal et al. 2006). The pH values also decreased with depth, varying from 9.4–6.9. These observations reflect primary production in the upper water column and respiration in the deeper water layers. Thus, the primary production was likely to have caused a decrease in pCO2 in the upper water column during the day. During winter, the water column tended to be well mixed to the depth of the deepest temperature sensor. However, when wind directions changed, near surface temperatures sometimes increased, and temperatures in the lower water column decreased. The former is indicative of advection, and the latter indicates a reservoir of cooler water at depth, which, based on the attributes of the reservoir, was likely enriched in pCO2. Nocturnal cooling would have entrained this water to the surface and contributed to the higher
Figure 2. Linear regressions between CO₂ fluxes and all heat fluxes during the cooling period (left panel) and between CO₂ fluxes and all heat fluxes during the heating period (right panel) with the same datasets used in figure 1. Negative heat flux denotes that the water surface loses heat to the atmosphere.

 nocturnal CO₂ fluxes (supplementary figure S4). During summer the daytime water column was thermally stratified. As winds picked up at night, the depth of the diurnal thermocline deepened and temperatures became uniform to the depth of the deepest sensor. On relaxation of the wind the following morning, cool water was again found at those depths. We computed the Wedderburn number, \( W = \frac{g \Delta \rho_w h^2}{\rho_w u_w L_f} \), which quantifies the relative significance of the buoyancy force in the water to the shear stress at the water-atmosphere interface (Imberger and Patterson 1990, MacIntyre et al 2009a). Here, \( g \) is gravitational acceleration, \( \rho_w \) is the water density, \( h \) is the mixed layer depth, \( u_w \) is water friction velocity computed from the air and water densities and measured \( u_e \) in air assuming the dynamic shear stress is equivalent on both sides of the air-water interface, and \( L_f \) is the effective horizontal length of the lake along the line of fetch. The Wedderburn numbers were of order 10 during the day (i.e. strong vertical stratification with minimal thermocline upwelling) and 1 at night (full water column upwelling and vertical mixing such that associated horizontal scale of variability in CO₂ concentrations cannot be ignored) (supplementary figure S5). Thus, in summer, the increased CO₂ fluxes at night would have resulted from the combination of convective mixing (Crill et al 1988), mixing associated with internal wave motions at low Wedderburn number (MacIntyre et al 2009b), and spatial variability of CO₂ in the footprint (Heiskanen et al 2014). CO₂ fluxes tended to be somewhat higher with lower values of \( u_e \) and \( U \). In summer, the winds tend to increase near mid-night and then decrease while winds were still changing direction. The independence of CO₂ fluxes from wind speed thus likely results from modifications of the related changes in concentration of CO₂ in the footprint as winds changed direction.

The relation between CO₂ fluxes, the total heat budget in the water surface, plus our calculations of the Wedderburn number (supplementary figure S5), indicates that heat loss and wind induced processes occurring at night explained approximately 31% of the variability in CO₂ efflux (figure 2). CO₂ effluxes slightly declined with the enhanced heating of the mixed layer in the day (figure 2).

3.2. CO₂ flux pulses and their contribution to CO₂ emissions

The seasonal measurements indicate that the diurnal variations of CO₂ effluxes were superimposed by large CO₂ flux pulses that occurred occasionally throughout the year. As shown by a CO₂ flux pulse example from April 11 to 16 (figure 3), each of these CO₂ flux pulses persisted for up to a few days. These pulses, accompanied mostly by sensible and latent heat flux pulses (hereafter H and LE pulses), were caused directly by high-wind events associated with synoptic weather activities such as passages of extratropical cyclones with windy, cold/cold, dry air masses immediately behind them (Liu et al 2009, Zhang and Liu 2013). In the analysis here, a ‘flux pulse’ is defined as occurring when the 24-h mean fluxes exceed 1.5 times the centered 10-day running mean (Liu et al 2009, Zhang and Liu 2013). The CO₂ flux pulses were taken to be the same periods as H and LE pulses. By examining synoptic weather charts for consecutive days (www.wpc.ncep.noaa.gov/dailywxmap/), we were able to verify that such pulse events were caused by synoptic weather events associated with cold front passages. As shown in figure 3, the cyclone passed over the site at about 12:00 LT on April 11, resulting in a shift in wind directions from southerly winds to northwesterly winds, an increase in wind speeds from 4 to 10 m s⁻¹, and a decrease in air temperature from 24 °C to 6 °C.
and vapor pressure from 2.2 to 0.6 kPa. Cold, dry air masses passing over the warm water surface enhanced temperature and humidity differences between the underlying water surface and the overlying atmosphere (i.e., an increase in $T_s - T_a$ and $e_s - e_a$), thereby enhancing convective mixing as reflected by the unstable stratification, and the windy conditions increased mechanical mixing, as compared with the pre- and post-pulse conditions. As a consequence, pulses in H, LE, and CO2 fluxes were produced. The mean fluxes during the pulse period were approximately $-10$, $6$, and $5$ times the pre- and post-pulse averaged fluxes, respectively for H, LE, and CO2 fluxes.

Driven by higher wind speeds and thus greater atmospheric mechanical turbulence, the friction velocity ($u_*$) during the pulse period was approximately

![Figure 3](image-url)

Figure 3. Changes in the surface energy budget components and meteorological variables after a cold front passage. The flux pulse started at approximately 12:00 LT on 11 April 2008 and ended on 16 April 2008. (a) H: sensible heat flux (W m$^{-2}$); LE: latent heat flux (W m$^{-2}$); Rn: net radiation (W m$^{-2}$); and CO$_2$ flux (μmol m$^{-2}$ s$^{-1}$). (b) U: wind speeds (m s$^{-1}$); WD: wind direction in degree. (c), $T_a$: air temperature (°C); $T_s$: water surface temperature (°C). (d) $T_s - T_a$; (e) $e_s - e_a$: vapor pressure (kPa) in the over-water atmosphere; $e_s$: saturation vapor pressure in the water-air interface (kPa). (f) $e_s - e_a$ (kPa).
mixing by convection likely co-occurred as in iod, the upwelling, internal wave induced mixing, and pulsed. During pulse events in the more stratified water column, the Wedderburn number could not be calculated. As the water column was well mixed to the depth of the sensors during the pulse event shown in Figure 4, the depth of the sensors during the pulse event shown is covered 58 days throughout the year (2009, covering 57 days). Annual CO2 effluxes were excluded. The fluxes, as compared with non-pulse periods. A total of 36 pulses were also identified for 2008, and in the equatorial Pacific (3°S, 125°W) for 15 days (McGillis et al. 2004). Methane fluxes are also observed to be greater at night than during the day over an Amazon floodplain (Grill et al. 1988) and over a Swedish lake (60°09′N, 17°20′E) for 16 days (Podgrajsek et al. 2014). This suggests that the greater carbon effluxes from water surfaces at night than during the day may be widespread. Year-round eddy covariance studies of lake-atmosphere interactions have increased over the past years (Vesala et al. 2006, Blanken et al. 2011, Huotari et al. 2011, Nordbo et al. 2011, Bouin et al. 2012, Liu et al. 2012, Zhang and Liu 2013). Also, diel cycles of stratification and mixing are well established for lakes at many latitudes (Melack and Kilham 1974, Imberger 1985, Xenopoulos and Schindler 2001, MacIntyre et al. 2002, 2009a, Pernica 2012, Zhang and Liu 2013).

3.3. Implications of greater nighttime effluxes and flux pulses to carbon emissions

Short-term eddy covariance measurements also reported greater CO2 effluxes at night than during daytime over Toolik Lake (68°37.9′N, 149°36.32′W) in Alaska, USA, Soppensee Lake (47°05.46′N, 8°05.00′E) in Switzerland for several days (Eugster et al. 2003), and in the equatorial Pacific (3°S, 125°W) for 15 days (McGillis et al. 2004). Methane fluxes are also observed to be greater at night than during the day over an Amazon floodplain (Grill et al. 1988) and over a Swedish lake (60°09′N, 17°20′E) for 16 days (Podgrajsek et al. 2014). This suggests that the greater carbon effluxes from water surfaces at night than during the day may be widespread. Year-round eddy covariance studies of lake-atmosphere interactions have increased over the past years (Vesala et al. 2006, Blanken et al. 2011, Huotari et al. 2011, Nordbo et al. 2011, Bouin et al. 2012, Liu et al. 2012, Zhang and Liu 2013). Also, diel cycles of stratification and mixing are well established for lakes at many latitudes (Melack and Kilham 1974, Imberger 1985, Xenopoulos and Schindler 2001, MacIntyre et al. 2002, 2009a, Pernica 2012, Zhang and Liu 2013).
et al 2014). These similarities indicate that the physical processes that moderate all lakes are similar with some variability likely in forcing terms as a function of latitude. Thus, the framework proposed here to evaluate periods with intensified gas fluxes applies to other inland water bodies.

If the enhanced nocturnal and pulse induced fluxes reported here are representative of those over lakes and reservoirs, our results imply that CO$_2$ emission rates from lakes and reservoirs obtained by indirect measurements are substantially underestimated. For our case, estimated fluxes would be approximately 42% too low. Our 42% estimate is conservative because the indirect methods consistently obtain overall lower CO$_2$ fluxes than the eddy covariance approach even during the daytime (Huotari et al 2011, Heiskanen et al 2014). Further, this reservoir is managed for reducing algal abundance by, e.g., water cleaning practices and enacting regulations. Many lakes without such management as well as more eutrophic water bodies, in general, would have higher levels of phytoplankton, higher photosynthesis during the daytime in the near surface, and higher respiration lower in the water column much of the time, leading to larger diel variabilities in pCO$_2$. Thus, the contrast in CO$_2$ efflux between day and night is likely to be even larger for these unmanaged systems.

H and LE flux pulses have been reported from other inland waters with different water surface areas and in different latitudes, including Great Slave Lake (Blanken et al 2000), a reservoir in southeast Queensland, Australia (McGloin et al 2014), a tropical reservoir (Curtarelli et al 2013), a medium-sized Mediterranean lagoon (Bouin et al 2012), a large southern lake in China (Deng et al 2013), Lake Ngoring over Tibetan Plateau (Li et al 2015), and an ocean gulf in China (Ma et al 2012), suggesting that the phenomenon is widespread. The CO$_2$ flux pulses were also observed in a small lake in Finland, though the reasons for these pulses were not analyzed (Huotari et al 2011). It is likely that flux pulse events are associated with a generic response of water bodies to persistent extratropical cyclone activities. One projection is that extratropical cyclone activity will be intensified under future climate change (Lambert and Fyfe 2006, Ulbrich et al 2009), consequently leading to increased CO$_2$ flux pulses from lakes and reservoirs. Accordingly, insufficient pCO$_2$ sampling of surface waters during pulse periods will bias CO$_2$ emissions low when fluxes are computed based on the indirect methods.

The global terrestrial land surface is an important carbon sink (Battin et al 2009, Ballantyne et al 2012). A significant part of this organic carbon initially sequestered as CO$_2$ by terrestrial ecosystems is laterally transported to inland waters (Battin et al 2009, Regnier et al 2013). A large fraction (approximately 30%) of the terrestrially sequestered carbon entering inland waters is emitted as CO$_2$ back to the atmosphere (Kling et al 1991, Cole et al 2007, Battin et al 2009, Raymond et al 2013). Thus, emissions from lakes and other inland waters can represent a missing component of the terrestrial sink (Cole et al 2013). Measurements reported here suggest that terrestrially derived CO$_2$ that outgases to the atmosphere through lakes and reservoirs may be greater than previously estimated due to the unaccounted for greater nighttime emissions and inadequate sampling of flux pulses during synoptic weather events. Therefore the terrestrial carbon sink, which is likely attributed to rising atmospheric CO$_2$ and nitrogen deposition, may have been substantially overestimated.

4. Conclusions

If sampled only during fair weather daytime conditions, our measurements indicate that CO$_2$ efluxes from Ross Barnett reservoir would be underestimated by about 42%. Consequently, these results suggest that published estimates of CO$_2$ emission rates from inland waters, using indirect methods are biased low due to insufficient sampling during night and during storm events. The findings here provide a blue-print on how to construct a conditional sampling framework that reduces potential biases when upscaling local inland water fluxes to regional budgets for CO$_2$ and CH$_4$.

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