



Global Biogeochemical Cycles

RESEARCH ARTICLE

10.1002/2015GB005286

Key Points:

- Surface CO₂ concentrations of three large lakes are assessed over the last 150 years
- Nutrient concentration has been the primary, long-term control of lakes surface CO₂
- Over the last decades, climate warming can take over nutrient control on lake CO₂

Supporting Information:

- Texts S1–S3, Figures S1–S4, and Tables S1–S6

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Citation:

Perga, M.-E., S. C. Maberly, J.-P. Jenny, B. Alric, C. Pignol, and E. Naffrechoux (2016), A century of human-driven changes in the carbon dioxide concentration of lakes, *Global Biogeochem. Cycles*, 30, 93–104, doi:10.1002/2015GB005286.

Received 11 SEP 2015

Accepted 3 JAN 2016

Accepted article online 6 JAN 2016

Published online 1 FEB 2016

A century of human-driven changes in the carbon dioxide concentration of lakes

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Abstract Now that evasion of carbon dioxide (CO₂) from inland waters is accounted for in global carbon models, it is crucial to quantify how these fluxes have changed in the past and forecast how they may alter in the future in response to local and global change. Here we developed a sediment proxy for the concentration of summer surface dissolved CO₂ concentration and used it to reconstruct changes over the past 150 years for three large lakes that have been affected by climate warming, changes in nutrient load, and detrital terrigenous supplies. Initially CO₂ neutral to the atmosphere, all three lakes subsequently fluctuated between near equilibrium and supersaturation. Although catchment inputs have supplied CO₂ to the lakes, internal processes and reallocation have ultimately regulated decadal changes in lake surface CO₂ concentration. Nutrient concentration has been the dominant driver of CO₂ variability for a century although the reproducible, nonmonotonic relationship of CO₂ to nutrient concentration suggests an interplay between metabolic and chemical processes. Yet for two of these lakes, climatic control of CO₂ concentrations has been important over the last 30 years, promoting higher surface CO₂ concentrations, likely by decreasing hypolimnetic carbon storage. This new approach offers the unique opportunity to scale, a posteriori, the long-term impact of human activities on lake CO₂.

1. Introduction

Most lakes today are supersaturated with CO₂ [Cole et al., 1994] and release amounts of CO₂ to the atmosphere that must be accounted for in global carbon (C) models [International Panel on Climate Change, 2013]. Naturally, such observations have urged scientists to constrain better the contribution of lake CO₂ emissions to the global C budgets [Alin and Johnson, 2007; Maberly et al., 2013; Sobek et al., 2005]. In addition to estimating the scale of their current emissions, addressing how much these fluxes have changed in the Anthropocene will improve understanding of the role of lakes in the global carbon cycle and how they are affected by environmental change [Cole et al., 2007; Tranvik et al., 2009].

Lake CO₂ concentration is controlled by multiple, interconnected physical, chemical, and biological mechanisms related to (1) external carbon inputs [Maberly et al., 2013; Marce et al., 2015; Sobek et al., 2005], (2) CO₂ redistribution by hydrodynamics [Aberg et al., 2010; Vachon and del Giorgio, 2014], and (3) internal carbon processing, including metabolism [Del Giorgio et al., 1999] and pH-controlled changes in carbonate equilibria [Finlay et al., 2009; Stets et al., 2009]. The relative importance of these mechanisms will vary depending on the geomorphological and climatic contexts [Kortelainen et al., 2006]. Besides, all these mechanisms are expected to be affected by human activities at local (e.g., land use and related human-driven nutrient inputs [Kortelainen et al., 2006; Maberly et al., 2013]) and global scales (i.e., climate change [Finlay et al., 2015; Lepisto et al., 2014; Yvon-Durocher et al., 2012]) to which they are likely to react in different directions, amplitudes, and with potential interactions. The complexity of intertwined processes acting on lake CO_{2aq} is revealed by the apparent divergence in lake CO₂ response to environmental change. For instance, increased nutrient concentrations (or lake primary production) can cause either an increase [Kortelainen et al., 2006] or a decrease [Balmer and Downing, 2011; Hanson et al., 2004; Schindler et al., 1997] in lake CO₂ concentrations, depending on the ultimate impact of nutrients on the balance between primary production and respiration at the whole lake scale. Similarly, climate change has been predicted to raise, lower, or have no effect on CO₂ concentrations [Finlay et al., 2015; Flanagan and McCauley, 2008; Kosten et al., 2010; Sobek et al., 2005] depending on the

relative consequences of climate change on water temperature, hydrodynamics, or indirect effects on dissolved organic carbon (DOC) export from the watershed. Actually, the final outcome of environmental changes on lake $\text{CO}_{2\text{aq}}$ will depend on the magnitude of these mechanisms (inputs, internal processing, or distribution) for a given lake typology (whether lakes are deep or shallow, for instance [Flanagan and McCauley, 2008]) and the relative scale at which they are affected by the ambient changes. Forecasting lake CO_2 response to global change requires these apparent idiosyncrasies of lake responses to environmental forcings to be understood and taken into account over a temporal perspective.

If multidecadal monitoring of lake $\text{CO}_{2\text{aq}}$ would be the key to this issue [Cole *et al.*, 2007], attempts have been seriously hampered by the dearth of long-term data series until now. Among the longest data series reported so far, those by Finlay *et al.* [2015] on Canadian lake cover less than 15 years and those by Maberly *et al.* [2013] on UK lakes cover 26 years but sampled at a 5 year frequency. Since climatic trends are defined over a 30 year period to filter out interannual anomalies (World Meteorological Organization, www.wmo.int), even longer data sets are required to disentangle adequately the actual role of climate and other human pressures on $\text{CO}_{2\text{aq}}$ long-term changes [Catalan *et al.*, 2009; Leavitt *et al.*, 2009] and how their relative contributions may shift over time. In this work, we explore the role that paleolimnological records could play in expanding the time frame of CO_2 monitoring data sets and therefore provide a unique opportunity to scale up the long-term consequences of human global and local changes on lakes CO_2 dynamics. The first step of this study was to develop a quantitative proxy for CO_2 concentrations in lake surface waters. Then the long-term history of CO_2 concentration was reconstructed for three temperate lakes that have undergone documented human modifications in hydrodynamics caused by climate change, internal processes caused by changes in nutrient load, and carbon inputs caused by alterations of their hydrological inflows. Finally, the temporal dynamics of environmental forcings and lakes CO_2 were confronted in order to assess the relative influence of each human-driven factor on lakes CO_2 variability over time.

2. Material and Methods

2.1. Study Sites

Lakes Annecy, Bourget, and Geneva are large (28–551 km²) and deep (82–309 m) temperate and monomictic lakes located at the French edge of the Western Alps (Figure 1a). Of comparable geomorphology and geochemical backgrounds, these neighboring lakes have clear and moderately alkaline waters (alkalinity = 1.5–2 meq L⁻¹) and long water residence time (4–15 years). Concentrations of dissolved organic carbon are low and fairly stable over the last decades (<1–2 mg C L⁻¹ [Rodríguez-Murillo and Filella, 2015]). The dissolved carbon pool is largely dominated by inorganic carbon (15–20 times more abundant than organic carbon). pH typically exceeds 8.1 in the epilimnion in summer (Text S1 and Table S1 in the supporting information). All three lakes have been exposed to similar climatic variability, with a 2.0°C increase in air temperatures over the twentieth century, i.e., twice the global average (Figure 1b), but no clear trend for mean annual precipitation [Perga *et al.*, 2015].

Despite their similar geomorphology and geographical proximity, the three studied lakes have not been equally thermally vulnerable to climate change over the last 30 years (Figures 1c and 1d) [Perga *et al.*, 2015]. Lake Annecy is the smallest of the three lakes, the most sheltered from winds, and the least hydrologically active. Consistently, it is the one for which the effects of climate warming on epilimnetic water temperatures are the strongest, with a +2.4°C increase between the early 1970s (as compared to +1.5°C for Lake Geneva over the same time period, Figure 1c) and the current period and a 2.5 m thermocline deepening over the last 20 years (Figure 1d). In lakes Geneva and Bourget, the thermal effects are weaker, with, however, different physical consequences. In Lake Geneva, surface waters warmed up more than in Lake Bourget (+1.2°C and +0.6°C, respectively, since the mid-1980s), but with no deepening of the thermocline, in contrast to Lake Bourget (+1.5 m over the last 20 years [Perga *et al.*, 2015], Figures 1c and 1d).

All lakes have endured well-documented and analogous local human activities on their watersheds over the twentieth century [Perga *et al.*, 2015], the main one being synchronous changes in total phosphorus (TP) inputs and lake concentrations (Figure 2a), as revealed by previous paleolimnological reconstructions [Berthon *et al.*, 2014]. Oligotrophic by the end of the nineteenth century, all three lakes became enriched in phosphorus from urban wastewater release as early as the 1920s, with a clear intensification of phosphorus

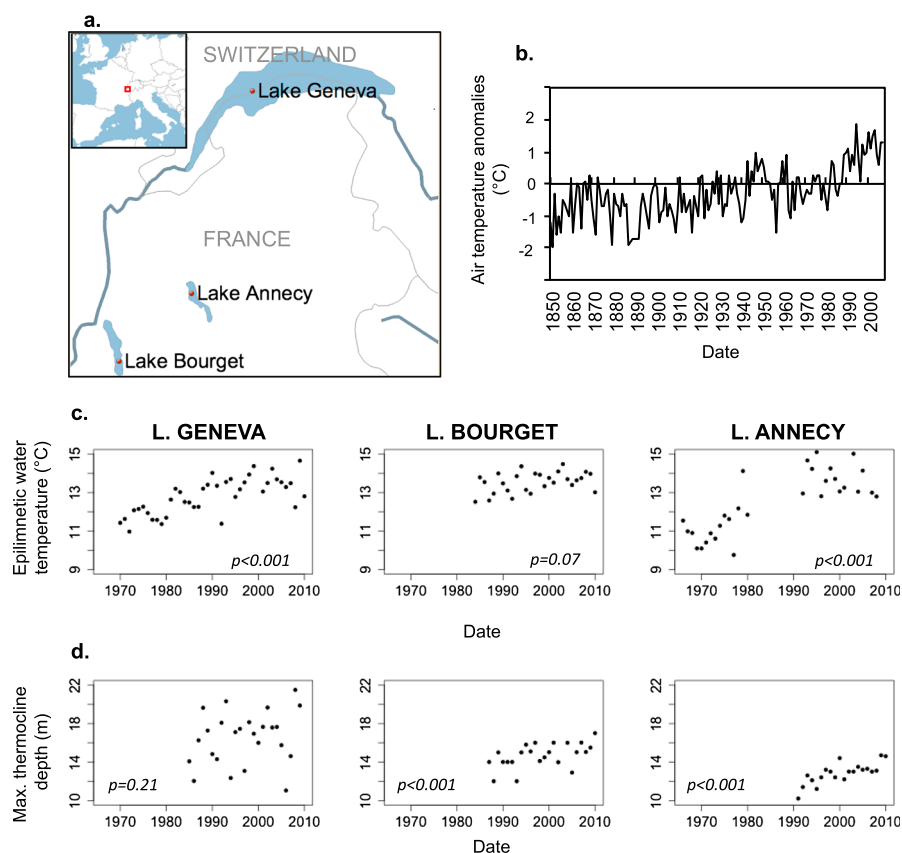


Figure 1. Lakes location, climate, and recent hydrological trends. (a) Lakes location. (b) Trends in air temperature anomalies for all three lakes, extracted from the HISTALP database. (c) Changes in lakes thermal characteristics over the last 25 years. Figure 1c shows annual surface (0–15 m) water temperatures. (d) Thermocline maximum depths over time, computed as the depth of the 14°C water layer at the end of summer for the three study lakes. p values are those associated to Mann-Kendall trend tests.

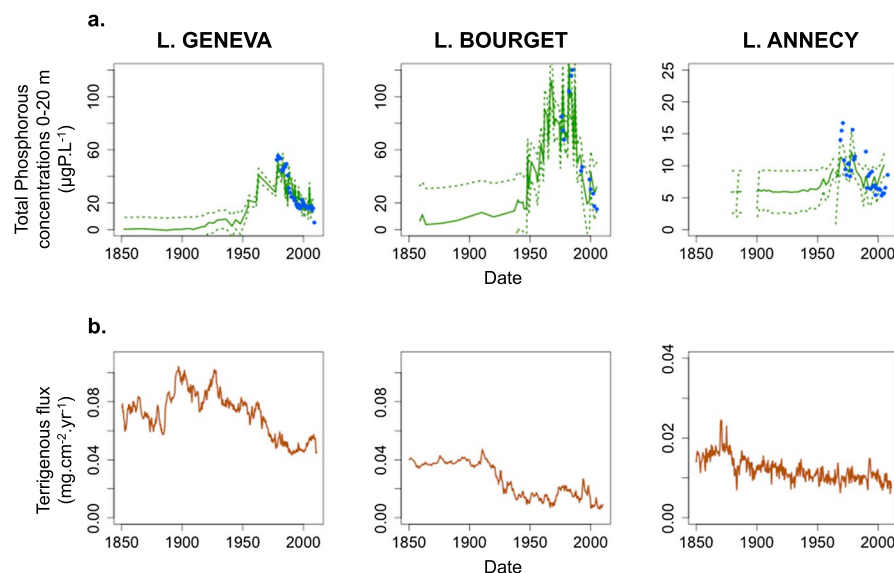


Figure 2. Dominant local environmental forcings for the three lakes. (a) Changes in surface TP for lakes Geneva, Bourget, and Annecy as reconstructed from a *Daphnia*-based transfer function (continuous green line; $\pm 95\%$ confidence interval [Berthon *et al.*, 2014]) and compared to actual measures (blue dots). (b) Changes in terrigenous fluxes for lakes Geneva, Bourget, and Annecy [Jenny *et al.*, 2014a]. Note changes in the y scale for Lake Annecy.

inputs from 1940 onward. Increased TP concentrations favored higher algal biomass [Jenny *et al.*, 2013; Lachavanne, 1980; Perga *et al.*, 2010] and triggered deep hypoxia [Jenny *et al.*, 2014a]. The three lakes reached different levels of maximum eutrophication (oligomesotrophic status for Lake Annecy in 1969 and eutrophic status by the late 1970s for the other two lakes; Figure 2a). Phosphorus reduction efforts proved successful in all three lakes. Based on their phosphorus concentrations, Lake Annecy is currently back to oligotrophy ($\text{TP} < 6 \mu\text{g P L}^{-1}$), whereas the other two are still oligomesotrophic ($\text{TP} < 20 \mu\text{g P L}^{-1}$, Figure 2a). Other significant local disturbance over the last century includes regulations of tributary discharges, with subsequent consequences on detrital inputs from terrigenous supplies [Jenny *et al.*, 2014a; Perga *et al.*, 2015]. Since 1880, terrigenous fluxes have decreased by 50%, 40%, and 45% for lakes Geneva, Bourget, and Annecy, respectively, caused by the sequential construction of dams built on the inflowing rivers to control floods and high river discharges, while the role of climate change on these declining fluxes was only marginal [Jenny *et al.*, 2014a]. The reconstructed terrigenous fluxes also confirm the contrasting hydrological conditions among the three lakes, with highest fluxes in Lake Geneva, medium in Lake Bourget, and lowest in Lake Annecy (Figure 2b).

2.2. Lake Coring and Core Analyses

Palaeolimnological data were collected from several short sediment cores (35 to 64 cm long) taken from the deepest zones of the lakes in 2009 (Lakes Bourget and Annecy) and 2010 (Lake Geneva) using a quadruple gravity corer (UWITEC, Mondsee, Austria). Accurate chronologies allowed for high-resolution sampling and estimates for accumulation rates [see Alric *et al.*, 2013]. Previous palaeolimnological studies conducted in the same program provided validated paleoproxies for TP (inferred from a transfer function based on absolute changes in the sediment flux of *Daphnia* remains and confronted to monitoring data when available [Berthon *et al.*, 2014]) and terrigenous supplies (inferred from titanium (Ti) fluxes measured by X-ray fluorescence and validated against flooding records from river discharge data [Jenny *et al.*, 2014a, 2014b]). Planktonic cladoceran remains (mainly *Bosmina* carapaces) were isolated from sediment samples as in [Perga, 2011], and $\delta^{13}\text{C}$ measurements were measured in the SINLAB, New Brunswick, Canada, on a Finnigan Delta Plus mass spectrometer interfaced via a Conflo II to a NC2500 elemental analyzer. Internal laboratory standard precision and accuracy were $<0.1\%$.

2.3. Calibration of the Paleoproxy for $\text{CO}_{2\text{aq}}$

CO_2 concentration is the dominant driver of plankton $\delta^{13}\text{C}$ in oceans and lakes [Degens *et al.*, 1968; Smyntek *et al.*, 2012], and we first tested whether this allows lake surface CO_2 concentrations to be determined quantitatively from changes in the $\delta^{13}\text{C}$ values of cladoceran remains retrieved from sediment cores. Our working hypothesis was that the $\delta^{13}\text{C}$ values of pelagic cladocerans (a zooplanktonic group herein dominated by algal consumers) would mirror changes in surface $\text{CO}_{2\text{aq}}$ in both contemporaneous and archived samples.

The monthly data for cladoceran $\delta^{13}\text{C}$ values were available for Lake Geneva in 2002–2004 [Perga and Gerdeaux, 2005], and for these dates, CO_2 concentrations in the top 5 m of the water column was computed from temperature, pH, alkalinity and ionic strength as in Cole *et al.* [1994] (Data copyright SOERE OLA-IS, INRA Thonon-les-Bains, CISALB, CIPEL, SILA, developed by Eco-Informatics ORE INRA Team). A log linear regression model linking surface lake CO_2 concentrations and cladoceran $\delta^{13}\text{C}$ values was computed from the Lake Geneva monthly monitoring data set (2002–2004) and compared with a model previously developed for Windermere [Smyntek *et al.*, 2012].

The ability of the model to predict past CO_2 concentrations was thereafter tested against the monitoring data; long-term trends in CO_2 concentrations (top 5 m) over the last 130 years were reconstructed from subfossil cladoceran $\delta^{13}\text{C}$ values using the model established in the previous step and compared with the CO_2 concentrations computed from the chemical data for years and lakes for which they were available (Data copyright SOERE OLA-IS, INRA Thonon-les-Bains, CISALB, CIPEL, SILA, developed by Eco-Informatics ORE INRA Team; 1978–2008 for Lake Geneva and 1967–1976 for Lake Annecy; there are no long-term data for Lake Bourget). Because cladoceran subfossil $\delta^{13}\text{C}$ records the isotope values of their parent populations in the summer [Perga, 2011], CO_2 concentrations, as reconstructed from subfossil remains, were expected to correspond to summer values. They were therefore compared to the CO_2 concentrations computed during June, July, and August of the corresponding year and the entire summer average (June–August) CO_2 concentrations.

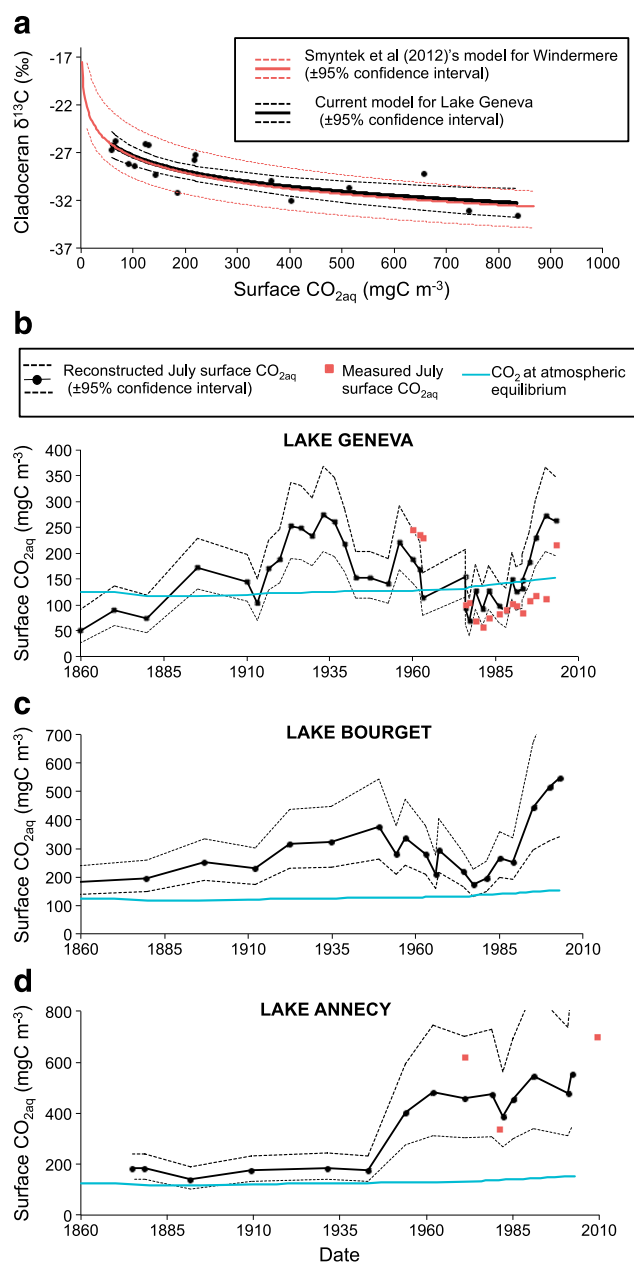


Figure 3. Quantitative reconstruction of historic lake CO₂ concentrations from $\delta^{13}\text{C}$ of cladoceran subfossils. (a) Model linking the $\delta^{13}\text{C}$ of contemporary pelagic cladocerans to average CO₂ concentrations between 0 and 5 m depths in Lake Geneva, 2002–2003, and comparison to the model previously built for Windermere (in red) [Smyntek et al., 2012]. (b–d) Temporal changes in surface CO₂ concentrations as reconstructed from $\delta^{13}\text{C}$ of subfossil cladocerans recovered from dated cores (continuous line, $\pm 95\%$ confidence interval) and comparison to measured July CO₂ concentrations over the 0–5 m depths (closed squares, averaged over 3–5 years) for lakes Geneva (Figure 3b) and Annecy (Figure 3c). Similar observational data were not available for Lake Bourget (Figure 3d). Blue lines represent changes in CO₂ concentration in equilibrium with the atmosphere.

2.4. Identifying Environmental Drivers of CO_{2aq} Over Time

Once the proxy validated, CO_{2aq} and subsequent lake CO₂ enrichment (expressed as CO_{2excess} relative to the atmosphere, in order to account for rising atmospheric CO₂ over time, www.esrl.noaa.gov/gmd/ccgg/trends/) were then reconstructed over the last 150 years for all three lakes. The isotopic consequence of the Suess effect (approximately 2‰ decline in atmospheric CO₂ $\delta^{13}\text{C}$ over the last 150 years) has been neglected since it only marginally affects the $\delta^{13}\text{C}$ of lake dissolved inorganic carbon (reported maximal effects are <1‰ in the oceans [Black et al., 2011]) which, in turn, seldom influences that of planktonic organic matter [Finlay, 2004]. Generalized additive models (GAMs) [Hastie and Tibshirani, 1990] were used to investigate the relationships between CO_{2excess} and external forcings as well as to separate, quantify, and identify time periods of their influences [Simpson and Anderson, 2009]. Long-term air temperature anomalies (www.zamg.ac.at/histalp/), reconstructed TP, and terrigenous supply were introduced as the predictor variables in the model. Both paleoproxies for TP and CO_{2excess} are provided by independent measures and are not mathematically derived from each other. GAM were run on all possible combination of factors and model selection procedures were based on percent of explained deviance, residual distribution and best fit between observed and modeled data.

The relationships between CO_{2excess} and external factors were then modeled using linear or polynomial regressions (order based on the estimated degrees of freedom of the terms of the GAM fitted models) and analysis of covariances (following linear or cubic models) [Huitema, 2011]. The most parsimonious models were chosen based on the Akaike information criterion and Bayesian information criterion (AIC-BIC). All tests were performed on R2.11.0 statistical software using dedicated packages.

| Table 1. Parameters of the Selected Generalized Additive Models Performed on $\text{CO}_{2\text{excess}}$ for All Three Lakes ^a | | | | |
|---|------------------------------|-----|----------------|--|
| Lake | Parameters of the Best Model | Edf | <i>p</i> value | Deviance Explained by the Best Model |
| Geneva | TP | 3.7 | 5.10^{-3} | 68% (60% for TP alone) |
| | Terrigenous flux | 2.1 | 0.059 | |
| Bourget | TP | 3.4 | 0.05 | 69% (70% for TP alone) |
| | July temperature | 1 | 0.03 | |
| Annecy | TP | 2.9 | $<2.10^{-7}$ | 90% (on univariate model) 32% (on univariate model) |
| | July temperature | 1 | 0.02 | |

^aDetails on selection procedures in Text S3. Edf: estimated degrees of freedom.

3. Results

3.1. Validation of Cladoceran Subfossil $\delta^{13}\text{C}$ as a Proxy for CO_2 Concentration

The strength of the relationship between cladoceran $\delta^{13}\text{C}$ and CO_2 concentrations was first validated with contemporary data (Figure 3a; log linear relationship, $y = -2.32 \ln x - 22.44$; $R^2 = 0.64$, $p = 6.10^{-5}$) yielding a strikingly similar result to that found before for Windermere ($y = -2.42 \ln x - 22.30$ [Smyntek *et al.*, 2012]). Second, historical trends of reconstructed CO_2 concentrations were compared to available monitoring data. Of the measured $\text{CO}_{2\text{aq}}$ values computed over the 0–5 m depths for Lakes Geneva and Annecy and averaged over the time resolution of the CO_2 paleoreconstructions (3–5 years) (Figures 2b and 2c), 60% fell within the 95% confidence interval of the fit. More importantly, the temporal trends derived from monitored and reconstructed data in Lake Geneva were significantly correlated in July (Spearman's rank correlation, $\rho = 0.55$,

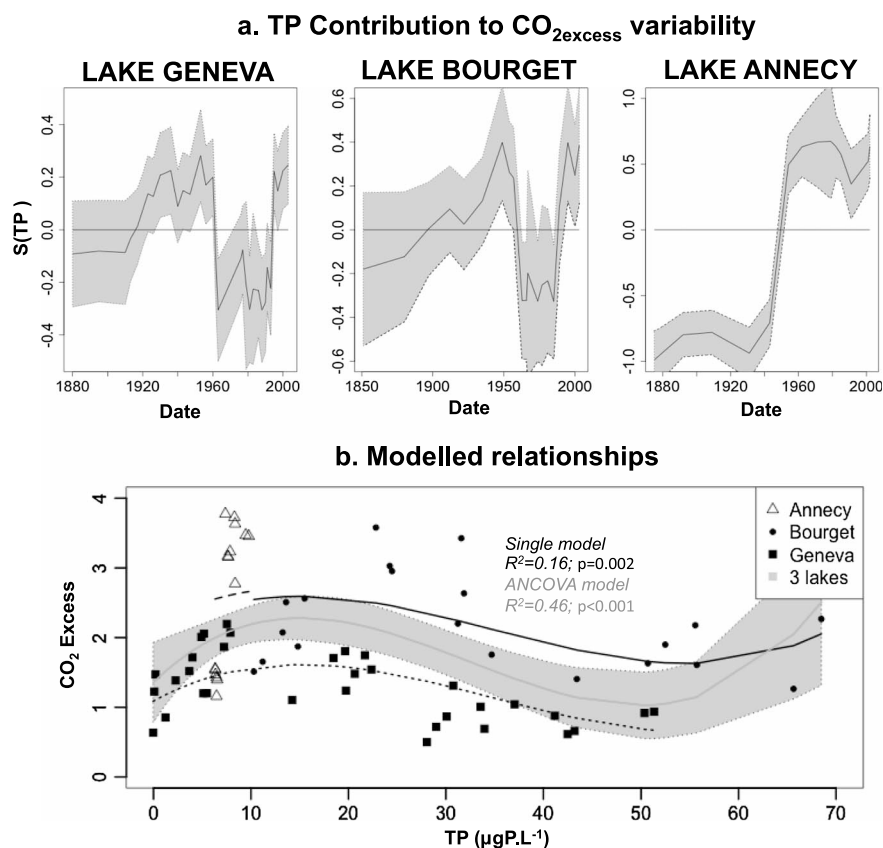


Figure 4. Relationships between $\text{CO}_{2\text{excess}}$ and lake concentrations of total phosphorus (TP) over the last century for Lakes Geneva, Annecy, and Bourget. (a) Contributions ($s(\text{TP})$; average \pm approximately 95% confidence interval) of changes in lake TP to the observed changes in $\text{CO}_{2\text{excess}}$ over time. Positive contributions indicate that TP was linked to higher $\text{CO}_{2\text{excess}}$ at a given time. (b) Single and ANCOVA models linking $\text{CO}_{2\text{excess}}$ to TP.

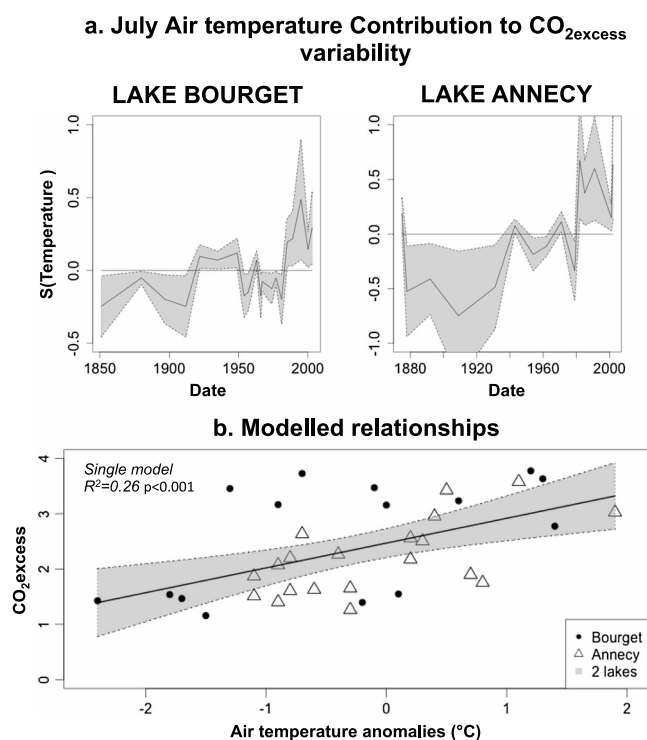


Figure 5. Relationships between CO₂^{excess} and air temperature anomalies over the last century for Lakes Annecy and Bourget. Note, air temperature did not significantly explain CO₂^{excess} over time for Lake Geneva. (a) Contributions (*s*(July temperature); average \pm approximately 95% confidence interval) of changes in air temperature to the observed changes in CO₂^{excess} in Lake Bourget and Lake Annecy. Positive contributions indicate that air temperature was linked to higher CO₂^{excess} at a given time. (b) Modeled relationship linking CO₂^{excess} to air temperature anomalies for both lakes.

Text S3). Estimated degrees of freedom of the TP term in the selected GAM were, in all cases, close to 3, indicating that the best fit between TP and CO₂^{excess} was cubic rather than linear. Cubic models were, for each lake, the most parsimonious as compared to quadratic and linear models, resulting in the lowest values of AIC and BIC (Table S3). The relationship relating CO₂^{excess} to TP over time indeed fitted a third-order polynomial regression in all three lakes, with yet significant between-lake differences within the model parameters (Figure 4d). The polynomial relationship between CO₂^{excess} and TP accounted for 46% of total CO₂ variability when lake identity was included as a grouping factor. The earlier eutrophication phase (TP increases below 15–25 $\mu\text{g P L}^{-1}$) caused the CO₂ concentrations in all three lakes to be twofold higher than atmospheric equilibrium (Figures 3b–3d). Above this 15–25 $\mu\text{g P L}^{-1}$ threshold (then only for Lakes Geneva and Bourget), CO₂^{excess} decreased (Figures 3 and 4) so that during their maximum eutrophication, in the summers of the 1970s and early 1980s, these two lakes returned to CO₂ equilibrium with the atmosphere. The decreasing TP concentrations because of TP abatement measures triggered the expected reversible response for CO₂^{excess}, i.e., returning the lakes to CO₂ supersaturation, until the lower TP threshold was reached again (Figures 3 and 4).

Air temperature also contributed substantially to changes in CO₂ concentrations of Lakes Annecy and Bourget where its contribution to driving CO₂ changes over the last 30 years was of a similar magnitude to that of TP (Table 1 and Figures 5a and 5b). Climate warming did not contribute significantly to the changes in CO₂ concentrations for Lake Geneva over the same period ($p = 0.3$). The linear model linking CO₂^{excess} to air temperature anomalies was common between Lakes Annecy and Bourget (Figure 4c). The common slope coefficient of $0.31^{\circ}\text{C}^{-1}$ (standard error = 0.07) reveals that the variability in air temperature over the twentieth century ($+2.0^{\circ}\text{C}$ in this region) could, alone, result in a 60% increase of CO₂ concentrations in July for these two lakes.

$p = 0.02$, not feasible for Lake Annecy due to the limited length of the data set), confirming that if absolute values might not be totally accurate, reconstructed CO₂ trends reliably reflect relative changes over time (Figures 2b and 2c). Measured CO₂ concentrations in July are 2–3 times lower than annual average values but follow very similar interannual trends (Text S2 and Figure S2). Therefore, the relative importance of the environmental factors controlling the temporal variability in annual and July CO₂ concentrations should be similar.

3.2. Long-Term Changes in CO₂^{aq} and Environmental Drivers

All three lakes were initially in near equilibrium with the atmosphere in the summers of the late 19th century but switched back and forth between equilibrium and supersaturation with CO₂ over the course of the 20th century and were supersaturated in the 21st century (Figures 3b–3d). GAMs on data from all three lakes identified TP as the dominant driver of CO₂^{excess} over the last 150 years, explaining alone between 65% and 90% of its variability over time (Table 1 and Figures 4a–4c; details for GAM selection procedures provided in

Terrigenous supply from rivers was not included as a driver of $\text{CO}_{2\text{excess}}$ in the retained models, except for Lake Geneva for which it was marginally significant (Table 1). For this lake, detrital inputs explained about 10% of the temporal deviance of $\text{CO}_{2\text{excess}}$ and time periods of high terrigenous supplies, prior to dams and regulation of high river discharges, coincided with higher $\text{CO}_{2\text{excess}}$ (S3).

4. Discussion

4.1. CO_2 Paleoproxy

Modern cladoceran $\delta^{13}\text{C}$ values were correlated with $\text{CO}_{2\text{aq}}$ and the isotopic record over decades (50 years for Lake Geneva and 20 years for Lake Annecy) consistently reflected changes in summer $\text{CO}_{2\text{aq}}$. The proxy is based on the dominant control that $\text{CO}_{2\text{aq}}$ exerts on phytoplankton $\delta^{13}\text{C}$ through isotope fractionation during carbon fixation (whether CO_2 or bicarbonate with different equilibrium isotopic values [Degens *et al.*, 1968; Smyntek *et al.*, 2012]), which is then further transmitted to phytoplankton consumers. Possible mechanisms supporting the log linear relationship are provided in Smyntek *et al.* [2012] and have been shown in culture for some marine algae [Burkhardt *et al.*, 1999]. They are therefore not repeated here. Although dissolved inorganic carbon (DIC) $\delta^{13}\text{C}$ values can vary considerably within and among lakes, it is not explicitly accounted for in the original [Smyntek *et al.*, 2012] model. Actually, the control by C-substrate limitation on isotope fractionation during photosynthesis is so strong that the final planktonic $\delta^{13}\text{C}$ is weakly influenced by DIC $\delta^{13}\text{C}$ and $\text{CO}_{2\text{aq}}$ is by far the dominant factor explaining planktonic $\delta^{13}\text{C}$ variability over space and time [Gu *et al.*, 2011]. Besides, both the Rayleigh effect (increased DIC $\delta^{13}\text{C}$ at low $\text{CO}_{2\text{aq}}$ due to selective removal of ^{13}C -depleted CO_2 by photosynthesis) and isotope effect during mineralization of organic matter (CO_2 regenerated by mineralization has low DIC $\delta^{13}\text{C}$) combine to create a strong, negative covariation of $\text{CO}_{2\text{aq}}$ and DIC $\delta^{13}\text{C}$ in lakes over space and time [Finlay, 2004; Gu *et al.*, 2011], which even reinforces the relationships between $\text{CO}_{2\text{aq}}$ and plankton $\delta^{13}\text{C}$. Therefore, omitting DIC $\delta^{13}\text{C}$ within the model shall affect its reliability at most marginally.

Over 500 mg C m^{-3} (42 mmol C m^{-3}), cladoceran $\delta^{13}\text{C}$ values are less sensitive to $\text{CO}_{2\text{aq}}$ than at lower concentration. However, this threshold exceeds the maximum summer averaged $\text{CO}_{2\text{aq}}$ in the 40 year monitoring of Lake Geneva (Figure S4) but could introduce uncertainty in $\text{CO}_{2\text{aq}}$ estimates for Lake Annecy. More generally, it might restrict the use of the proxy to lakes with low to moderate $\text{CO}_{2\text{aq}}$.

A prerequisite for the use of subfossil cladoceran $\delta^{13}\text{C}$ as a proxy for $\text{CO}_{2\text{aq}}$ is that the phytoplankton is the dominant carbon source for the cladocerans for the entire study period. All three lakes studied here are deep, and their bathymetry is concave, and cladoceran subfossil communities were strongly dominated (75–100%) by planktonic species at all times [Alric *et al.*, 2013]. The only exception was for the period during 1880–1912 for Lake Geneva when *Sida cristallina* (a littoral species) was quite abundant ($\approx 40\%$), but this period did not correspond to any clear break in the isotope records for Lake Geneva. Furthermore, restricting the data set to the time of overwhelming planktonic dominance (post-1920) did not modify the overall conclusions. The assimilation of terrestrial carbon by zooplankton could further blur the isotope records [Jones *et al.*, 1998], but previous studies on these lakes did not provide evidence of allochthony for the cladocerans in these lakes, even at seasons of very low primary production [Perga and Gerdeaux, 2006; Perga *et al.*, 2009]. In shallow, small, and humic lakes in which methane oxidizing bacteria can constitute a significant food source for pelagic cladocerans, the $\delta^{13}\text{C}$ of *Daphnia* was shown to be more sensitive to CH_4 rather than CO_2 concentrations [Schilder *et al.*, 2015] but this is unlikely to be important in our study lakes. Overall, the high similarity of the relationships linking CO_2 and modern cladoceran $\delta^{13}\text{C}$ between Lake Geneva and Windermere supports the general applicability of the proxy in relatively deep lakes with low to moderate CO_2 concentrations. However, although promising, further application of the proxy to other lakes will require further validation.

4.2. Causes of CO_2 Supersaturation

On an annual base, the studied lakes are presently supersaturated with CO_2 (Figures 2 and S2) and hence sources to the atmosphere. Nevertheless, the planktonic communities of all three lakes are net autotrophic, providing further evidence that elevated concentrations of CO_2 do not necessarily indicate heterotrophy [Maberly *et al.*, 2013]. In these lakes, inputs of terrestrial organic matter represent less than 8% of the total primary production and are totally counterbalanced by outflows (Table 2). Organic carbon concentrations in inflowing rivers are low (close to $1\text{--}2 \text{ mg L}^{-1}$) and have been fairly stable over the last decades at least for

Table 2. Annual Estimates of Main Carbon Fluxes and Pools for the Three Study Lakes^a

| C Pool and Flux | Lake Geneva (Large Basin) | Lake Bourget | Lake Annecy |
|--|---|----------------------------------|------------------------------------|
| Average net primary production (Gg C yr ⁻¹) | 100–175 (range over 1998–2010) ^b | 50 (2005)–23 (2011) ^b | 6.1 (1998)–4.6 (2011) ^b |
| Allochthonous organic carbon inputs (Gg C yr ⁻¹) | 14 (1996)–11.3 (2010) ^b | 0.5 (2006–2011) ^b | 0.2 ^b |
| Exported organic carbon (Gg C yr ⁻¹) | 10 (2010) ^b | 0.5 ^b | 0.2 ^b |
| Organic carbon accumulation (Gg C yr ⁻¹) | 8 (2000–2010) | 1.2 (2000–2009) | 0.2 (2000–2006) |
| Inorganic carbon accumulation (Gg C yr ⁻¹) | 16 (2000–2010) | 4.3 (2000–2009) | 1.5 (2000–2006) |
| Pelagic metabolism | Likely autotrophic ^c | Autotrophic ^d | Autotrophic ^e |

^aPrimary production has been assessed through incorporation of inorganic ¹⁴C as part of the long-term monitoring of the three lakes. Organic carbon inputs and outputs were estimated as the product of inflows and outflows discharges and concentrations. Organic and inorganic carbon accumulations were estimated as the product of sediment accumulation rate (in dry weight) by percent sediment content in organic or inorganic matter as measured by Rock-Eval pyrolysis.

^bData copyright SOERE OLA-IS.

^cHanson et al. [2004].

^dGroleau et al. [2000].

^eJanjua and Gerdeaux [2009].

the main tributaries of Lake Geneva as for similar rivers across nearby Switzerland [Rodríguez-Murillo et al., 2015]. Although rates of organic matter burial suggest that more than 90% of the lake organic matter gets oxidized within the lake water column, mineralization alone cannot explain the current C supersaturation and CO₂ efflux.

Instead, CO₂ supersaturation of these lakes arises from catchment inputs of inorganic carbon, and considering their alkalinity (>1 meq L⁻¹) and the geology of the surrounding catchment, likely through carbonate weathering [Marce et al., 2015]. The CO₂ concentrations in the two dominant tributaries of Lake Geneva are consistently higher than in the lake (Figure S4), and their role as the main source of DIC to the lake has been confirmed from isotope-based mass budgets [Vennemann et al., 2006]. Monitored long-term changes in the rivers and lake CO_{2aq} are, however, unrelated (Figure S4) because the lakes have long water residence time (3.8–15 years), and an internal control of decadal changes in surface CO₂ (i.e., through processes occurring within the lakes) is more plausible [Bade et al., 2004], as also supported by DIC δ¹³C data [Vennemann et al., 2006]. Consistently, decadal variability in terrigenous supplies was not a significant driver of CO_{2excess} over time. Yet its marginal significance in Lake Geneva, which is the most hydrologically active of these lakes, suggests that high detrital inputs from rivers might affect the lake carbon budget during time periods marked by high flooding regime or extreme flooding events. Recent studies have indeed pinpointed the role of intense precipitation events in lake CO₂ dynamics [Vachon and del Giorgio, 2014] although the current monitoring data do not allow the underlying mechanisms (e.g., inputs of DOC, CO₂, or reallocation of hypolimnetic CO₂ to the surface [Vachon and del Giorgio, 2014]) whereby episodes of high river discharge may increase lake surface CO_{2aq}. Nevertheless, the fact that the paleorecords, in spite of their low temporal resolution, could capture their contribution to the lake CO_{2aq} variability reinforces the confidence in the sensitivity of the developed method.

4.3. Impacts of Nutrient Load on Lake CO_{2aq}

The concentration of TP was found to be the major factor controlling summer concentrations of CO_{2aq} in these lakes, over the last century. While valid in these P-limited lakes [Finger et al., 2013] with long water residence time, it might not be true for lakes with shorter flushing rates, for which TP loads were shown to covary with DIC [Maberly et al., 2013] or DOC [Kortelainen et al., 2006] inputs from their watersheds. Consistently, the TP concentration in the Rhone river in 1975–2011, the main tributary of Lake Geneva, was not related to its concentration of CO₂ ($R^2 = 0.01$; $p = 0.25$ on linear and $R^2 = 0.06$; $p = 0.30$ on cubic fit) nor DOC ($R^2 < 0.01$; $p = 0.27$).

The nonmonotonic relationship of CO₂ to TP implies that underlying mechanisms might be more complex than usually envisaged. First, TP acts on CO₂ concentrations through its positive influence on primary production, causing direct CO₂ removal by photosynthetic carbon fixation [Schindler et al., 1997]. Therefore, productive lakes are usually expected to be CO₂ undersaturated in summer [Balmer and Downing, 2011]. Second, respiration also increases with higher lake trophic status, so that the final relationship linking metabolism to TP might be hump shaped, inverting at TP concentrations typical for mesotrophic status (20–30 μg P L⁻¹ [Del Giorgio and Peters, 1994; Prairie et al., 2002]), as we observed here. Third, calcite

precipitation induced by a photosynthetic-driven pH increase is a significant source of CO_2 to the epilimnion in even moderately alkaline lakes [Stets *et al.*, 2009]. Calcite precipitation has been estimated to provide $40\text{--}60\text{ g C m}^{-2}$ as CO_2 in summer for all three lakes as compared to the $150\text{--}250$, $120\text{--}240$, and $40\text{--}60\text{ g C m}^{-2}$ of CO_2 fixed by primary production in Lakes Geneva, Bourget, and Annecy, respectively (Table 2). Fourth, coprecipitation of phosphate with calcite (as apatite) may produce a negative feedback reducing primary productivity and CO_2 removal [Murphy *et al.*, 1983]. Fifth, calcite precipitation is inhibited by TP with threshold values ($>20\text{ }\mu\text{g P L}^{-1}$ [House, 1990]) that coincide with our observations since phosphate coprecipitation with calcite contributes to limit internal inputs of CO_2 by calcite precipitation at TP concentrations $>20\text{ }\mu\text{g P L}^{-1}$. The model suggested a further increase in CO_2 for TP $>50\text{ }\mu\text{g P L}^{-1}$. However, observational data are scarce above this TP threshold and further investigations would be required to evaluate whether the model predictions are realistic for more eutrophic situations. Regardless of the precise mechanism, an increase in nutrient concentration ($<20\text{ }\mu\text{g P L}^{-1}$) appears to first promote and then diminish (TP $>20\text{ }\mu\text{g P L}^{-1}$) lake CO_2 concentrations, through a complex combination of biogeochemical processes, the outcome of which can be reproduced by a polynomial relationship. Threshold values need further investigation and may vary among lakes, depending on the relative importance of the processes involved.

4.4. Impacts of Atmospheric Warming on Lake $\text{CO}_{2\text{aq}}$

Air temperature also contributed substantially to changes in CO_2 concentrations of Lakes Annecy and Bourget where its effect on CO_2 concentration over the last 30 years was of a similar magnitude to that of TP (Figure 4). There is evidence that lakes Geneva and Annecy have become warmer over the last decades, and this could increase surface CO_2 concentrations through temperature dependency of internal processes (metabolism [Yvon-Durocher *et al.*, 2012] and calcite precipitation [Homa and Chapra, 2011]) even though increasing temperature reduces CO_2 solubility. However, effects of increasing water temperature on CO_2 production might not be the only or major process explaining the link between $\text{CO}_{2\text{excess}}$ and air temperature, especially since the warmer surface waters of Lake Geneva did not show any climate-driven increase in their CO_2 over the last decade (Figure 1). The further consequences of climate warming on thermal stratification and the depth of the mixed layer may also affect CO_2 vertical transport and ultimately summer surface CO_2 [Macintyre *et al.*, 2013]. Climate warming has been shown to reinforce the stability of the summer stratification in Lake Geneva [Perroud and Goyette, 2010]. Higher epilimnetic stability could counteract the warming effect on surface CO_2 production by reducing summer entrainment of water from depth with elevated concentrations of CO_2 [Aberg *et al.*, 2010].

In the other two lakes, the thickness of the epilimnetic layer has increased over the last 25 years, while in Lake Geneva, the epilimnetic thickness did not exhibit any clear temporal trend (Figure 1). Downward epilimnion expansion can increase CO_2 concentrations of the surface water as a result of liberation of hypolimnetic stores [Aberg *et al.*, 2010]. Indeed, surface CO_2 concentrations in Lakes Annecy and Bourget are currently 360 and 240 mg C m^{-3} higher than expected based on the relationship between CO_2 concentrations and TP, suggesting an additional CO_2 input of 4.3 and 3.6 g C m^{-2} , respectively, to the surface waters (considering initial epilimnetic depths of 12 and 14 m). Considering the hypolimnetic concentrations of CO_2 concentrations (measured at 1.0 and 1.2 g C m^{-3} for Lake Annecy in 2008–2011 and Lake Bourget in 2011, respectively), a 2.5 and 2 m deepening of the metalimnion would liberate an additional 2.5 and 2.4 g C m^{-2} of CO_2 to the surface waters of Lakes Annecy and Bourget, respectively. A liberation of part of the hypolimnetic stores, and therefore decreased C storage capacities, would account for about 57 to 71% of the excess CO_2 concentrations attributed to climate change.

5. Conclusion

Despite uncertainties inherent in any sediment archive, the carbon-isotope-based CO_2 paleoproxy we developed herein provides the first quantitative assessment of the actual effect of human local and global activities on lake long-term CO_2 dynamics. The results show that the concentration of CO_2 is strongly affected by human activities. Overall, lake surface CO_2 concentrations have been modified by a factor of $2\text{--}3$ over the last 150 years, under the primary control of nutrient-driven changes on internal processes, which were supplanted by the thermal and hydrodynamics consequences of climate change for two of the three lakes over recent decades.

Besides, for the first time, the effects of climate change could be distinguished from local human impacts using observation data. This was previously a challenge because climate effects on CO₂ concentrations are confounded by local, catchment background signals in meta-analyses using latitude as a proxy for a climatic gradient [Alin and Johnson, 2007; Kosten et al., 2010]. Such long-term reconstructions, although less accurate, offer therefore a new and complementary approach to scale better and understand lake CO₂ dynamics in response to climate change. Although our approach is basically correlative and cannot completely address which are the underlying processes ultimately regulating lake CO₂, it clearly helps targeting the drivers to be tested further in future experimental or modeling approaches.

Acknowledgments

Authors are thankful to Y.M. Prairie for his valuable comments on a previous version of this manuscript. Comments from two anonymous reviewers such as the editor, S. Trumbore, really contributed to improve this manuscript. This represents a contribution to the IPER-RETRO program of the French National Research Agency (grant ANR-VUL 005). S.C.M.'s research is supported by the Natural Environment Research Council. DI-TP is included as three tables in the supporting information file; reconstructed terrigenous flux was included in the supporting information file of Jenny et al. [2014a]. Monitoring data (physical and chemical data) from the three lakes are provided by the Observatory of Alpine Lakes (data available upon request and following registration at <https://si-ola.inra.fr>) and EAWAG database for the Rhône River (http://www.eawag.ch/forschung/wut/schwerpunkte/chemievon-wasserressourcen/naduf/datendownload_EN). Climate data were obtained from the HISTALP data sets (<http://www.zamg.ac.at/histalp/datasets.php>). Isotopic data and reconstructed CO_{2aq} may be obtained from MEP (marie-elodie.perga@thonon.inra.fr).

References

- Aberg, J., M. Jansson, and A. Jonsson (2010), Importance of water temperature and thermal stratification dynamics for temporal variation of surface water CO₂ in a boreal lake, *J. Geophys. Res.*, **115**, G02024, doi:10.1029/2009JG001085.
- Alin, S. R., and T. C. Johnson (2007), Carbon cycling in large lakes of the world: A synthesis of production, burial, and lake-atmosphere exchange estimates, *Global Biogeochem. Cycles*, **21**, GB3002, doi:10.1029/2006GB002881.
- Alric, B., J. P. Jenny, V. Berthon, F. Arnaud, C. Pignol, J.-L. Reyss, P. Sabatier, and M.-E. Perga (2013), Local forcings affect zooplankton responses to climate warming, *Ecology*, **94**(12), 2767–2780.
- Bade, D. L., S. R. Carpenter, J. J. Cole, P. C. Hanson, and R. H. Hesslein (2004), Controls of δ¹³C-DIC in lakes: Geochemistry, lake metabolism, and morphometry, *Limnol. Oceanogr.*, **49**(4), 1160–1172.
- Balmer, M. B., and J. A. Downing (2011), Carbon dioxide concentrations in eutrophic lakes: Undersaturation implies atmospheric uptake, *Inland Waters*, **1**(2), 125–132.
- Berthon, V., B. Alric, F. Rimet, and M.-E. Perga (2014), Sensitivity and responses of diatoms to climate warming in lakes heavily influenced by humans, *Freshwater Biol.*, **59**(8), 1755–1767.
- Black, D., R. Thunell, K. Wejnert, and Y. Astor (2011), Carbon isotope composition of Caribbean Sea surface waters: Response to the uptake of anthropogenic CO₂, *Geophys. Res. Lett.*, **38**, L16609, doi:10.1029/2011GL048538.
- Burkhardt, S., U. Riebesell, and I. Zondervan (1999), Effects of growth rate, CO₂ concentration, and cell size on the stable carbon isotope fractionation in marine phytoplankton, *Geochim. Cosmochim. Acta*, **63**(22), 3729–3741.
- Catalan, J., S. Pla, J. Garcia, and L. Camarero (2009), Climate and CO₂ saturation in an alpine lake throughout the Holocene, *Limnol. Oceanogr.*, **54**(6), 2542–2552.
- Cole, J. J., N. F. Caraco, G. W. Kling, and T. K. Kratz (1994), Carbon dioxide supersaturation in the surface waters of lakes, *Science*, **265**(5178), 1568–1570.
- Cole, J. J., et al. (2007), Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget, *Ecosystems*, **10**, 171–184.
- Degens, E. T., M. Behrendt, B. Gotthard, and E. Reppmann (1968), Metabolic fractionation of carbon isotopes in marine plankton—II. Data on samples collected off the coasts of Peru and Ecuador, *Deep Sea Res.*, **15**, 11–20.
- Del Giorgio, P. A., and H. P. Peters (1994), Patterns in planktonic P:R ratios in lakes: Influences of lake trophy and dissolved organic carbon, *Limnol. Oceanogr.*, **39**(4), 772–787.
- Del Giorgio, P. A., J. J. Cole, N. F. Caraco, and R. H. Peters (1999), Linking planktonic biomass and metabolism to net gas fluxes in northern temperate lakes, *Ecology*, **80**(4), 1422–1431.
- Finger, D., A. Wüest, and P. Bossard (2013), Effects of oligotrophication on primary production in peri-alpine lakes, *Water Resour. Res.*, **49**, 4700–4710, doi:10.1002/wrcr.20355.
- Finlay, J. C. (2004), Patterns and controls of lotic algal stable carbon isotope ratios, *Limnol. Oceanogr.*, **49**(3), 850–861.
- Finlay, K., P. R. Leavitt, B. Wissel, and Y. T. Prairie (2009), Regulation of spatial and temporal variability of carbon flux in six hard-water lakes of the northern Great Plains, *Limnol. Oceanogr.*, **54**(6), 2553–2564.
- Finlay, K., R. J. Vogt, M. J. Bogard, B. W. B. Tutolo, G. L. Simpson, and P. L. Leavitt (2015), Decrease in CO₂ efflux from northern hardwater lakes with increasing atmospheric warming, *Nature*, **519**, 215–218.
- Flanagan, K. M., and E. McCauley (2008), Warming and depth interact to affect carbon dioxide concentration in aquatic mesocosms, *Freshwater Biol.*, **53**(4), 669–680.
- Groleau, A., G. Sarazin, B. Vincon-Leite, B. Tassin, and C. Quiblier-Lloberas (2000), Tracing calcite precipitation with specific conductance in a hard water alpine lake (Lake Bourget), *Water Res.*, **34**(17), 4151–4160.
- Gu, B., C. Schelske, and M. Waters (2011), Patterns and controls of seasonal variability of carbon stable isotopes of particulate organic matter in lakes, *Oecologia*, **165**(4), 1083–1094.
- Hanson, P. C., A. I. Pollard, D. A. Bade, K. Predick, S. R. Carpenter, and J. A. Foley (2004), A model for carbon evasion and sedimentation in temperate lakes, *Global Change Biol.*, **10**, 1285–1298.
- Hastie, T., and R. Tibshirani (1990), *Generalized Additive Models*, 352 pp., CRC Press, London.
- Homa, E. S., and S. C. Chapra (2011), Modeling the impacts of calcite precipitation on the epilimnion of an ultraoligotrophic, hard-water lake, *Ecol. Modell.*, **222**, 76–90.
- House, W. A. (1990), The prediction of phosphate coprecipitation with calcite in freshwaters, *Water Res.*, **24**, 1017–1023.
- Huitema, B. E. (2011), Nonlinear ANCOVA, in *The Analysis of Covariance and Alternatives*, pp. 285–296, John Wiley.
- International Panel on Climate Change (2013), *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, edited by T. F. Stocker et al., 1535 pp., Cambridge Univ. Press, Cambridge, U. K., and New York.
- Janjua, M. Y., and D. Gerdeaux (2009), Preliminary trophic network analysis of subalpine Lake Annecy (France) using an Ecopath model, *Knowl. Manage. Aquat. Ecosyst.*, **39**(2), 02.
- Jenny, J. P., et al. (2013), A spatiotemporal investigation of varved sediments highlights the dynamics of hypolimnetic hypoxia in a large hard-water lake over the last 150 years, *Limnol. Oceanogr.*, **58**(4), 1395–1408.
- Jenny, J. P., F. Arnaud, B. Alric, J. M. Dorioz, P. Sabatier, M. Meybeck, and M. E. Perga (2014a), Inherited hypoxia: A new challenge for reoligotrophicated lakes under global warming, *Global Biogeochem. Cycles*, **28**, 1413–1423, doi:10.1002/2014GB004932.
- Jenny, J. P., B. Wilhelm, F. Arnaud, P. Sabatier, C. G. Covex, A. Melo, B. Fanget, E. Malet, E. Ployon, and M. E. Perga (2014b), A 4D sedimentological approach to reconstructing the flood frequency and intensity of the Rhône River (Lake Bourget, NW European Alps), *J. Paleolimnol.*, **51**(4), 469–483.

- Jones, R. I., J. Grey, C. Quarmby, and D. Sleep (1998), An assessment using stable isotopes of the importance of allochthonous organic carbon sources to the pelagic food web of Loch Ness, *Proc. R. Soc. B*, **265**, 105–111.
- Kortelainen, P., M. Rantakari, J. T. Huttunen, T. Mattsson, J. Alm, S. Juutinen, T. Larmola, J. Silvola, and P. J. Martikainen (2006), Sediment respiration and lake trophic state are important predictors of large CO₂ evasion from small boreal lakes, *Global Change Biol.*, **12**(8), 1554–1567.
- Kosten, S., F. Roland, D. M. L. Da Motta Marques, E. H. van Nes, N. Mazzeo, L. S. L. Sternberg, and J. J. Cole (2010), Climate-dependent CO₂ emissions from lakes, *Global Biogeochem. Cycles*, **24**, GB2007, doi:10.1029/2009GB003618.
- Lachavanne, J. B. (1980), Les manifestations de l'eutrophisation des eaux dans un grand lac profond: le Léman (Suisse), *Schweiz. Z. Hydrol.*, **42**(2), 127–154.
- Leavitt, P. R., et al. (2009), Paleolimnological evidence of the effects on lakes of energy and mass transfer from climate and humans, *Limnol. Oceanogr.*, **54**(6), 2330–2348.
- Lepistö, A., M. N. Futter, and P. Kortelainen (2014), Almost 50 years of monitoring shows that climate, not forestry, controls long-term organic carbon fluxes in a large boreal watershed, *Global Change Biol.*, **20**(4), 1225–1237.
- Maberly, S. C., P. A. Barker, A. W. Stott, and M. M. De Ville (2013), Catchment productivity controls CO₂ emissions from lakes, *Nat. Clim. Change*, **3**, 391–394.
- Macintyre, S., W. Eugster, and G. W. Kling (2013), The critical importance of buoyancy flux for gas flux across the air-water interface, in *Gas Transfer at Water Surfaces*, edited by M. A. Donelan et al., pp. 135–139, AGU, Washington, D. C.
- Marce, R., B. Obrador, J.-A. Morgui, J. Lluís Riera, P. Lopez, and J. Armengol (2015), Carbonate weathering as a driver of CO₂ supersaturation in lakes, *Nat. Geosci.*, **8**(2), 107–111.
- Murphy, T. P., K. J. Hall, and I. Yesaki (1983), Coprecipitation of phosphate with calcite in a naturally eutrophic lake, *Limnol. Oceanogr.*, **28**(1), 58–69.
- Perga, M.-E. (2011), Taphonomic and early diagenetic effects on the C and N stable isotope composition of cladoceran remains: Implications for paleoecological studies, *J. Paleolimnol.*, **46**(2), 203–213.
- Perga, M.-E., and D. Gerdeaux (2005), "Are fish what they eat" ... all year long?, *Oecologia*, **144**(4), 598–606.
- Perga, M.-E., and D. Gerdeaux (2006), Seasonal variations in zooplankton species isotopic composition in two lakes of different trophic status, *Acta Oecol.*, **30**, 69–77.
- Perga, M. E., A. Bec, and O. Anneville (2009), Origins of carbon sustaining the growth of whitefish *Coregonus lavaretus* early larval stages in Lake Annecy: Insights from fatty-acid biomarkers, *J. Fish Biol.*, **74**(1), 2–17.
- Perga, M. E., M. Desmet, D. Enters, and J. L. Reyss (2010), A century of bottom-up- and top-down-driven changes on a lake planktonic food web: A paleoecological and paleoisotopic study of Lake Annecy, France, *Limnol. Oceanogr.*, **55**(2), 803–816.
- Perga, M.-E., et al. (2015), High-resolution paleolimnology opens new management perspectives for lakes adaptation to climate warming, *Front. Ecol. Evol.*, **3**, 72.
- Perroud, M., and S. Goyette (2010), Impact of warmer climate on Lake Geneva water-temperature profiles, *Boreal Environ. Res.*, **15**, 255–278.
- Prairie, Y. T., D. F. Bird, and J. J. Cole (2002), The summer metabolic balance in the epilimnion of southeastern Quebec lakes, *Limnol. Oceanogr.*, **47**(1), 316–321.
- Rodriguez-Murillo, J. C., and M. Filella (2015), Temporal evolution of organic carbon concentrations in Swiss lakes: Trends of allochthonous and autochthonous organic carbon, *Sci. Total Environ.*, **520**, 13–22.
- Rodriguez-Murillo, J. C., J. Zobrist, and M. Filella (2015), Temporal trends in organic carbon content in the main Swiss rivers, 1974–2010, *Sci. Total Environ.*, **502**, 206–217.
- Schilder, J., D. Bastviken, M. van Hardenbroek, M. Leuenberger, P. Rinta, T. Stotter, and O. Heiri (2015), The stable carbon isotopic composition of *Daphnia* ephippia in small, temperate lakes reflects in-lake methane availability, *Limnol. Oceanogr.*, **60**(3), 1064–1075.
- Schindler, D. E., S. R. Carpenter, J. J. Cole, J. F. Kitchell, and M. L. Pace (1997), Influence of food web structure on carbon exchange between lakes and the atmosphere, *Science*, **277**, 248–250.
- Simpson, G. L., and N. J. Anderson (2009), Deciphering the effect of climate change and separating the influence of confounding factors in sediment core records using additive models, *Limnol. Oceanogr.*, **54**(6), 2529–2541.
- Smyntek, P. M., S. C. Maberly, and J. Grey (2012), Dissolved carbon dioxide concentration controls baseline stable carbon isotope signatures of a lake food web, *Limnol. Oceanogr.*, **57**(5), 1292–1302.
- Sobek, S., L. J. Tranvik, and J. J. Cole (2005), Temperature independence of carbon dioxide supersaturation in global lakes, *Global Biogeochem. Cycles*, **19**, GB2003, doi:10.1029/2004GB002264.
- Stets, E. G., R. G. Striegl, G. R. Aiken, D. O. Rosenberry, and T. C. Winter (2009), Hydrologic support of carbon dioxide flux revealed by whole-lake carbon budgets, *J. Geophys. Res.*, **114**, G01008, doi:10.1029/2008JG000783.
- Tranvik, L. J., et al. (2009), Lakes and reservoirs as regulators of carbon cycling and climate, *Limnol. Oceanogr.*, **54**(6), 2298–2314.
- Vachon, D., and P. del Giorgio (2014), Whole-lake CO₂ dynamics in response to storm events in two morphologically different lakes, *Ecosystems*, **17**(8), 1338–1353.
- Vennemann, T., R. Piffarerio, L. Favre, and W. Walter (2006), Hydrologic balance of Lake Geneva: Insights from hydrogen and oxygen stable isotope compositions of water and carbon isotope compositions of dissolved inorganic carbonate, in *4th Swiss Geoscience Meeting*, Bern.
- Yvon-Durocher, G., et al. (2012), Reconciling the temperature dependence of respiration across timescales and ecosystem types, *Nature*, **487**(7408), 472–476.