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Catchment productivity controls CO₂ emissions from lakes

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Most lakes are oversaturated with CO$_2$ and are net CO$_2$-sources to the atmosphere, yet their contribution to the global carbon-cycle is poorly constrained$^{1-4}$. Their CO$_2$-excess is widely attributed to in-lake oxidation of terrestrially-produced dissolved organic carbon (DOC)$^5$. Here we use data collected over 26 years to show that the CO$_2$ in 20 lakes is primarily delivered directly via inflowing streams rather than being produced in situ by degradation of terrestrial carbon. This implies that high CO$_2$ concentrations and atmospheric emissions are not necessarily symptoms of heterotrophic lake ecosystems. Instead, the annual mean CO$_2$ concentration increased with lake productivity and was proportional to the estimated net primary productivity of the catchment. Overall, about 1.6% of net primary productivity (range 1.2 to 2.2%) was lost to the atmosphere. Extrapolating globally this is equivalent to CO$_2$ losses of ~0.9 Pg C yr$^{-1}$ (range 0.7 to 1.3), consistent with existing estimates. These data and our catchment productivity hypothesis re-enforce the high connectivity found between lakes, their catchment and the global C-cycle$^6$. They indicate that future concentrations of CO$_2$ in lakes, and losses to the atmosphere, will be highly sensitive to altered catchment management and concomitant effects of climate change that modify catchment productivity.
The generally elevated concentration of CO₂ in lakes has led to the belief that they are heterotrophic systems that oxidise terrestrially-produced DOC⁵. While this is undoubtedly true at some locations, it is less likely in relatively clear-water lakes. An additional hypothesis, that we examine here, is that high CO₂ concentrations can also result from direct inputs of CO₂, fixed and broken-down in the terrestrial catchment and delivered via hydrological pathways. Moreover, we hypothesise that CO₂ concentrations in lakes are a consequence of the catchment carbon cycle implying that catchment processes, driven by land use, will regulate the contribution of lakes to the global carbon cycle⁶,⁷.

Twenty lakes in the English Lake District were sampled quarterly (January/February, April, July and October) in 1984, 1991, 1995, 2000, 2005 and 2010. The average rainfall on these catchments (2.34 m yr⁻¹) and catchment slope (277 m km⁻¹) are high and the geology largely comprises impermeable slates, shales and igneous rocks that do not support major groundwater aquifers (See Supplementary Fig. 1) so inflow of water is dominated by surface-flow and potentially soil throughflow and interflow. The lakes have a low alkalinity (mean 0.21 equiv m⁻³, range 0.05 to 0.54 equiv m⁻³ in 2010) and relatively low concentrations of DOC (mean 0.13 mol m⁻³, range 0.06 to 0.22 mol C m⁻³ ⁸ Supplementary Table 1) and hence have relatively clear-water. Their productivity is largely controlled by the availability of phosphorus⁹. The concentration of CO₂ varied significantly with lake trophic status, as expressed using measured total P (Fig. 1) and verified by the morpho-edaphic index¹⁰ that excludes point-sources of P (See Supplementary Information). There was little variability in the concentration of CO₂ in unproductive, oligotrophic lakes, where concentrations of total P were less than about 10 mg m⁻³. In contrast, there was a large dynamic range of CO₂ concentration in the more productive lakes, with minima in summer when productivity was high² and maxima in the autumn when CO₂ produced by mineralisation of organic carbon at
depth\textsuperscript{11} is mixed into the surface waters on breakdown of stratification. On average, these
lakes were about 2-fold oversaturated with CO\textsubscript{2}, in broad agreement with previous
surveys\textsuperscript{1,3,4}.

Paradoxically however, the annual mean concentration of CO\textsubscript{2} increased with lake
productivity, despite summer CO\textsubscript{2}-depletion and high productivity indicated by elevated
concentrations of chlorophyll and oxygen in the surface waters during the growing season.

We hypothesise that the large CO\textsubscript{2}-excess in the more productive lakes results from them
receiving large subsidies of carbon from productive terrestrial ecosystems. This hypothesis
was tested using the ratio of $^{13}\text{C}$ to $^{12}\text{C}$ ($\delta^{13}\text{C}$) to trace inputs of terrestrial carbon fixed by C\textsubscript{3}
photosynthesis which is depleted in $^{13}\text{C}$. Our spot-sample data from 2005 show that the $\delta^{13}\text{C}$
value of dissolved inorganic carbon (DIC, $\delta^{13}\text{C}\text{DIC}$) decreased with increasing concentration of
total P (Fig. 2a) consistent with an increasing contribution of terrestrially-fixed carbon to the
inorganic carbon pool in productive lakes. Moreover, a time-integrated estimate of $\delta^{13}\text{C}$ based
on analysis of proteins within the silica frustules of epilithic lake diatoms ($\delta^{13}\text{C}_{\text{diatom}}$),
confirmed the strong negative relationships between $\delta^{13}\text{C}_{\text{diatom}}$ and lake P concentration (Fig.
2a). The lake $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{diatom}}$ values were also strongly correlated with other measures
of lake productivity: the mean concentration of phytoplankton chlorophyll $a$ (Pearson
correlation coefficient: $r= -0.70$ for DIC and $-0.92$ for diatoms, $P<0.001$ for both) and Secchi
depth (Pearson correlation coefficient: $r= 0.46$, $P<0.05$ for DIC and $r =0.88$, $P<0.001$ for
diatoms) (See Supplementary Fig. 2).

These carbon isotope data are consistent with our hypothesis that aquatic systems within
productive catchments receive more allochthonous biogenic carbon, relatively depleted in $^{13}\text{C}$,
than those in unproductive catchments. Furthermore, in each month and overall, high
concentrations of CO₂ are associated with the most negative values of δ¹³C_DIC (Fig. 2b) which suggests that high concentrations of CO₂ are linked to input from terrestrial C₃-fixed carbon. A similar relationship has been found for lakes in the North America and Finland sampled prior to ice-melt. The conventional explanation for excess CO₂ in a lake is in situ mineralisation of organic carbon produced in the catchment. This is unlikely in lakes where the concentration of DOC is low such as in the lakes studied here and an alternative hypothesis is that the CO₂ is produced in the catchment and brought in directly via water transfer. Hydrological pathways that link the terrestrial and aquatic components of a catchment often contain high concentrations of CO₂ which our hypothesis would predict. In other regions where aquifers contribute significantly to the water budget of a lake, CO₂ can be delivered by groundwater and emitted from the lake.

The source of CO₂ in these lakes was determined by a survey of the 33 streams entering 19 of lakes (excluding Thirlmere reservoir with many small inflowing streams). The δ¹³C_DIC values of the inflowing streams (Fig. 2a) also decreased in proportion to the P concentration in a nearly identical way to that of the lakes. These spot water samples were extended temporally by analysing the δ¹³C of stream bryophytes, which lack roots and are unable to use HCO₃⁻ as a carbon source requiring them to derive their inorganic carbon from CO₂ in water. Bryophyte δ¹³C also declined with total P (Fig. 2a) and the relationship between bryophyte δ¹³C and stream δ¹³CO₂ (See Supplementary Information for method of calculation) was close to 1:1 with an average discrimination of 14.3 ‰ against CO₂ (linear regression with standard errors in parenthesis, Bryophyte δ¹³C‰ = -14.3 (4.75) + 1.09 (0.26) stream δ¹³CO₂‰; adjusted R² = 0.45, P<0.001). These data support the direct input of CO₂ to lakes from
inflowing streams because the retention time in these short (typically less than 10 km), high-slope streams is too little for substantial oxidation of DOC. Furthermore, the mean stream concentration of DIC (0.37, SD = 0.24 mol m\(^{-3}\)) is nearly three times greater than the mean concentration of DOC (0.13, SD = 0.06 mol m\(^{-3}\)).

These data strongly suggest that the source of the excess CO\(_2\) lies in the terrestrial catchment. There was a strong positive relationship between the CO\(_2\) concentration in each lake and terrestrial Net Primary Productivity (NPP) i.e., lakes with higher mean concentrations of CO\(_2\) lie in more productive catchments (Fig. 3a). To estimate the proportion of carbon fixed by catchment NPP that is lost at the lake surface, CO\(_2\) efflux was estimated from the measured CO\(_2\) concentrations for each lake using a gas transfer velocity of 5.43 cm hr\(^{-1}\) based on annual mean wind speed measured at five of the lakes (see Supplementary Information for more detail on derivation). Excluding four lakes with a major lake upstream, there was a significant relationship between lake CO\(_2\)-efflux and NPP in the lake’s catchment (Fig. 3b). In contrast, stepwise regression showed that other possible explanatory variables including mean catchment slope, rainfall, discharge, stream length, residence time and concentration of DOC did not contribute significantly to explaining the variation in CO\(_2\)-efflux among lakes (Supplementary Information Table 4a). On average, 1.6% of the carbon fixed in the catchment is lost at the lake surface (linear regression with standard errors in parenthesis: net CO\(_2\) efflux = -0.85 \(10^{-2}\) (3.29 \(10^{-2}\)) + 1.56 \(10^{-2}\) (0.19 \(10^{-2}\)) * total catchment NPP; adjusted \(R^2\) = 0.84, \(P<0.001\); units are Gg C yr\(^{-1}\)). Using the minimum and maximum mean gas transfer coefficients in Supplementary Table 3, this ranged between 1.2 and 2.2% of catchment NPP. The mean loss of CO\(_2\) to the atmosphere is about 16-times larger from lakes than the loss of CO\(_2\) in the outflow river (Fig. 3b) assuming that the CO\(_2\) exiting the lake reaches atmospheric equilibrium during the passage downstream.
The global CO₂-efflux from lakes has been estimated previously from the product of the average CO₂ concentration (converted to an efflux using a gas transfer velocity as above) and an estimate of the global number of lakes and their size-distribution which is poorly constrained²⁰. This approach produces an estimate of 0.53 Pg C yr⁻¹. If the hypothesised link between catchment productivity and CO₂ losses from lakes is broadly correct and applicable globally, the product of global terrestrial NPP and our estimates of proportionate losses should produce a similar value. Using a value of CO₂-losses from lakes of 1.6% of NPP and an estimated global terrestrial NPP of 56.4 Pg C yr⁻¹, global CO₂-losses from lakes are about 0.9 Pg C yr⁻¹. The similar magnitude of the two estimates is consistent with the hypothesis that there is a broad link between catchment productivity and CO₂-losses from lakes. Work on CO₂-concentration in streams and rivers in the USA which found a strong positive, but likely indirect, correlation between CO₂ evasion and annual precipitation¹⁶ could also be explained by this hypothesis since precipitation and NPP are generally positively correlated over larger spatial scales²².

Our results reinforce the established link between lakes, their catchment and the global carbon-cycle.⁶,⁷. While the focus hitherto has been on the in situ oxidation of terrestrially-produced DOC as the cause of high concentrations of CO₂ in lakes, the results presented here demonstrate that high concentrations of CO₂ can also derive from terrestrially-fixed carbon broken down in the soil, and entering lakes directly. The lakes analysed in the present work had a maximum DOC concentration of 0.22 mol m⁻³ and lie in the lower quartile of a dataset of 7500 lakes where the median DOC concentration was 0.48 mol m⁻³. It is likely that in lakes where the DOC concentration is low the direct input of CO₂ will be important and vice versa, but further research is needed to define the relative importance of these two routes of carbon entry in different types of lakes.
Understanding these contrasting routes to CO₂ excess is critical in understanding the role of lakes in the global carbon cycle. The strong coupling of lakes to their terrestrial catchment mean that large scale factors that increase terrestrial productivity, such as increasing regional temperature and nitrogen deposition, plus local change in land use and management, will potentially increase the supply of CO₂ to lakes. This will consequently increase aquatic emissions of CO₂ to the atmosphere, potentially reducing gains in carbon sequestration made by enhanced terrestrial productivity. The concentration of CO₂ in lakes is much more likely to be controlled by land use than by rising atmospheric CO₂ concentrations, or temperatures²⁵. Increasing atmospheric CO₂ will consequently have little direct ecological impact on all but the most unproductive systems. At the largest scale, our hypothesis is highly relevant to global carbon-cycling models by providing a quantitative explanation of the link between terrestrial productivity and CO₂ losses from lakes. Recent studies²⁶ have concluded that experimental observations cannot quantify the impacts of land-cover changes on the global carbon cycle, so studies such as this are essential to understand processes delivering carbon through lake catchments and back to the atmosphere.

Methods

Depth-integrated lake water samples were collected with a 5 or 7 m tube. Alkalinity was measured by Gran titration and pH with a combination electrode. Total P was measured following²⁷. Carbon species were calculated following², using an estimate of ionic strength from the cation and anion analysis made in 2005. As a result of the low concentrations of DOC in these lakes⁸, DOC anions are estimated to have contributed on average 5.5% of alkalinity²⁸ which will not have had a major effect on the calculations of carbon speciation.
In 2005, water for stable isotope analysis was collected sub-surface in the 20 lakes on four occasions and for the 33 major inflowing streams in July. The carbon isotope ratio $^{13}\text{C}/^{12}\text{C}$ ($\delta^{13}\text{C}$) was analysed on the dissolved inorganic carbon (DIC). Submerged mosses or liverworts were collected in July 2005 from inflowing streams where present (22 of the 33 streams). Lacustrine diatoms were collected from five randomly selected stones at approximately 30 cm water depth in fourteen of the lakes in July 2005. The cleaned samples of diatom frustules were dried at 40°C for 24 h. Stable isotope analysis of proteins within the silica frustule was undertaken by high temperature combustion in an elemental analyser coupled to a ‘continuous flow’ isotope ratio mass spectrometer.

The land cover of each catchment was allocated to one of nineteen categories using the CEH satellite-based land cover map LCM2000. Net primary productivity (NPP) of the different land cover types is given in Supplementary Table 2 and catchment NPP was calculated as the product of cover and NPP, summed for each land cover category. Further details are available in the Supplementary Information.

Concentrations of CO$_2$ were converted to rates of CO$_2$ exchange estimated from hourly wind speed measurements at five of the lakes and four different relationships between wind speed and gas transfer (Supplementary Table 3).

Further details of all the methods are available in the Supplementary Information.

**References**


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Author contributions

S.C.M. conceived the work, led the analysis and co-wrote the manuscript. P.A.B. undertook the diatom isotope work and analysis and co-wrote the manuscript. A.W.S. undertook the remainder of the isotope measurements. M.M.D.V. led the field work.

Competing Financial Interests

There are no competing financial interests.

Figure legends
Figure 1 Effect of lake productivity on concentration of CO$_2$. Mean (●), maximum (▲) and minimum (■) concentrations of free CO$_2$ and approximate CO$_2$-excess for 20 lakes sampled four times a year in 1984, 1991, 1995, 2000, 2005 and 2010 vs mean concentration of total P between 1984 and 2010. The horizontal grey-line represents the mean air-equilibrium concentration (CO$_2$-excess equals 1) calculated from lake temperature and annual mean atmospheric partial pressure of CO$_2$ from ftp://ftp.cmdl.noaa.gov/ccg/co2/trends/co2_annmean_mlo.txt. The error bars represent one standard deviation. The regression lines relate the concentration of CO$_2$ to total P. The regression for mean CO$_2$ is (standard errors in parentheses): CO$_2$ (mol m$^{-3}$) = 0.0216 (0.0021) + 0.0012 (0.0001) total P (mg m$^{-3}$), adjusted $R^2 = 0.87$, $P<0.001$.

Figure 2 Relationship between inorganic and organic δ$^{13}$C values in lakes and streams and productivity and CO$_2$ concentration. a) Relationship between δ$^{13}$C of dissolved inorganic and organic carbon and mean concentration of Total P in lakes and streams and b) relationship between δ$^{13}$C of dissolved inorganic carbon and lake concentration of CO$_2$. Values of δ$^{13}$C for lake dissolved inorganic carbon for January (●), April (●), July (●) and October (●); solid regression line average for all months (all individual months also significant $P<0.05$ in July and $P<0.001$ in the other months). Results from July for stream dissolved inorganic carbon (▲, dashed regression line), organic carbon from lake epilithic diatom frustules (♦, solid regression line) and organic carbon from stream bryophytes (■, dashed regression line). All data from 2005.

Figure 3 Links between lake CO$_2$ concentration, CO$_2$-efflux and catchment productivity. a) Relationship between mean CO$_2$ concentration measured four times a year in 1984, 1991, 1995, 2000, 2005 and 2010 and mean NPP estimated from area of different land cover categories in the catchment; b) estimated CO$_2$-efflux from the lake surface (●) and loss of...
CO₂ to the downstream river (○) for lakes without another major lake upstream. The grey horizontal line in a) is the approximate mean air-equilibrium concentration.
Figure 1
Figure 2.
Figure 3.

**a**
- Mean CO$_2$ (mol m$^{-3}$) vs. Mean NPP in catchment (g C m$^{-2}$ yr$^{-1}$)
- $y = 1.76E-04x - 2.13E-02$
- $R^2 = 0.61$
- $P<0.001$

**b**
- Net CO$_2$-efflux (Gg C yr$^{-1}$) vs. Total catchment NPP (Gg C yr$^{-1}$)
- $y = 1.56E-02x - 8.46E-03$
- $R^2 = 0.85$
- $P<0.001$

$y = 9.56E-04x + 2.53E-04$
- $R^2 = 0.93$
- $P<0.001$