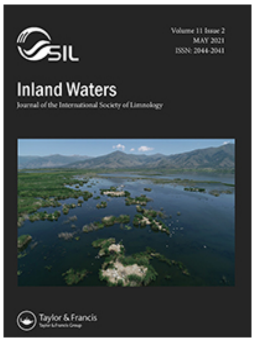

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Late summer peak in pCO_2 corresponds with catchment export of DOC in a temperate, humic lake

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ABSTRACT

Humic lakes play a key role in the processing of organic carbon (OC) mobilised from their catchments, but knowledge of OC dynamics in lakes within maritime temperate climates is limited. Climate exerts a significant influence on mechanisms of OC capture, storage, and processing on the wet and cloudy west coast of Ireland. We examined a high-frequency dataset of partial pressure of CO_2 (pCO_2) in the surface waters of Lough Feeagh collected over 1 year. The annual pattern in pCO_2 ranged between 491 and 1169 µatm and was strongly related to allochthonous riverine OC inputs. In contrast to observations in colder climates, a single peak in pCO_2 occurred in Lough Feeagh in early September. Generalised additive mixed modelling revealed that 2 variables, inflow water colour concentration (a reliable proxy for DOC concentrations) and lake Schmidt stability, together explained 68% of pCO_2 variability. Both the statistical analysis and timing of the peaks in inflow DOC and pCO_2 strongly suggested that catchment carbon export drove pCO_2 supersaturation in the lake, and hence CO_2 emissions. We estimated that between 217 and 370 t CO_2-C (0.55–0.94 t/ha) was emitted during the study period. These results highlight the interplay between catchment OC fluxes and climate in determining pCO_2 dynamics in maritime temperate lakes.

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carbon; catchment; CO_2 emission; lake; pCO_2; temperate maritime climate

Introduction

Lakes actively process terrestrial carbon (C) and, as a consequence, are important emitters of greenhouse gas to the atmosphere (Cole et al. 2007, Tranvik et al. 2009, Bastviken et al. 2011, Deemer et al. 2016). The contribution of carbon dioxide (CO_2) from lakes and impoundments has been estimated to be equivalent to almost 20% of global anthropogenic fossil fuel emissions, ranging between 503 and 810 Tg yr^{-1} of CO_2-C (DelSontro et al. 2018). When rivers and streams are included in these calculations the contribution of C from freshwater systems in their entirety increases to 2.1 Pg yr^{-1} (Raymond et al. 2013). Factors such as nutrient status, lake hydrology and morphology, catchment properties, and climate are known to determine lake C processing and cycling characteristics (Tranvik et al. 2009, Lewis 2011, Weyhenmeyer et al. 2015).

Soil organic carbon (OC) tends to accumulate in areas where precipitation dominates over potential evaporation by a ratio of about 3:1, and subsequently primary production exceeds the decomposition of soil organic matter (Wieder and Vitt 2006). This imbalance in accrual over decomposition for soil OC is particularly common in temperate maritime climate zones and results in the accumulation of peat soils (Moore and Bellamy 1974) as blanket bog, common in Ireland and Scotland, reflecting the strong influence of the Atlantic Ocean in both countries (Coll et al. 2014). Blanket peatlands are recognised as threatened by excessive erosion from harvesting, burning and grazing (Renou-Wilson 2011), and climate change (Gallego-Sala and Prentice 2013). Freshwater aquatic systems in these C-rich peatland environments are the principal conduits conveying OC to the ocean (Hope et al. 1997, Tipping et al. 1997, Ryder et al. 2014). While much of the literature is focused on C processing in upland peatland streams (Hope et al. 1997, Dawson et al. 2002), less is known about C processing and CO_2 partial pressure (pCO_2) dynamics of peatland lakes within temperate maritime climate zones.

The Republic of Ireland has ∼12 200 lakes >0.001 ha (10 m^2) with a total cumulative lake surface area of 1288 km^2, or 1.8% of the total land area (Dalton 2018). Geographically, the greatest concentrations of lakes are in the northwest and west of the country (Dalton 2018). This spatial concentration of lakes in Ireland largely overlaps with catchments dominated by blanket peatland,

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which is also spatially biased toward the west of Ireland. It is therefore important to gain a better understanding of lake C processing within this geographical setting and in peatland catchments in temperate regions generally.

Lake epilimnetic pCO_2 is driven by the interplay of numerous drivers over a range of timescales, with photosynthesis and respiration central to the process (Dodds and Cole 2007). Variation in pCO_2 at daily time scales is predominantly linked to biological activity in the water column. Primary producers in lakes fix inorganic C during photosynthesis, thus reducing water column pCO_2 (Williamson et al. 2009). Conversely, the oxidation of OC during respiration by both heterotrophic and autotrophic organisms increases lake water column pCO_2 (Cole et al. 1994, Jonsson et al. 2001). The observed diel variation of pCO_2 in lakes results from the continuous oscillation between both photosynthesis and respiration during the day and respiration only at night (del Giorgio et al. 1997, Sobek et al. 2005, Huotari et al. 2009). Physical processes may also cause diel variation in pCO_2; for example, convective nighttime mixing causes upwelling of deeper CO_2-rich water as a result of differences in air temperature between day and night (Åberg et al. 2010). The drivers of pCO_2 may also be abiotic, such as sunlight-related photochemical reactions (Bertilsson and Tranvik 1998), wind-related water column mixing (Czikowsky et al. 2018), and discharge-related direct CO_2 inflow to the lake from rain events, surface water, and groundwater (Jonsson et al. 2007).

When considering the variation of pCO_2 at longer, multi-seasonal time scales, other factors become important. As biological processes, both photosynthesis and respiration are directly affected by hydrologically driven inputs of dissolved or total OC (DOC/TOC; Jonsson et al. 2003, Lapierre and del Giorgio 2012, Weyhenmeyer, Fröberg et al. 2012), inorganic C from the catchment (Weyhenmeyer et al. 2015, Wilkinson et al. 2016), and factors such as temperature and nutrient status of the water column (Dodds and Cole 2007). Any given lake will function as either a net source of CO_2 to the atmosphere (when the water is supersaturated with CO_2 with respect to the atmosphere) or as a sink of CO_2 from the atmosphere (when the water is CO_2 undersaturated) (Tranvik et al. 2009), depending on the relative rates of these biological processes within each system. Lake C inputs are sensitive to regional climate variation such as variations in precipitation (Rantakari and Kortelainen 2005, Marotta et al. 2010) and temperature (Staehr and Sand-Jensen 2007) and to individual lake and catchment-related properties such as area, morphometry, productivity, and land use (Roehm et al. 2009, Staehr et al. 2012, Maberly et al. 2013, Raymond et al. 2013, Ferland et al. 2014).

High-resolution pCO_2 datasets have been used to explore lake and reservoir C processing dynamics in boreal (Laas et al. 2016, Denfeld et al. 2018), temperate (Morales-Pineda et al. 2014), and tropical (Junger et al. 2019) climates. To the best of our knowledge, no similar studies have been published for peatland lakes within temperate maritime climate zones. Lough Feeagh's geographic setting within a peatland-dominated catchment and temperate maritime climate zone on the west coast of Ireland makes it an interesting case study from a C dynamics perspective. Previous studies suggest that OC is stored in abundance in the surrounding catchment soils and continuously supplied to the lake, driven mainly by the catchment's hydrologic regime (e.g., Ryder et al. 2014, Doyle et al. 2019). Within-lake OC processing is not disrupted during the winter because the relatively warm winters experienced locally prevent ice-over. Therefore, in contrast to boreal or temperate-continental climate lakes, no major OC release occurs in spring during an ice-out or turnover event. The almost continual tracking of Atlantic weather fronts over the region, bringing clouds and wind, generally ensures a relatively weak stratification during the summer months and a mixed water column for the rest of the year (de Eyto et al. 2016, Andersen et al. 2020). The turbulence of the lake combined with the relatively cool summers are also in direct contrast to many studied boreal and temperate-continental lake systems where calm conditions and hot summers predominate.

Using data from an in situ CO_2 sensor deployed in this temperate humic lake in the maritime temperate region of Europe, we investigated temporal changes in pCO_2 in the lake surface water over 1 year. We assessed the relationships between these changes and a range of potential environmental drivers of pCO_2 variability. Our aims were to (1) investigate the temporal variation in pCO_2 between February and November 2017, a 10-month study period; (2) determine the principal environmental drivers of pCO_2 in the system; and (3) calculate the magnitude of CO_2 evasion from the lake over the study period. We hypothesised that the lake was net heterotrophic and supersaturated with CO_2 due to high year-round inputs of coloured allochthonous OC from the catchment, which would both stimulate ecosystem respiration and restrict net ecosystem production. We also hypothesised that pCO_2 in the lake would peak during late summer and early autumn, responding to the regular, strong, annual peak in DOC concentrations observed in the main catchment streams entering the lake in previous studies (Ryder et al. 2014, Doyle et al. 2019, Jennings et al. 2020).

Materials and methods

The study site

The Burrishoole research station, run by the Irish Marine Institute, is a centre for the study of diadromous aquatic species such as salmon, sea trout, and eel in the North Atlantic (e.g., McGinnity et al. 2009, de Eyto et al. 2016, Poole et al. 2018). As a key element of this research, the Marine Institute maintains a network of high resolution instrumentation in the catchment in tandem with a programme of long-term ecological monitoring (http://burrishoole.marine.ie). Essential to the present study was the use of data from their network of high resolution monitoring equipment, especially the automatic biogeochemical sensors deployed throughout the catchment. The multi-seasonal and high-frequency datasets captured during the study were critical for assessing pCO_2 dynamics and examining the underlying processes (Hanson et al. 2006).

Lough Feeagh (53°56′44″N, 9°34′40″W; Fig. 1) is a freshwater lake located at the base of the Burrishoole catchment (~84 km^2). It has an area of 3.92 km^2 and mean and maximum depths of 14.5 and 46 m, respectively (Table 1). The 2 main inflows into Lough Feeagh are the Black and Glenamong rivers, which supply the lake with most of its water. Two short outflows from the lake, Millrace and Salmon Leap, are each ~200 m in length and drop ~10 m in elevation over this distance. Both outflows discharge to Lough Furnace, a tidal lagoon to the south of Feeagh, before entering the sea through a tidal estuarine river. The catchment has a flashy hydrological regime, mainly due to the temperate maritime climate and subsequent high temporal variability of rainfall. Frontal Atlantic rain systems continually cross the catchment, and occasional extreme storm events cause dramatic flooding (de Eyto et al. 2016, Kelly et al. 2020). The Newport Met Éireann automatic weather station, located between Lough Feeagh and Lough Furnace (Fig. 1) and operating since 2005, recorded an average (standard deviation [SD]) annual rainfall of 1533 (182) mm yr^{-1} between 2005 and 2017. Long-term average monthly rainfall at the station indicates that the driest month of the year is generally April (mean monthly total 85 mm) while December is the wettest (mean monthly total 168 mm). The temperate maritime climate in the region manifests in both mild winters and summers with a mean December–February 2005–2018 air temperature of 6.0 °C and a mean June–August 2005–2018 air temperature of 14.3 °C (Met Éireann; www.met.ie). The area also experiences a regular diurnal sea breeze with mean wind speeds of ~5 m s^{-1} (Kelly et al. 2018).

The Environmental Protection Agency (2005) defined 12 categories of Irish lakes using 3 separate factors: alkalinity, depth, and size. Under this system, Lough Feeagh is classified as low alkalinity (<20 mg L^{-1} calcium carbonate [$CaCO_3$]), deep (>4 m average depth and >12 m maximum depth), and large (>0.5 km^2). The lake is considered oligotrophic (Table 1), with low productivity associated with low phosphorus and nitrogen, and humic with highly coloured water resulting in a mean Secchi disk depth of 1.7 m (e.g., Calderó-Pascual et al. 2020). The 2 main rivers supplying the lake, the Black and Glenamong, have alkalinities of 15–20 and 2.7–7.5 mg L^{-1} $CaCO_3$, respectively. These ranges (<35 mg L^{-1} $CaCO_3$) categorise the river chemistry as soft water and the catchment geology bedrock as effectively 100% siliceous (EPA 2005).

Land cover in the Burrishoole catchment was reported by Doyle et al. (2019), using CORINE data, as comprising 52% blanket peat, 15% forestry, and the remaining 33% transitional woodland and scrub, natural grasslands, and agricultural land. The catchment top soils are predominantly humic, with blanket peatlands covering upland slopes and high C content soils including poorly drained gleys, podzols, and alluvial soils on the valley floors (May and Place 2005).

pCO_2, meteorological and ancillary measurements

An Automatic Water Quality Monitoring System (AWQMS) on Lough Feeagh, positioned over the deepest point of the lake (46 m), collects and transmits high-frequency sensor information to the Marine Institute's research station (Fig. 1; http://burrishoole.marine.ie). The lake water pCO_2 was measured at the AWQMS every 15 min using a membrane-covered optical CO_2 sensor (AMT Analysenmesstechnik GmbH, Joachim-Jungius-Strasse 9D-18059, Rostock, Germany) suspended at 1 m depth. The sensor was deployed on 16 February 2017 until 5 December 2017 and ran continually except for 3 data gaps of 95, 216, and 77 h in August, October, and November, respectively. A multi-parameter sonde (Hydrolab DS5, OTT, Kempton, Germany) deployed on the AWQMS at 0.9 m below the water surface measured pH, specific conductivity (mS cm^{-1}), temperature (°C), and dissolved oxygen (DO; mg L^{-1} and % of saturation) every 2 min for the same period. Vertical temperature profiles below the AWQMS were measured during the study period using a chain of 12 platinum resistance thermistors (PRTs: Lab facility PT100 1/10DIN 4 wire sensor, www.labfacility.co.uk, Labfacility Ltd., Bognor Regis, UK). The chain spanned the full water column with sensors at depth intervals of 2.5, 5, 8, 11, 14, 16, 18, 20, 22, 27, 32, 42 m, all recording every 2 min. Sensors on the AWQMS were cleaned fortnightly, and DO on the multi-parameter sonde was calibrated once per month.

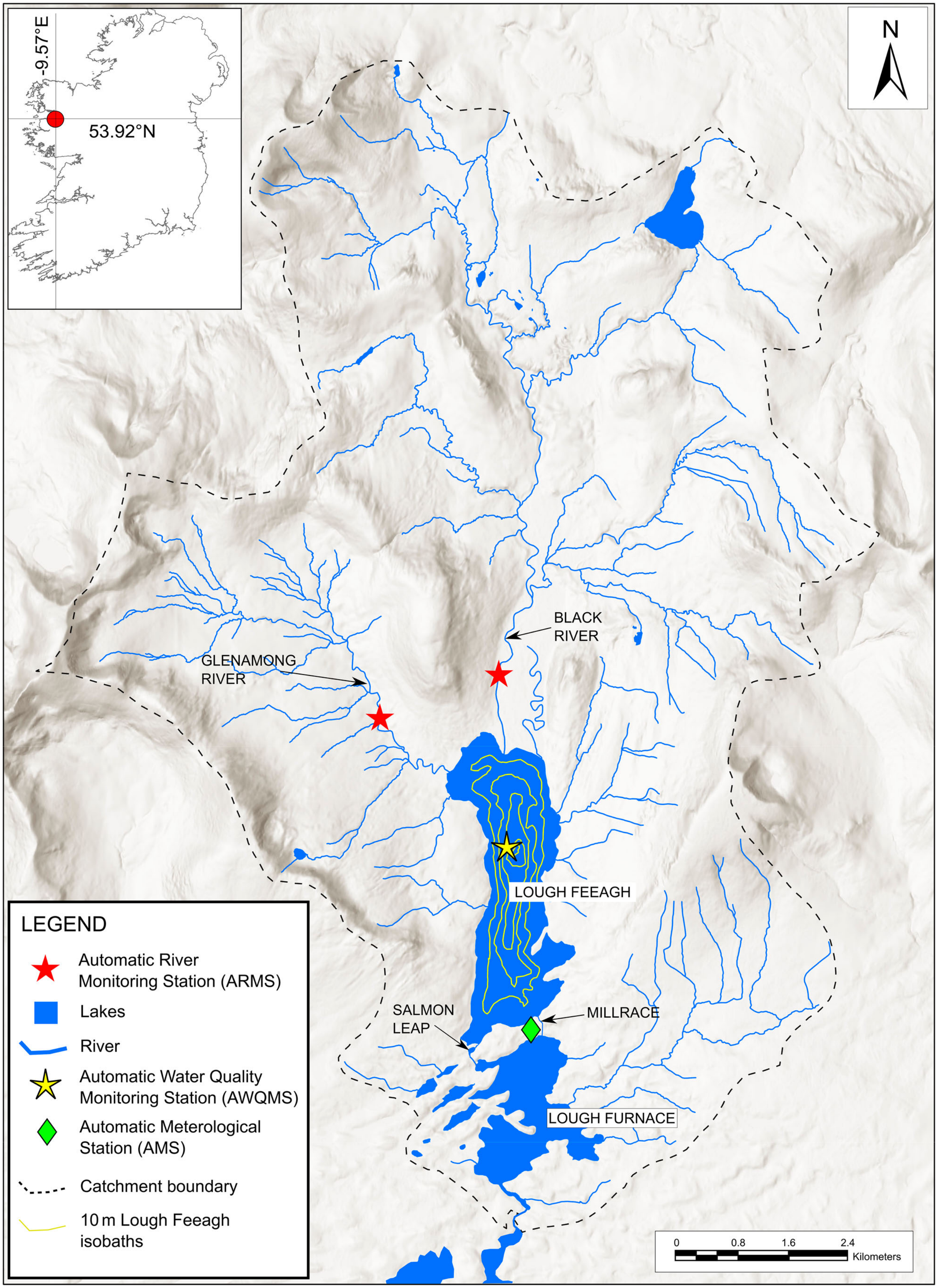

Figure 1. Geographical position of Lough Feeagh and the location of the automatic meteorological station (AMS) and lake and river monitoring stations: the automatic water quality monitoring station (AWQMS) and the automatic river monitoring station (ARMS). Flow direction is from north to south.

Table 1. Location and general characteristics of Lough Feeagh and the Burrishoole catchment.

General characteristics of Lough Feeagh		Characteristics of the Burrishoole catchment		
Latitude	53°56′44″N	Latitude	53°55′N	
Longitude	9°34′40″W	Longitude	9°34′W	
Lake area (km^2)	3.92	Area (km^2)	18.2	
Maximum depth (m), mean depth (m), mean volume (m^3)	46, 14.5, 5.9×10^7	Geology	Quartzite and schist, also interbedded volcanics, marble, dolomite, and schist	
Mixing type	Monomictic	Blanket peat (%)	52	
Mean retention time (yr)	0.47	Forestry (%)	15	
Chlorophyll *a* (µg L^{-1})	0.52–2.01	Minimum altitude (m)	8	
Secchi depth (m)	1.0–2.2	Maximum altitude (m)	710	
Water characteristics of Lake Feeagh		**Water characteristics of Burrishoole rivers**		
			Black	Glenamong
pH range	6.5–7.4	pH range	4.0–8.0	3.5–7.3
Colour (mg L^{-1} PtCo)	62–114	Colour (mg L^{-1} PtCo)	15–257	24–211
DOC (mg L^{-1})	7.7–11.7	DOC (mg L^{-1})	2.3–25.8	3.6–21.5
Total phosphorus (µg L^{-1})	4.8–10.1	–	–	–
Total nitrogen (mg L^{-1})	0.13–0.78	–	–	–
Mean discharge (m^3 s^{-1})	4.37	Mean discharge (m^3 s^{-1})	3.56	0.67
Water temperature range (°C)	5.3–18.8	Water temperature range (°C)	−0.05–26	−0.03–26

An array of instruments on the surface platform of the AWQMS measured meteorological parameters. Wind speed and direction were measured with Vector Instruments A100L2-WR and W200-P-WR, respectively (www.windspeed.co.uk, Windpeed Ltd., Rhyl, North Wales, UK), and photosynthetically active radiation (PAR) was estimated using a pyranometer (Kipp & Zonen CMP6, www.kippzonen.com). Pyranometer data (W m^{-2}) were converted to PAR by multiplying by 0.45 (45% of the light measured by a pyranometer falls into the PAR region) and converting to µmol m^{-2} s^{-1} (1 W m^{-2} = 4.6 µmol m^{-2} s^{-1}) . Lake water level (m) was recorded every 15 min using an OTT Hydrometry Orpheus Mini water level logger (https://www.ott.com). Air temperature (°C), air pressure (hPa), solar radiation (kWh m^{-2}), relative humidity (%), daily rainfall amount (mm), and mean soil temperature (°C) measurements were available from an automatic meteorological weather station operated by Met Éireann (www.met.ie) and situated at the Marine Institute's research station (Fig. 1).

In addition to these data, manual river water samples were taken at weekly intervals from the 2 main rivers entering the lake, the Black and Glenamong, and 1 river exiting the lake, the Millrace. These rivers were analysed for true water colour (mg L^{-1} PtCo) within hours of sampling using a HACH Dr 2000 (Loveland, CO, Germany) spectrophotometer at 455 nm on water filtered through Whatman GF/C filters (pore size ~1.22 µm). Wavelength accuracy was ±2 nm from 400 to 700 nm. DOC concentration (mg L^{-1}) was estimated from water colour concentration (mg L^{-1} PtCo) using a linear model developed between water colour and DOC from the Glenamong River between April 2010 and September 2011 (Ryder 2015). A strong linear relationship was found between colour and DOC ($r^2 = 0.88$, $p \leq 0.001$, $n = 366$), indicating that water colour measurements are a good proxy for DOC concentrations in the catchment rivers.

Data collation and analysis

Continuous in situ measurements of surface water CO_2 concentrations were used to estimate CO_2 emission (F-CO_2, mmol m^{-2} d^{-1}) from the lake by applying the following equation (Cole and Caraco 1998):

$$F\text{-}CO_2 = k[CO_{2water} - CO_{2sat}], \tag{1}$$

where k is the gas transfer velocity (cm h^{-1}), CO_{2water} is the CO_2 concentration in the water (µatm L^{-1}), and CO_{2sat} is the CO_2 concentration at equilibrium with the atmosphere, calculated from Henry's constant (Weiss 1974). For CO_{2sat} a constant pCO_2 in equilibrium with the atmosphere of 400 µatm was assumed (http://co2now.org/). The gas transfer velocity k was estimated from k_{600} values derived from wind speed based on the following formula as described by Cole and Caraco (1998);

$$k_{600} = 2.07 + 0.215U_{10}^{1.7}, \tag{2}$$

where k_{600} is the gas transfer velocity at 20 °C (cm h^{-1}), and U_{10} is the wind speed over the lake at 10 m height (m s^{-1}). A temperature-dependent Schmidt number (defined as the kinematic viscosity of water divided by diffusion coefficient of the gas) for CO_2 was calculated according to Jähne et al. (1987) using the following equation;

$$Sc = 1841 \times e^{(-0.0549 \times t)}, \tag{3}$$

where Sc is the Schmidt stability and t is the water temperature in °C.0 Sc was used to recalculate k_{600} (Wanninkhof 1992) using the following equation;

$$k = k_{600}/(600/Sc)^{-0.66}. \quad (4)$$

In addition to the Cole and Caraco (1998) model used to estimate gas transfer velocity (k), we also reported CO_2 emissions using an alternative bilinear approximation model described by Crusius and Wanninkhof (2003).

Raw data from the instruments on the AWQMS and the water level recorders were visually checked, cleaned, and adjusted when necessary by referring to the Marine Institute's maintenance logs and using Hydras 3 v10.1software (www.ott.com/products/software-solutions/ott-hydras-3-basic). Any outliers identified in the data were removed, and drift that could be attributed to biofouling of sensors between calibration periods (particularly in the DO dataset) was corrected using the sliding correction feature in Hydras 3. Indices of lake physical structure (Schmidt stability and Brunt-Väisälä buoyancy frequency) were calculated using the *r* Lake Analyzer package 1.11.4.1 (Winslow et al. 2014) through R 3.6.2 (R Core Team 2019). Schmidt stability was calculated as defined by Schmidt (1928) as the amount of work required to transform a waterbody to a uniform density. The Brunt-Väisälä frequency, or simply buoyancy frequency, measures fluid stability against vertical displacements such as those caused by convection (Gilmour 1973).

An estimate of the autochthonous C contribution was calculated using primary productivity in the lake. Daily estimates of gross primary production (GPP), respiration (R), and net ecosystem production (NEP) were made using the R *LakeMetabolizer* package (Winslow et al. 2016), applying the maximum likelihood estimate method, a process-error-only model with parameters fitted via maximum likelihood estimation (Solomon et al. 2013). *LakeMetabolizer* was run with a 2 min time step over the study period when data (DO, water temperature, PAR, and wind speed) were available, producing estimates of daily GPP and R ($mg\ m^{-2}\ d^{-1}\ O_2$), and NEP (GPP − R). Negative values of GPP and positive values of R were removed from the dataset, assuming that the model fit was poor or that some other process not included in the model was acting that day (e.g., physical entrainment of O_2 from other depths).

A comparison of lake CO_2 flux with NEP on a daily scale was used to provide insight into the contribution of aerobic in-lake metabolism to the net CO_2 efflux. Daily NEP values ($mg\ L^{-1}\ d^{-1}\ O_2$) were converted to aerial units ($mg\ m^{-2}\ d^{-1}\ O_2$) and converted to CO_2 assuming a respiratory quotient of 1. The daily CO_2 amounts were summed over the study period and the estimated mass of C reported.

The DOC load to the lake over the study period was calculated for the Black and Glenamong subcatchments by multiplying the calculated river discharge volume for each week by the weekly estimated DOC concentration using water colour data converted to DOC concentration, and summing the totals.

Predictors of pCO_2 dynamics

To identify the principal explanatory drivers of pCO_2 in the lake, a generalised additive mixed model (GAMM) with cubic regression smoothing splines and q-Gaussian distributions was developed using the *mgcv* package (Wood 2006) in R 3.6.2, (R Core Team 2019). Variance inflation factors (VIFs) >3 were used to exclude closely related variables (Montgomery and Peck 1992, Zuur et al. 2009). All models were tested for violations of the assumptions of homogeneity, independence, and normality, and correlation or variance structures were included as appropriate using the protocol described in Zuur et al. (2009). The response variable was the lake pCO_2 data. Potential explanatory variables included a set of climatic, hydrological, and lake metabolic data. Because water colour was available at a weekly time step only, weekly means were calculated for all other variables for each sampling week. The climate variables included were mean air temperature (°C), total daily precipitation ($mm\ d^{-1}$), wind speed ($m\ s^{-1}$), relative humidity (%), air pressure (hPa), and solar irradiance using a pyranometer ($W\ m^{-2}$). Hydrological and metabolic explanatory variables included lake level (cm), conductivity ($mS\ cm^{-1}$), DO ($mg\ L^{-1}$), pH, chlorophyll *a* (RFU), colour in the Black River ($mg\ L^{-1}$ PtCO), PP ($mg\ L^{-1}\ d^{-1}\ O_2$), R ($mg\ L^{-1}\ d^{-1}\ O_2$), NEP ($mg\ L^{-1}\ d^{-1}\ O_2$), Schmidt stability, and thermocline depth (m).

The original 15 min pCO_2 dataset was converted to a mean hourly time step and examined using seasonal trend decomposition using *loess* (STL; Cleveland et al. 1990) in R (R Core Team 2019), but no periodicity in the dataset was uncovered. A manual decomposition technique previously described by Morales-Pineda et al. (2014) was applied to the hourly pCO_2 dataset based on 2 frequencies assumed (a priori) to show maximum lake pCO_2 variation. The 2 chosen frequencies were 24 h and 48 h, the former frequency highlighting the variation in pCO_2 due to photosynthesis and the latter frequency highlighting pCO_2 variation due to weather events. Storm event duration in the Burrishoole catchment averaged 54.0 h during winter and 46.4 h during summer (Andersen et al. 2020), which was rounded to 48 h to encompass the entire year. The daily component (pCO_{2daily}) was calculated by removing the 24 h moving average ($24h_{avg}$) from the hourly pCO_2 dataset (equation 3). The 48 h component ($pCO_{2,48h}$) was calculated by removing the 48 h moving average ($48h_{avg}$) from the 24 h moving average ($24h_{avg}$, equation 4). The remaining seasonal component ($pCO_{2seasonal}$) was calculated by removing the pCO_2 time series data average (pCO_{2avg}) from the 48 h moving average (equation 5). These equations are expressed as follows:

$$pCO_{2daily} = pCO_2 - 24h_{avg}, \tag{5}$$

$$pCO_{2,48hr} = 24h_{avg} - 48h_{avg}, \text{ and} \tag{6}$$

$$pCO_{2seasonal} = 48h_{avg} - pCO_{2avg}. \tag{7}$$

The hourly pCO_2 dataset can be described mathematically as:

$$pCO_2 = pCO_{2avg} + pCO_{2seasonal} + pCO_{2,48h} + pCO_{2daily}. \tag{8}$$

Results

Data overview

From a possible 43 020 separate measurements, 39 456 valid pCO_2 measurements at 15 min resolution were taken during the 303 d study period (11 Feb to 11 Dec 2017). Data gaps accounted for 8.3% of the total dataset, with 3 main gaps occurring between 10 and 14 August (95 h), 11 and 20 October (216 h), and 19 and 22 November (77 h). The pCO_2 ranged from a minimum of 491 µatm recorded on 10 May to a maximum of 1169 µatm recorded on 10 September. The average (SD) pCO_2 for the whole study period was 803 (122) µatm, and the lake was supersaturated throughout the study period. The pCO_2 had a general seasonal cycle, with lower values in the earlier part of the record, reaching a maximum value in autumn. Concentrations climbed steadily during the first 3 months, from ~600 µatm in early February, reaching concentrations of just over 800 µatm in late April (Fig. 2a). Concentrations then declined sharply for 3 weeks, with concentrations just above 500 µatm recorded in the second week of May. From this low point, concentrations climbed and plateaued at ~750 µatm until the end of July, then climbed steadily reaching a maximum in early September with values of >1100 µatm, and thereafter declined to ~800 µatm in late November.

Mean water colour concentrations in the 2 rivers entering the lake, the Black and the Glenamong, were 109 (54) mg L^{-1} PtCo ($n = 44$) and 96 (43) mg L^{-1} PtCo ($n = 44$), respectively (Fig. 2b). Maximum and minimum PtCo values of 236 and 19 mg L^{-1} were recorded in the Black while those for the Glenamong were 216 and 31 mg L^{-1}. Temporally, the colour concentrations in both inflowing rivers were broadly synchronous over the study period. From February until the beginning of May, colour concentrations in the Black and Glenamong averaged 71 and 63 mg L^{-1} PtCo, respectively. Minimum colour concentrations for both inflowing rivers during the study period were recorded in early May, which also corresponded with a minimum lake level recorded at this time. Colour concentrations recovered rapidly from this low point in late spring, climbing to the maxima recorded for the 2 rivers in mid to late August (Fig. 2b).

The Schmidt stability of Lough Feeagh began to climb in early April and reached a peak of ~250 J m^{-2} at the start of June. Schmidt stability values fell and did not peak again until mid-July. From this point, values fell until around mid-September when the lake was fully mixed and Schmidt stability values remained at 0 for the remainder of the study period (Fig. 2d). Greater peaks of wind speed were noticeable during January and February and also during September. A calm period also occurred during late April and early May and coincided with the onset of thermal stratification (Fig. 2d).

Water temperature at the lake surface ranged between 5.3 °C (27 Feb) and 18.8 °C (17 Jul) with a mean water temperature of 12.3 (3.3) °C over the study period. Temperature averaged just over 16 °C during August and declined steadily to temperatures ~7.7 °C at the end of the study period. The water column in the lake was mixed until 19 April when thermal stratification commenced. The lake was thermally stratified until 20 September when the water column began to mix following a series of storm events (Fig. 2e).

An estimated total DOC load to the lake of 1182 t of C during the study period (11 Feb to 11 Dec) was calculated for the Black and Glenamong subcatchments.

Estimated C emission as atmospheric CO_2 from the lake surface varied depending on the model applied. Using the Cole and Caraco (1998) model, C emission ranged from 2.8 to 195.0 mmol m^{-2} d^{-1} (mean [SD]= 28.1 [15.5] mmol m^{-2} d^{-1}), and using the model proposed by Crusius and Wanninkhof (2003) C emission ranged from 0.5 to 83.1 mmol m^{-2} d^{-1} (mean 16.5 [8.2] mmol m^{-2} d^{-1}; Fig. 3a). The total estimated C emission over the study period from the lake was 369.6 t using the Cole and Caraco (1998) and 216.9 t using the Crusius and Wanninkhof (2003) models. The estimated emissions therefore represent 31.3% or 18.3% of the calculated DOC load entering the lake, depending on the model applied.

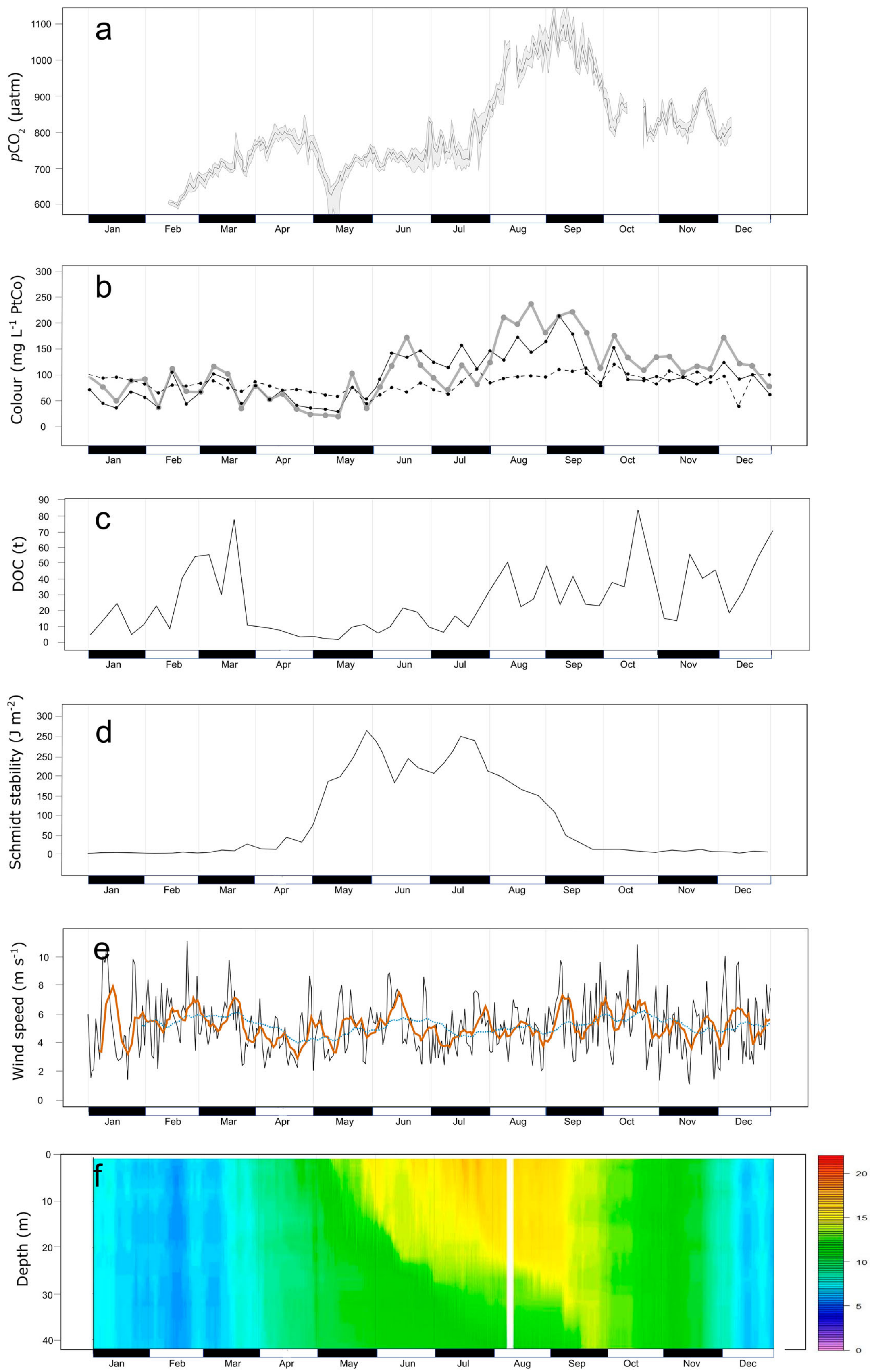

Figure 2. (a) Average daily pCO_2 (black line) within daily maximum and minimum (shaded area); (b) = river inflow and outflow colour concentrations (black line = Black River, grey line = Glenamong River, dashed line = Millrace outflow); (c) = catchment OC load in tonnes DOC per week to the lake; (d) = Schmidt stability; (e) = average daily wind speed (black line), average weekly wind speed (orange line), and average monthly wind speed (dashed blue line); (f) = lake temperature profile (the temperature scale bar is in °C); the x-axis for all panels = time (2017).

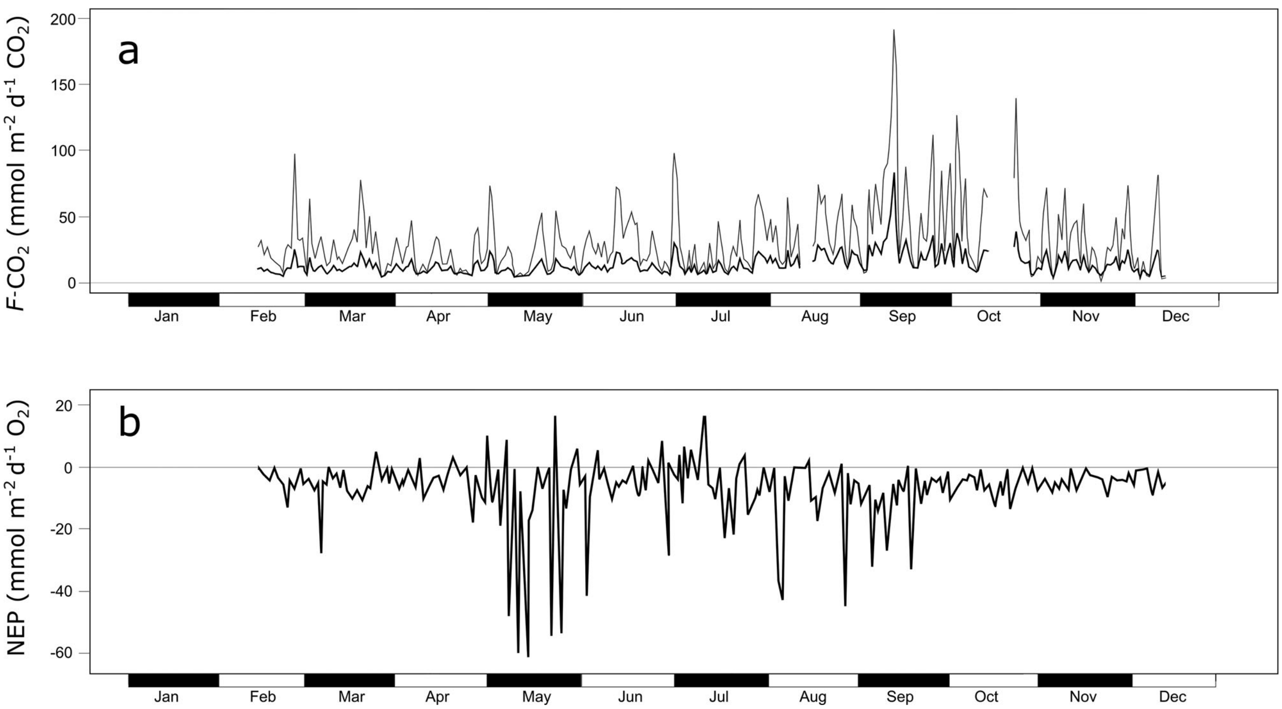

Figure 3. (a) Water to air fluxes of CO_2 from Lough Feeagh during the study period. The dark black line corresponds to Crusius and Wanninkhof (2003) bilinear relationship and the grey line corresponds to Cole and Caraco (1998) power relationship, the fluxes equate to 217 and 370 t C respectively. (b) Net ecosystem production (NEP) during the study period. Daily NEP converted to CO_2, summed over the study period and assuming a respiratory quotient of 1, was estimated to amount to 67.92 t C; the x-axis for both panels = time (2017).

NEP (GPP−R) was predominantly negative, in agreement with the almost continuous O_2 under-saturation observed throughout the study period. Daily NEP O_2 values (mmol m^2 d^{-1}; Fig. 3b), converted to CO_2 assuming a respiratory quotient of 1 and summed over the study period, were estimated at 67.92 t of C. This value is considered to be the contribution of aerobic in-lake metabolism to the net CO_2 efflux and equates to 18.3–31.3% of the total C emission to the atmosphere during the study period, depending on the model applied.

Predictors of pCO_2 dynamics

The optimal GAMM for pCO_2 in Lough Feeagh included 2 significant smoothers, colour concentrations in the Black River and Schmidt stability of the water column in Lough Feeagh. This model explained 67.8% of the variance in pCO_2 over the study period (Table 2). The smoother for colour concentration in the Black River indicated a linear, positive relationship with pCO_2, indicating that, in general, the pattern of pCO_2 follows the inflowing water colour concentrations during the study period (Fig. 4a). The relationship between Schmidt stability and pCO_2 in the lake was more complicated, with the smoother showing a wave-like pattern (Fig. 4b). The pattern indicated a positive relationship between pCO_2 and Schmidt stability when the lake was fully mixed, with Schmidt stability values close to 0. However, as Schmidt stability values increased above ∼100 J m^{-2} the relationship with pCO_2 became negative. At Schmidt stability values >250 J m^{-2} the relationship between the 2 variables again became positive. An alternative model, using solely colour concentration in the Black River versus pCO_2, resulted in an r^2 value of 0.60, indicating that this explanatory variable explains ∼60% of the variance in the optimal model and confirms that colour in the Black River, and by proxy DOC from the surrounding catchment, is the most important driver of pCO_2 in the model.

pCO_2 time series decomposition

The mean hourly pCO_2 signal was decomposed into 3 temporal components, a 24 h or daily component, pCO_{2daily} (Fig. 5a); a 48 h component, $pCO_{2,48h}$ (Fig. 5b); and a seasonal component, $pCO_{2seasonal}$ (Fig. 5c). Following careful visual inspection of the pCO_{2daily} data, no strong, regular pattern of diel variation was observed (suggesting variation in pCO_2 due to photosynthesis), except during one 4-week long period between April and May (S1 in Fig. 5a). During this

Table 2. Results of generalised additive mixed model (GAMM) applied to pCO_2 in Lough Feeagh over the study period in 2017. s = the scaled smoother for each explanatory variable; s(black_col) = the scaled smoother for colour concentrations in the Black River, and s (Schmidt stability) = the scaled smoother for Schmidt stability of Lough Feeagh during the study period.

	pCO_2 – Black river		R^2 (adj) = 0.678, scale est. = 4276.2, $n = 44$	
	Estimate	Standard error	*t*-value	Pr (>|*t*|)
Intercept	804.131	9.972	80.64	$<2.0 \times 10^{-16}$
Approximate significance of smooth terms:	edf	Ref.df	*F*	*p*-value
s(black_col)	1.000	1.000	61.801	1.47×10^{-10}
s(Schmidt stability)	3.751	3.751	3.895	0.0133

period, a strong and regular trend of diel pCO_{2daily} variation is apparent in the time series, synchronous with an extended period of sunny and calm weather (i.e., high pyranometer values and wind speeds below ~4 m s^{-1}). Large dips and spikes in the pCO_{2daily} component can be observed from the end of June to around mid-August, but these variations seem to be random in time, and when viewed alongside the wind and lake-level data they seem to be related to individual storm events. The water level in the lake fluctuated considerably over the study period, responding to periods of high and low rainfall in the catchment. A maximum level of 1.19 m was recorded on 18 March and a minimum level of 0.18 m on 12 May. The mean lake level was 0.47 (0.18) m and the overall level of the lake varied by 1.01 m over the study period (Fig. 5b).

The duration of the 48 h component was chosen to highlight how storm events might affect pCO_2 variability. Many of the major dips and spikes in the $pCO_{2,48h}$ data seemed to be synchronous with peaks of wind speed and abrupt rises in lake level following heavy rain (shaded areas in Fig. 5b). The seasonal component, $pCO_{2seasonal}$, shows the pCO_2 variability when both the 24 h and 48 h components are removed from the mean hourly pCO_2 dataset (Fig. 5c).

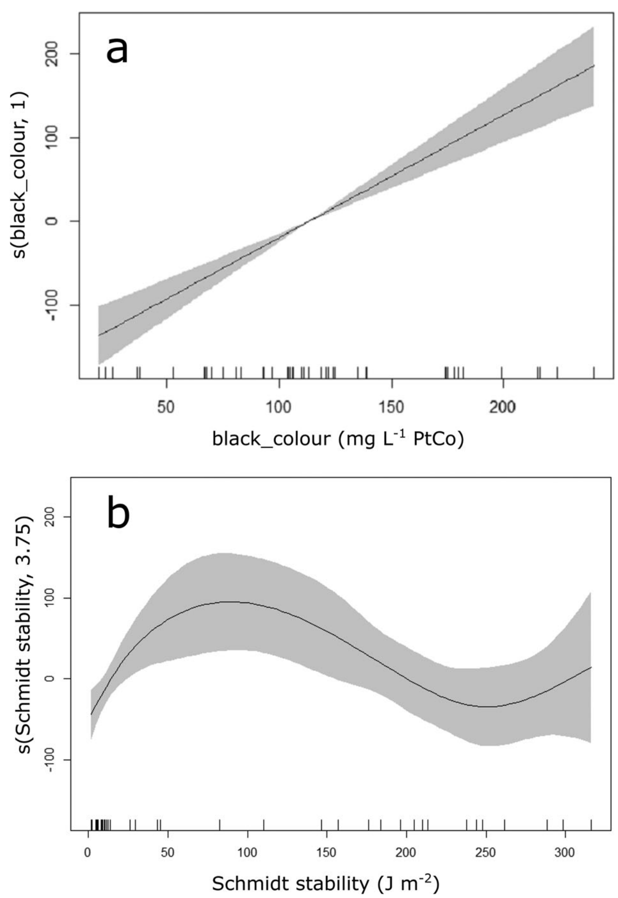

Figure 4. Selected smoothers for the contribution of explanatory variables for the optimal GAMM explaining pCO_2 in the Lough Feeagh: (a) colour concentrations in the Black River, (b) Schmidt stability in Lough Feeagh. The solid line is the smoother, and the shaded area shows the 95% confidence bands. The y-axis units are the scaled smoother (s) for each explanatory variable with the variable name followed by the estimated degrees of freedom (edf) within the parentheses. Vertical dashes on the inside of the horizontal axes show the location of individual data points.

Discussion

Freshwater aquatic systems, including lakes, are recognised as important regulators of C transport and transformation along the continuum of inland waters (Cole et al. 2007, Tranvik et al. 2009, Raymond et al. 2013, Engel et al. 2019), and many are net contributors of C to the atmosphere (Cole et al. 1994, Bastviken et al. 2011). The pCO_2 levels we report here confirmed that Lough Feeagh was continuously emitting CO_2 during the study. More interesting, however, was the temporal pattern of pCO_2 in Lough Feeagh, which had a peak in late summer/early autumn with levels then dropping again toward winter. To our knowledge, this pattern has not been reported from other climate zones where data were available over the annual cycle. For example, in Boreal climate zones, pCO_2 has been observed to generally peak twice during the year, once following ice melt when CO_2 is released, having built up beneath the ice during the winter (Ducharme-Riel et al. 2015), and again in autumn when lake mixing brings CO_2-rich bottom water to the surface (Ojala et al. 2011,

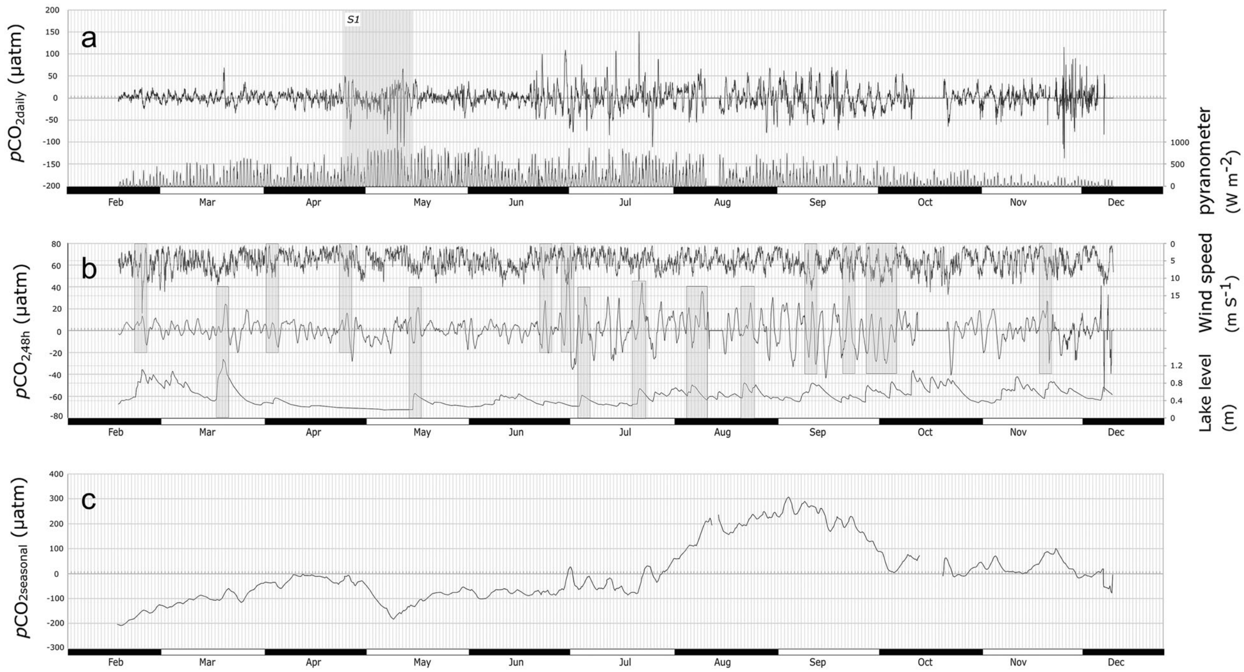

Figure 5. Decomposition of the original pCO_2 signal to (a) daily pCO_2 component (pCO_{2daily}) and pyranometer measurements (lower right axis). Shaded section (S1) highlights a period where diurnal periodicity is evident. (b) 48 h pCO_2 component ($pCO_{2,48hr}$) with wind speed (upper right axis) and lake level (lower right axis). Areas shaded highlight peaks in $pCO_{2,48hr}$ with concurrent peaks in either wind speed or lake level. (c) Seasonal pCO_2 component ($pCO_{2seasonal}$). Note: Shaded areas were identified by visual examination. Power for pCO_2 component is at the seasonal scale (c), followed by the daily scale (a), and finally the intermediate scale (b). the x-axis for all panels = time (2017).

Weyhenmeyer, Kortelainen et al. 2012). Ice formation on Lough Feeagh is an extremely rare and brief occurrence because of the temperate maritime climate of the region, and the hydrological pattern therefore differs considerably from boreal sites, with highest inflows throughout the autumn–winter and into early spring.

Surface water pCO_2 in Lough Feeagh did not fall below 491 µatm at any time during the measurement cycle. At 803 µatm, mean lake pCO_2 was approximately double that of atmospheric CO_2 levels in 2017 (http://co2now.org/). Surprisingly, given the humic status of the lake, the mean pCO_2 values from Lough Feeagh were on the low end of the scale compared with directly measured pCO_2 values reported from other climate zones. In a study of temporal dynamics of pCO_2 in 2 Mediterranean reservoirs, for example, mean concentrations of 695 and 1529 µatm were reported using high-frequency data over the summer months (Morales-Pineda et al. 2014). In boreal climate zones, 33 lakes in Sweden sampled 4 times during the year had a mean pCO_2 of 1762 µatm (Sobek et al. 2003), and a more recent study by Yang et al. (2015) reported a mean pCO_2 of 1100 µatm in 75 lakes in Norway and Sweden sampled once during July and August.

Two other studies showed pCO_2 similar to those in Lough Feeagh. Larsen et al. (2011) presented mean pCO_2 levels of 774 µatm for 112 lakes in Norway sampled once in October, and a mean pCO_2 of 631 µatm was reported by Roehm et al. (2009) from a 3-year sampling campaign of 78 Boreal lakes in Canada. Most lakes in the latter study were, however, sampled only once during summer or early autumn. Only one other study that presented lake pCO_2 in temperate maritime zones was found in the literature. Whitfield et al. (2011) reported a median pCO_2 in the region of 1080 µatm for 121 lakes in Ireland in a study where each lake was again sampled only once during early summer, and 20 were found to be undersaturated. Although most of the sampled lakes were situated in peatland catchments, they were also much smaller than Lough Feeagh (median = 2.0 ha) and predominantly located above 200 m in altitude. The results of our study suggest that the timing of the one-off sampling period in the Whitfield study coincided with a period of the year that pCO_2 would have been lower.

In Lough Feeagh, pCO_2 climbed steadily during summer when the lake was stratified (Fig. 2a and f). Conversely, in studies from other climate zones, the onset of lake thermal stratification was reported to suppress

pCO_2 in the epilimnion by reducing the volume of water in which mineralisation of allochthonous OC can occur (e.g., Jonsson et al. 2007). Also, in boreal and continental temperate climates, lake thermal stratification generally coincides with periods of low discharge, resulting in a reduction of allochthonous C inputs to lakes. During their study in a boreal lake, for example, Jonsson et al. (2007) reported an anomalous high-rainfall/discharge event in late July where a large input of DOC-rich water entered the lake, causing a spike in pCO_2 that declined slowly. The authors noted that typical low discharge pCO_2 levels were not reached until 1 month after the peak discharge was recorded. We assumed that the high rainfall regime experienced at Lough Feeagh results in the lake being continuously "topped up" with allochthonous C from the surrounding catchment throughout the year, which can be observed by the relatively high loading of DOC to the lake (Fig. 2b–c; Ryder et al. 2014, Doyle et al. 2019). We suggest that this almost constant and regular OC supply allows pCO_2 in Feeagh to climb even during the main period of thermal stratification.

One of the most striking features in the pCO_2 time series for the study year was the sharp decrease that occurred between mid-April and mid-May, where values dipped to 491 µatm, the minimum values recorded over the study period (Fig. 2a). This period of sharply suppressed pCO_2 coincided with a 30 d rain-free period, a relatively rare occurrence in this catchment, and corresponded to minimum values for the lake-level gauge. River colour concentrations in the inflowing rivers also dropped to their lowest levels during this period. The coincident reduction of pCO_2, water colour, and discharge highlights the connectivity between catchment hydrology and OC availability in this lake. During such low-discharge periods, the lowered water table and processes such as drought-induced acidification serve to break the connection between the source of DOC production, the surrounding peatland soils, and its destination, the catchment's aquatic continuum (Clark et al. 2005). A drought effect was previously reported in the Glenamong catchment for early summer, whereby low river DOC concentrations were associated with a dry weather event (Ryder et al. 2014). For the 30 d period described here, we assumed that the lake epilimnion was increasingly deprived of allochthonous C inputs, and pCO_2 in the lake dropped accordingly. However, pCO_2 in the lake rapidly rebounded following the return of rain in mid-May.

Following peak pCO_2 observed in early September when concentrations reached >1100 µatm, they declined relatively quickly to concentrations between 800 and 900 µatm. Interestingly, this period of declining pCO_2 coincided with the breakdown of thermal stratification in the lake. In other climate zones, downward epilimnion expansion has been associated with an increase in pCO_2 when CO_2 contained in the hypolimnion is released. For example, Morales-Pineda et al. (2014) reported increasing pCO_2 in one Spanish reservoir during early autumn as downward epilimnion expansion facilitated release of CO_2 trapped beneath the thermocline. We suggest that because bioavailable C was not limited in the epilimnion of Lough Feeagh during the period of breakdown of thermal stratification, no major spike in pCO_2 occurred at that time.

A link between diel variations in pCO_2 and solar radiation due to the changing day–night balance between production and respiration is well described in the literature (Carignan 1998, Hanson et al. 2006, Huotari et al. 2009). However, the expected regular pattern of increase in pCO_2 during night, as respiration dominates production in plankton metabolism, appeared only sporadically in the Lough Feeagh record. Careful visual examination of the daily pCO_2 component (pCO_{2daily}) and concurrent wind speed and pyranometer data indicated that these distinct diel fluctuations only occurred when wind speed remained consistently below ~4 m s^{-1} and solar radiation levels were high. Such calm, sunny conditions did not occur often during the study period but did between mid-April and mid-May, giving rise to a strong diel pCO_2 signal with sharp peaks in pCO_2 at night and dips during the day. This strong signal notably occurred when overall pCO_2 levels in the lake were falling sharply. Our results show that the regular diel pCO_2 oscillation reported from waterbodies in other climate zones (e.g., Morales-Pineda et al. 2014) were generally intermittent and weak in Lough Feeagh over the study period.

The 2 main predictors of pCO_2 dynamics in the lake were colour concentrations in the incoming Black River and the Schmidt stability of the lake water column. The optimal model explained 67.8% of pCO_2 variance during the study period, and the relationship between colour in the Black River and pCO_2 in the lake was positive and linear (Fig. 5a). This result suggests a close dependence between input of allochthonous DOC and heterotrophic respiration in Lough Feeagh. A regular pattern of strong, annual peaks in colour/DOC concentrations during the late summer/early autumn were found in a recent 6-year study on colour concentrations in the main streams entering Lough Feeagh (Doyle et al. 2019). These peaks were found to be predominantly driven by soil temperature in the catchment and to a lesser extent by soil moisture levels, stream discharge, and climate. Especially notable in the current study was the annual peak of colour/DOC in both the Black and Glenamong rivers corresponding closely to the annual peak pCO_2 levels in the lake (Fig. 2a). Numerous studies, mostly from northern, boreal lakes, highlight the relationship between the biological mineralisation of allochthonous C and excess CO_2 in lake waters (e.g., del Giorgio and Peters 1994, Sobek et al. 2003, Duarte and Prairie 2005, Lapierre et al. 2013).

The Schmidt stability of Lough Feeagh generally followed a predictable and regular pattern every year, closely following the solar cycle and peaking in July (de Eyto et al. 2016). Note, however, that the annual peak in Schmidt stability was not synchronous with the annual peak in pCO_2. Presumably the offset in timing between the peak in the Schmidt stability of the lake and the peak in pCO_2 gives rise to the complicated relationship evident in the model (Fig. 5b). Also of note is the absence of any in-lake or autochthonous drivers of pCO_2 variability in the optimal model. While daily estimates of lake GPP, R, and NPP were included as explanatory variables, they were excluded from the final model because they were not statistically linked to pCO_2 variability in the lake over the study period. The estimate of autochthonous-derived C also shows that primary production in the lake contributed between ~18% and 31% of the total OC mineralisation.

The $pCO_{2,48h}$ data showed strong variation at this time step, and much of the variation seemed to be concurrent with storm events that occur over a similar time duration in the catchment. Although elevated wind speeds may have suppressed variability of pCO_2 over a daily time period, it seems to be a significant forcing factor over longer time periods. Visual examination of the $pCO_{2,48h}$ graph, in conjunction with wind speed, showed that many of the larger peaks in pCO_2 corresponded to wind speed peaks. Presumably during these storm events, downward expansion of the epilimnion released pCO_2 in the hypolimnion, rapidly increasing pCO_2 levels. A similar episodic relationship between wind speed and pCO_2 was described by Morales-Pineda et al. (2014) in 2 reservoirs in southern Spain. Variability in $pCO_{2,48h}$ also seems to be linked with major rainfall events in the catchment (Fig. 5b). A repeated pattern of pCO_2 variation appears with these rainfall event, with an initial dip of pCO_2 as fresh water arrives in the lake followed immediately by a sharp peak of pCO_2. The initial dip in pCO_2 may be explained by the rapid dilution of the epilimnion and, the subsequent peak occurs as a result of increased respiration as the bacterial and planktonic communities responds to the pulse of DOC and nutrients from the catchment.

Estimating the water-to-air fluxes of C from pCO_2 provides important information on the C budget of the lake and is useful when comparing with other freshwater systems. Two air–water flux (F-CO_2) models, one described by Cole and Caraco (1998) and a bilinear approximation model described by Crusius and Wanninkhof (2003), were applied to hourly averaged pCO_2 over the study period. Both models are based on empirical relationships between gas transfer velocity and wind speed and are commonly used to calculate F-CO_2. Carbon emission estimates from the lake varied considerably depending on the model applied. The total estimated mass of C emission over the study period almost doubled between the Crusius and Wanninkhof (2003) and the Cole and Caraco (1998) models at 217 and 370 t of C, respectively (Fig. 4). Note that both models were developed based on empirical measurements from small, wind-sheltered lakes in the boreal climate zone of North America, and as such are not entirely comparable to the more exposed conditions at Lough Feeagh. However, in an examination of pCO_2 dynamics in 2 reservoirs in southern Spain by Morales-Pineda et al. (2014), these 2 models were also applied, and the Crusius and Wanninkhof (2003) model was found to more accurately capture F-CO_2 dynamics in their systems. In particular, short spikes in F-CO_2 were linked to decreases in pCO_2 during windy events, processes not accurately captured by the Cole and Caraco (1998) model. This result perhaps signals that the Crusius and Wanninkhof (2003) model may be a better fit when applied to more turbulent systems, such as Lough Feeagh. The estimated total DOC load to the lake of 1182 t of C during the study period is equivalent to a catchment load of 14.7 t km^{-2}, comparable to previous load estimates to the lake from the catchment (Doyle et al. 2019).

There is a dearth of data on C processing in Irish lakes, which is unfortunate given the >12 000 lakes in the Irish Republic covering ~1.8% of the land surface. Their role in C processing and C emission to the atmosphere is vastly disproportionate to their surface coverage, particularly because most Irish lakes are located in humic, high soil OC catchments. Lake C emissions are not captured in national emissions budgets for Ireland (EPA 2019), and we consider that this study greatly improves existing knowledge and will assist with constraining national CO_2 emission inventories. However, further work is required on lakes within a range of sizes, trophic states, and morphometries to form a broader, regional understanding of pCO_2 dynamics and CO_2 emissions.

Conclusions

This investigation of temporal variation in pCO_2 highlighted the role of the local temperate maritime climate on the temporal dynamics of lake pCO_2 and the potential for using high frequency data to inform these patterns. Most importantly, we showed that lakes in these regions can have a different temporal pattern than sites in boreal and continental regions, with late-summer/autumn peaks driven predominantly by catchment inflows of C and changes in thermal stratification. Both of our hypotheses were also confirmed: that ecosystem respiration exceeded primary production in the lake and that pCO_2 peaked in the early autumn, coinciding with an annual DOC concentration peak in the incoming rivers. Our investigation also showed that the lake was supersaturated with CO_2 and was a net emitter of CO_2 to the atmosphere during the study period. This study contributes to lake C cycling literature by broadening understanding of the interactions between lake pCO_2 dynamics and climate.

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