



Heterogeneous responses of lake CO₂ to nutrients and warming in perialpine lakes imprinted in subfossil cladoceran δ¹³C values

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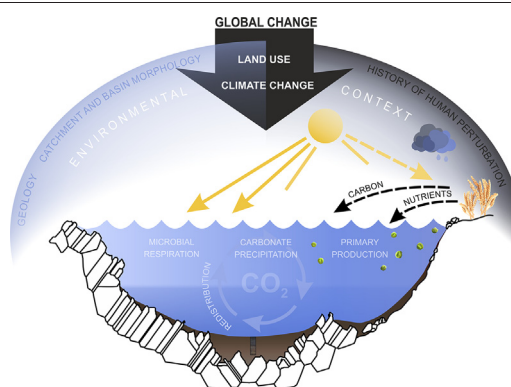
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HIGHLIGHTS

- Effects of global change on lake CO₂ concentrations are poorly understood
- Sedimentary cladoceran δ¹³C trace multidecadal CO₂ trends in seven perialpine lakes
- In most lakes δ¹³C patterns are tightly connected to cultural eutrophication
- Impact of warming on δ¹³C patterns is discernible but comparatively weaker
- Hydrogeomorphic features shape δ¹³C responses to global and local human pressures

GRAPHICAL ABSTRACT



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ABSTRACT

Global change transforms processes regulating carbon dioxide (CO₂) concentrations in lakes, yet our understanding of the broad-scale responses of lake CO₂ to global and local human perturbation across heterogeneous landscapes and multidecadal time scales is limited. We examined decadal variability in the carbon isotope (δ¹³C) composition of subfossil zooplankton (Branchiopoda: Cladocera) in seven large clear perialpine lakes, including three previously studied sites, to decipher different patterns in summer surface CO₂ concentrations. Generalized additive models were used to examine whether and how these patterns connect to changing nutrient regimes and anthropogenic warming over the past century. In all but one of the lakes shifts in cladoceran δ¹³C values coincided with turning points in the eutrophication history, broadly implying decreasing summer surface CO₂ concentrations driven by phosphorus fertilization of pelagic primary production. Yet where nutrient concentrations remained below mesotrophic levels, the positive relationship between δ¹³C and phosphorus diminished indicating that the strong biotic control of CO₂ concentrations was overwritten, probably by catchment inorganic carbon inputs and internal biochemical processes. Even under extensive nutrient loading, the connection was further weakened in lakes with high catchment to lake area ratio attributable to increased catchment interference and shorter water residence times. Warming of the perialpine region was also imprinted in the isotope records, yet the temperature effects appeared modest and were restricted to three smaller lakes with lower drainage ratios. In these lakes, warming contributed to declining cladoceran δ¹³C values likely partially driven by epilimnetic

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deepening increasing CO₂ in surface waters. Overall, our results manifest the broad heterogeneity of lake responses to global change and point to the importance of hydrogeomorphic context in shaping the sensitivity and responses of lake CO₂ to changing nutrient regimes and warming at the regional scale.

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1. Introduction

Global environmental change is altering carbon dioxide (CO₂) concentrations in freshwater lakes (Finlay et al., 2009; Balmer and Downing, 2011; Yvon-Durocher et al., 2017) with repercussions for aquatic carbon balance and CO₂ evasion. The vulnerability and responses of lakes to global and local human perturbations, however, vary dynamically with the environmental context and scale of observation challenging attempts to understand the broad-scale effects of global change on lake CO₂ dynamics (Zwart et al., 2019). Concerted research efforts have expanded our knowledge of underlying environmental determinants, such as lake water dissolved organic carbon (DOC) concentrations (Prairie et al., 2002) or lake size gradients (DelSontro et al., 2018), unveiling broad geographic patterns in the control of aquatic carbon cycling (Seekell et al., 2018). Yet, CO₂ concentrations display also substantial fluctuations through time (Finlay et al., 2009; Natchimuthu et al., 2017) and the temporal element of variability is rarely addressed even though it can fundamentally alter the perceived response of lake CO₂ to environmental perturbation (Klaus et al., 2019). We may be increasingly better equipped to trace fine scale fluctuations in aquatic CO₂ fluxes, however, observational time series extending beyond annual let alone decadal time scales are few, dispersed and discontinuous. This is a critical limitation as the effects of pressing human disturbances, such as land use or anthropogenic climate change, often develop over multidecadal time scales (Smol, 2019). The problem is further exacerbated as lakes are increasingly confronted with multiple interacting human pressures that may superimpose or amplify the effect of one another (Nöges et al., 2016; Bruel et al., 2018). Approaches incorporating the long-term temporal perspective are therefore needed to elicit patterns and control of lake CO₂ under growing human perturbation.

Stable carbon isotope composition ($\delta^{13}\text{C}$) of pelagic cladoceran exoskeletons can be used to gain retrospective insights into aquatic carbon cycling and CO₂ dynamics, acting as a time-integrated measure of the carbon source of the parent population (Perga, 2010, 2011) which often corresponds to phytoplankton $\delta^{13}\text{C}$ over the growing season (Marty and Planas, 2008). Algal $\delta^{13}\text{C}$ values in turn are often tightly linked to surface CO₂ concentrations in aquatic environments across lotic (Finlay, 2004) and lentic systems (France et al., 1997; Gu et al., 2011, 2006) and marine environments (Laws et al., 1995). The relationship may arise from the interplay of a number of processes, such as lowered physiological fractionation or changes in the photosynthetic mechanism (CO₂ versus HCO₃⁻ utilization), however, these will all generally lead to an increase in $\delta^{13}\text{C}$ under depletion of the inorganic carbon pool (Finlay, 2004; Smyntek et al., 2012). In support, quantitative models linking cladoceran $\delta^{13}\text{C}$ with surface CO₂ concentration, validated against limnological monitoring data, have proven efficient in capturing temporal variability in lake CO₂ (Smyntek et al., 2012; Perga et al., 2016). Without validated local models, shifts in $\delta^{13}\text{C}$ cannot be used to quantify changes in CO₂ concentrations as the processes triggered by the depletion or replenishment of the dissolved inorganic carbon pool may vary along with the isotope effect, even if generally uniform in direction (Fogel and Cifuentes, 1993; Smyntek et al., 2012). The approach may nevertheless be employed to explore broad temporal patterns in lake CO₂ and their connections to long term environmental change, given consideration of the underlying methodological assumptions. Overall, the sedimentary approach is not implicitly process based and comes with its inherent limitations, yet it provides a unique means

to overcome the long-term temporal blind spot of modern limnological approaches (Herzschuh et al., 2010; McGowan et al., 2016; Smol, 2019).

Prediction of lake CO₂ responses to global change is also hindered by spatial biases in lake carbon research (Seekell et al., 2018). A strong focus over the past decades has been on comparatively small and shallow boreal lakes where allochthonous organic carbon derived from the surrounding terrestrial environment imposes strong control over aquatic carbon cycling (Tranvik et al., 2018), while larger water bodies dominated by inorganic carbon have received less attention. Here large and clear perialpine lakes, impacted by both local and global anthropogenic forcing (Tolotti et al., 2018), provide ideal systems to study the complex effects of multiple human pressures on lake CO₂. The perialpine region has been heavily influenced both by cultural eutrophication and marked warming over the past century (Auer et al., 2007; Perga et al., 2015) with myriad effects on biogeochemical and physical processes regulating lake CO₂. In these lake environments, internal biological, physical and chemical controls of carbon cycling may be considered especially important due to their vast pelagic waters and depth coupled with a relatively weaker catchment connection (DelSontro et al., 2018). The few available sedimentary studies on decadal scale inorganic carbon dynamics in perialpine lakes indeed point to a strong metabolic nutrient response driving either decreases or increases in CO₂ concentrations (Teranes and Bernasconi, 2005; Perga et al., 2016) depending on the eventual influence of the nutrient stimulus on photosynthetic carbon drawdown (Balmer and Downing, 2011) and microbial respiration (Hollander and Smith, 2001). This biotic control of lake CO₂ can, however, be offset by other mechanisms that regulate carbon cycling, such as carbonate weathering and precipitation dynamics that become relevant already at moderately low alkalinity levels (Marce et al., 2015; Khan et al., 2020). Eventually, such mechanisms could limit the biotic control of lake CO₂ to situations of extensive nutrient loading (Marce et al., 2015; Müller et al., 2016; Perga et al., 2016). Moreover, catchment and basin size and other hydrogeomorphic characteristics are likely to modulate the relative importance of the various controls of lake CO₂ under fertilization by regulating the rate of hydrological inputs, including nutrients and other solutes, and their fate in the water column (Jones et al., 2018; DelSontro et al., 2018). For instance, where nutrient input could result in increased CO₂ flux in smaller lakes, larger lakes may be more likely to show an opposite response related to enhanced photosynthetic carbon drawdown in the extensive pelagic waters (DelSontro et al., 2018). Correspondingly, where warming is generally considered to stimulate microbial respiration and mineralization and thus CO₂ production in lakes (Gudasz et al., 2010; Yvon-Durocher et al., 2017), the relative importance of the metabolic response may vary between lakes depending on the physicochemical and hydrological context (Finlay et al., 2009; Åberg et al., 2010). For example, Perga et al. (2016) found an increase in surface CO₂ in response to decadal scale warming in two perialpine lakes while a third lake, similarly exposed to warming, showed no apparent temperature response potentially related to increased stability of summer stratification limiting CO₂ entrainment from deeper waters. With these complexity of multiscaled and often interconnected processes underway, prone to push lake CO₂ to opposing directions, upscaling within and across regions becomes a challenging endeavor particularly with the limited spatial and temporal breadth of available data.

Building on the inherent link between CO₂ concentrations and cladoceran carbon isotope records archived in lake sediments, we investigated how changing nutrient regimes intertwined with anthropogenic

climate change have shaped aquatic carbon cycling in large clear perialpine lakes over the past century. Specifically, our aim was to assess if summer surface CO₂ concentrations have changed through time in response to shifting phosphorus loading and warming, and whether the changes have been uniform in strength and direction across the region. Our aim was further to identify landscape (hydrological context) and anthropogenic (history of environmental perturbation) factors driving variability in lake sensitivity and responses to either forcing. For these aims, seven perialpine lakes with variable eutrophication histories and hydrological characteristics (defined by basin and catchment hydrogeomorphic features) were chosen for the analysis, including three previously studied systems (Perga et al., 2016) as comparison points of systems affected by low to moderate nutrient enrichment. Our temporal focus extends from the pre-eutrophication to reoligotrophication period for each lake, also covering major warming trends of the past century in the greater perialpine region. We expected the variable characteristics and disturbance histories of the lakes to forge variability in their vulnerability and decadal responses related to varying importance of internal (metabolism, carbonate chemistry and hydrodynamics) and external (catchment material inputs) controls on surface CO₂ concentrations. In particular, we expected to find a strong photoautotrophic metabolic response to eutrophication promoting CO₂ drawdown in the extensive pelagic waters. We further suspected that this response will be most prominent in the heavily nutrient impacted sites and in larger basins with weakest catchment connection where pelagic primary production can be considered especially important for lake CO₂ regulation. Warming was anticipated to generally increase CO₂ concentrations in the surface waters, while the strength of the response was expected to vary depending on the hydrological context and, in particular, thermal stratification regimes that control CO₂ distribution in the water column. Importantly, although we do not focus here on the method of using cladoceran δ¹³C values to trace phytoplankton δ¹³C and eventually past CO₂ trends, there are a number of underlying methodological assumptions that must be carefully considered. We have thus included a brief review in Supplementary material 1 considering their validity and caveats in the studied lakes, building on earlier literature and knowledge of the studied systems. Overall, we consider the cladoceran δ¹³C patterns to reflect temporal trends in dissolved inorganic carbon availability in each lake with sufficient accuracy to outline broad-scale responses of lake CO₂ to nutrients and warming. The results should advance our understanding of lake CO₂ regulation in the perialpine region and contribute to the identification of key drivers of summer surface CO₂ in large inorganic carbon dominated lakes.

2. Material and methods

2.1. Study region

Seven large perialpine lakes with similar limnological attributes but variable hydrogeomorphic characteristics (Table 1) were selected from across Italy, Switzerland and France, including lakes Lugano (southern basin), Varese, Zürich (western basin), Joux, Geneva, Bourget and

Table 1

Hydrogeomorphic characteristics of the studied perialpine lakes. WRT stands for theoretical water residence time and drainage ratio refers to catchment area to lake area ratio.

	Surface area km ²	Drainage ratio	Mean depth m	Max depth m	WRT y	Volume km ³
Varese (IT)	15	8	11	26	1.9	1.6
Annecy (FR)	27	10	40	65	4.0	1.1
Bourget (FR)	45	12	80	147	8.0	3.6
Lugano (CH, IT)	20	14	55	95	1.4	1.1
Geneva (CH, FR)	580	14	154	309	11.4	89.0
Joux (CH)	9	24	18	32	0.8	0.1
Zürich (CH)	68	27	51	136	1.4	3.4

Annecy (Fig. 1). The lakes have characteristic transparent and alkaline (~1.5–3 meq L⁻¹) waters with low concentrations of dissolved organic carbon (DOC, typically around 2 mg L⁻¹). Climate in the region is sub-continental temperate with cool and wet winters and warm and dry summers. All the lakes have been exposed to the recent warming displayed as uniform air temperature trends across the perialpine region, while no marked changes have occurred in precipitation (Fig. 2). The lakes are at present characterized as dimictic (Joux), monomictic (Varese, Zürich, Bourget, Annecy), or oligomictic (Geneva, Lugano southern basin) (Bouffard et al., 2019). All of the lakes have further undergone eutrophication to a varying degree over the past century, with most pronounced nutrient enrichment between the 1950s and the 1990s (Perga et al., 2015; Bruel, 2018). In Lake Zürich, eutrophication was initiated much earlier and the lake was already eutrophic by the turn of the 20th century. For our analysis, lakes Joux and Annecy represent systems exposed to low nutrient forcing (total phosphorus <30 µg L⁻¹ during peak eutrophication), lakes Bourget and Geneva those under moderate nutrient enrichment (<150 µg L⁻¹), and lakes Zürich, Varese and Lugano systems that have undergone major eutrophication (>150 µg L⁻¹) (Fig. 3). Driven by nutrient abatement measures, all of the lakes are currently on a path to recovery.

2.2. Carbon isotope composition in subfossil Cladoceran remains

Stable carbon isotope (δ¹³C) analysis of cladoceran remains was undertaken on sediment sequences from lakes Varese, Lugano, Joux and Zürich. The cores were collected between years 2010 and 2013 from the deepest parts of the lake basins using gravity corers. Core chronologies were established based on shortlived radionuclides for Lakes Varese and Lugano, on varve counting for Lake Zürich, and by correlating magnetic susceptibility profiles between our core and a previously dated one for Lake Joux. Details on dating procedures are provided in Supplementary material 2. From each core, sedimentary cladoceran samples were prepared applying the protocol detailed in Perga (2011). Briefly, sediment samples were heated with 10% KOH for half an hour to remove organic material and coating from the chitinous remains. Remaining material was subsequently rinsed on a 100 µm sieve followed by HCl treatment to avoid potential effects of carbonate contamination. Coarse mineral matter was removed using physical separation by swirling and decanting and fine mineral matter was reduced by sieving. Planktonic cladoceran (*Bosmina* sp. and *Daphnia* sp. ephippia) exoskeletons were extracted combining sieving, centrifuging, and manual separation with fine forceps under a stereomicroscope. Final sample weights varied between ~50–150 µg. The selective use of planktonic bosminid remains should ensure that the isotopic composition of the exoskeletons reflects that of phytoplankton over the growing season, while the contribution of terrestrial detritus to the cladoceran diet is considered low due to the depth of the lakes and the extent of their pelagic waters (Supplementary material 1). *Daphnia* ephippia were in some cases included to ensure adequate sample size yet this should cause minimal interference to the δ¹³C values (Perga, 2010, Supplementary material 1). Stable carbon isotope analysis of the cladoceran samples was performed at the Stable Isotope Laboratory of the University of Lausanne by elemental analysis/isotope ratio mass spectrometry. The results were reported in the delta (δ) notation as variations of the molar ratio (R) of ¹³C to ¹²C isotopes relative to an international standard:

$$\delta^{13}\text{C}_{\text{sample/standard}} = \frac{R(^{13}\text{C}/^{12}\text{C})_{\text{sample}}}{R(^{13}\text{C}/^{12}\text{C})_{\text{standard}}} - 1$$

For δ¹³C values, the standard is the Vienna Pee Dee Belemnite limestone (VPDB), and the unit is per mil (‰). For calibration and normalization of the measured carbon isotope ratios to the international scales (VPDB-LSPVEC lithium carbonate scale), a 3-point calibration

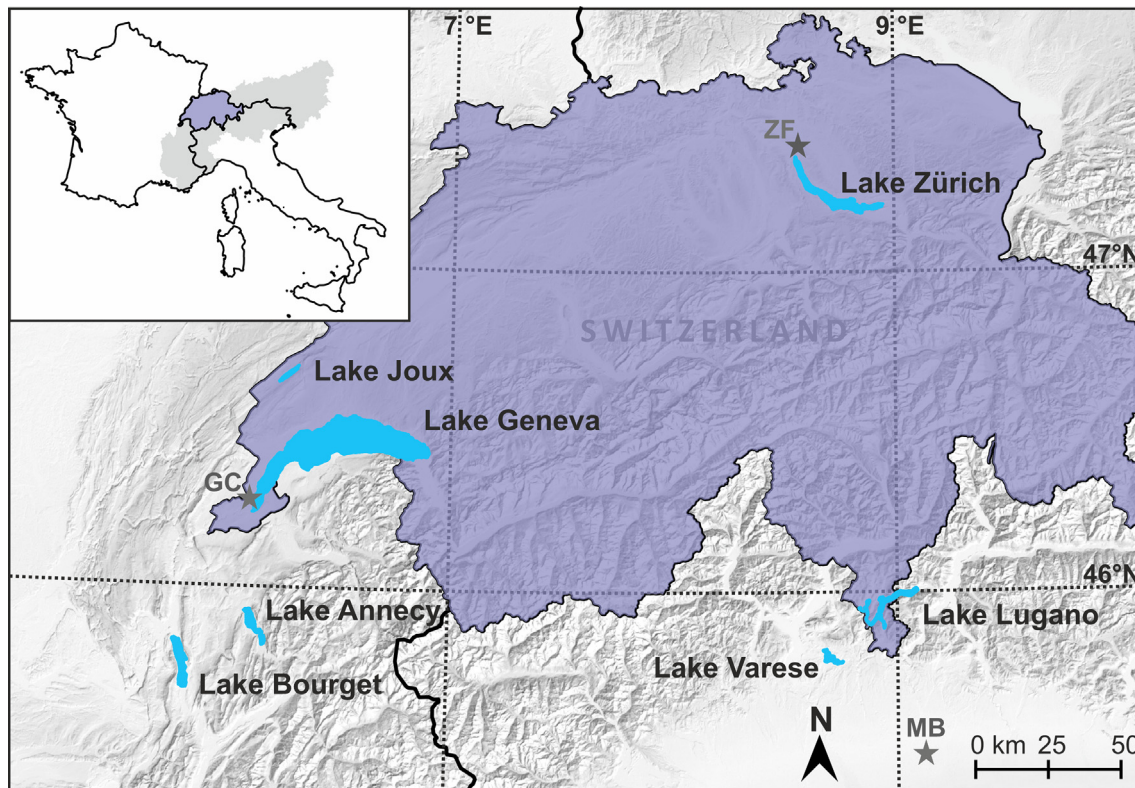


Fig. 1. Location of the studied seven lakes in the perialpine region, including the previously studied lakes Geneva, Annecy and Bourget (Perga et al., 2016). Grey shaded area in the index map depicts the extent of the Alps. Location of the weather stations Genève-Cointrin (GC), Zürich-Fluntern (ZF) and Milan-Brera (MB) are indicated.

was used with international reference materials (RMS) and the UNIL in-house urea standards (Spangenberg and Zufferey, 2019). The repeatability and intermediate precision, determined by replicated analyses of RMS and samples, were better than 0.05‰. The accuracy of the $\delta^{13}\text{C}$ measurements was monitored through the analysis of international RMS. Sample preparation and analysis from the previously published isotope records from lakes Geneva, Annecy and Bourget followed similar procedures (Perga et al., 2016).

2.3. Sediment organic content

Measurements of sediment organic content were included to provide additional insights into decadal scale carbon dynamics in the

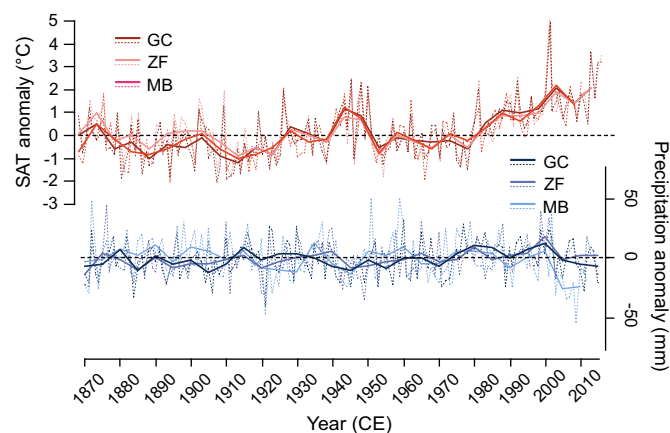


Fig. 2. Mean summer air temperature (SAT) and annual precipitation anomalies expressed relative to the 1901–2000 baseline (dashed line) for Genève-Cointrin (GC), Zürich-Fluntern (ZF) and Milan-Brera (MB) weather stations. Solid lines depict 5 year moving averages.

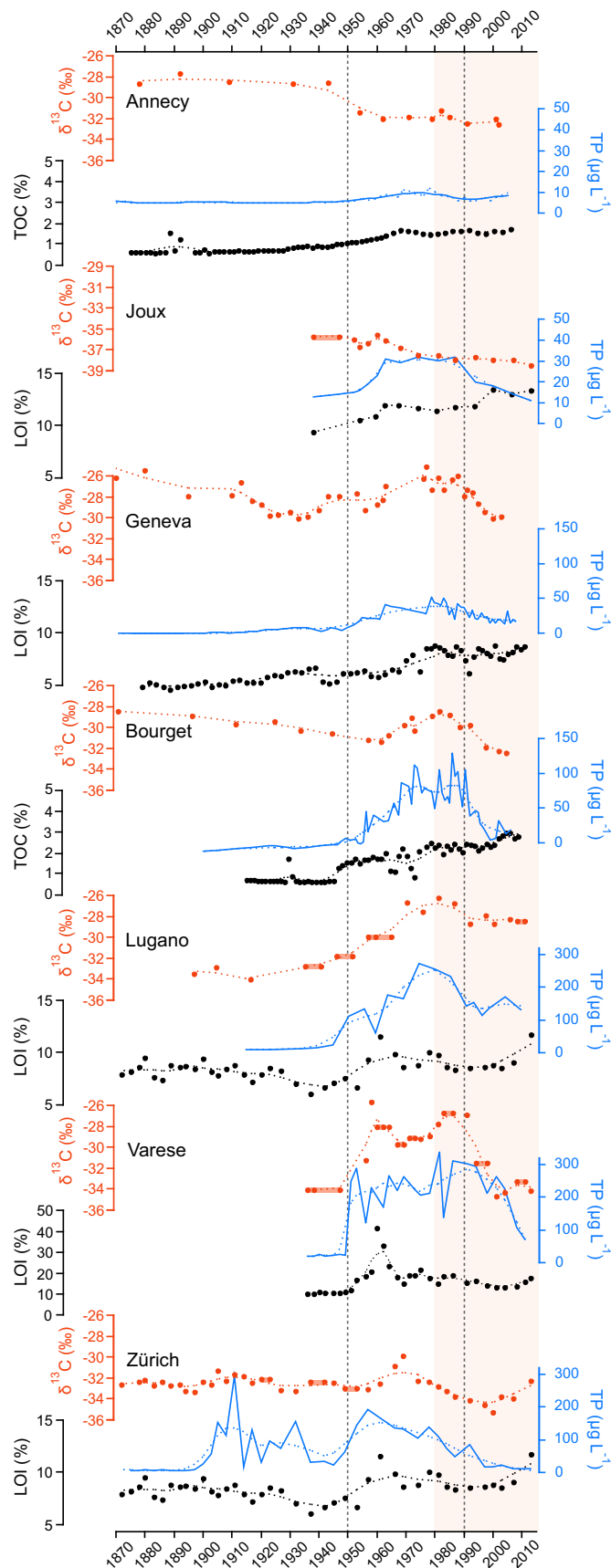
studied lakes. Relative changes in sediment organic matter content were determined by loss on ignition (LOI) for all lakes but Bourget and Annecy. The analysis was performed at 550 °C and the results are expressed as percentages of total dry mass. For lakes Bourget and Annecy, sediment total organic carbon (TOC) content was measured by Rock Eval pyrolysis (Espitalié et al., 1985) with a Model 6 device (Vinci Technologies).

2.4. Temporal patterns in nutrients and temperature

Temperature and precipitation data were retrieved from the MeteoSwiss database for the Swiss and French lakes (Genève and Zürich weather stations) and from the HISTALP database (Auer et al., 2007) for the Italian lakes (Milan weather station). Precipitation data were not considered in further analyses as they showed no distinct trends. Summer mean temperature values were calculated from the monthly (June to August) data and were converted into summer air temperature (SAT) anomalies relative to 1901–2000 baseline (Fig. 2). Total phosphorus (TP) concentrations were reconstructed based on fossil diatom assemblages for lakes Lugano and Zürich (Supplementary material 3) and based on *Daphnia* abundances for lakes Geneva, Annecy and Bourget (Berthon et al., 2014). For Lake Varese, the TP model was constructed based on diatom assemblages and carotenoid pigments (Bruel et al., 2018). TP values for Lake Joux were obtained combining monitoring data (1981–2013) with inferences based on sediment phosphorus concentrations (1938–1974) as detailed in Supplementary material 3. The inferred TP trends showed high consistency with modern measurements during periods for which observational data were available (Perga et al., 2016; Bruel, 2018; Bruel et al., 2018).

2.5. Numerical analyses

Generalized additive models (GAMs) were used to decipher nutrient and temperature effects on cladoceran $\delta^{13}\text{C}$ values evaluating variability



in their relative importance as well as in the direction of the response between lake ecosystems and through time. Sedimentary cladoceran $\delta^{13}\text{C}$ values were included as response variables with reconstructed TP concentrations and measured SAT anomalies as predictor variables. Hierarchical GAMs (HGAMs) were further tested to seek common structures in lake responses. When autocorrelation in the residuals of GAMs were detected, a first-order autocorrelation structure was included using a generalized additive mixed model. The GAMs were performed using R software (R Core Team, 2020) and the mgcv package (Wood, 2011). While we are ultimately interested in lake CO_2 , we did not attempt reconstructing absolute changes in summer surface CO_2 concentrations since no local models, such as the one previously employed for lakes Geneva, Bourget and Annecy (Perga et al., 2016), were available for all of the studied lakes. This was either necessary as we focus here on the dynamic relationship between cladoceran $\delta^{13}\text{C}$ and environmental forcing precluding the need to translate the observed changes in $\delta^{13}\text{C}$ into amounts of CO_2 gain or loss. Importantly, the slopes of the regression lines for $\delta^{13}\text{C}$ versus nutrient loading or temperature should consequently be treated with caution as they may in part reflect interlake variation in the relationship between phytoplankton $\delta^{13}\text{C}$ and CO_2 (France et al., 1997; Supplementary material 1). Accordingly, while the amplitude of $\delta^{13}\text{C}$ change can provide some cues into respective changes in lake CO_2 concentrations, we focus here on the direction of the $\delta^{13}\text{C}$ response as well as the strength of the relationship indicating variability in the responses and sensitivity of summer surface CO_2 concentrations to environmental forcing. To evaluate the influence of landscape context on the isotopic patterns, we assessed monotonic relationships between the model parameters and hydrogeomorphic characteristics, that provide useful summary metrics for lake hydrological setting (Jones et al., 2018), with correlation analyses. False discovery rate using the Bonferroni correction was employed to correct for multiple comparison ($q = 0.05$).

3. Results

3.1. Cladoceran $\delta^{13}\text{C}$ responses to nutrients and warming

Cladoceran $\delta^{13}\text{C}$ values showed considerable variability between and within lake, ranging from -38.5 to -24.1% in the studied lakes between the late 19th and the early 21st century. There were further differences in the reference $\delta^{13}\text{C}$ values prior eutrophication, with lakes Varese, Lugano and Joux showing more ^{13}C depleted values relative to the other lakes. Within a lake, the amplitude of change through time varied between ~ 3 and 10% . For most lakes, the changes occurred in distinct synchrony with inferred TP patterns (Fig. 3). In lakes Lugano, Varese, Bourget and Geneva, $\delta^{13}\text{C}$ values began tracing rapidly increasing phosphorus concentrations around the 1950s indicating reduced summer surface CO_2 concentrations upon eutrophication. The subsequent reoligotrophication initiated in the 1980s was accordingly mirrored as decreasing $\delta^{13}\text{C}$ values implying increasing CO_2 concentrations. Lakes Joux and Annecy displayed a declining $\delta^{13}\text{C}$ trend over the eutrophication period suggesting gradually increasing CO_2 concentrations through the latter half of the past century. In both lakes, nutrient levels remained at mesotrophic levels even during peak eutrophication. In Lake Zürich, $\delta^{13}\text{C}$ values showed no strong trends and only a weak connection to shifting nutrients despite high TP concentrations peaking first in the early 1900s and again in the 1950s.

Fig. 3. Temporal patterns in sedimentary cladoceran carbon isotope values ($\delta^{13}\text{C}$), inferred total phosphorus (TP), and sediment organic carbon (LOI) or total organic carbon (TOC) content. Connected dots indicate pooling of adjacent samples for cladoceran $\delta^{13}\text{C}$ analysis where remains were too few otherwise. Dotted lines depict lowest smooth curves (span 0.2). Note that there are some differences in the scales between lakes. The vertical dashed lines delimit the main eutrophication period and the shaded area indicates the period of most intensive warming in the perialpine region.

Table 2

Model parameters for generalized additive models performed on cladoceran $\delta^{13}\text{C}$ with total phosphorus (TP) concentrations and mean summer air temperature (SAT) anomalies as predictor variables. For lakes Annecy, Lugano and Joux, TP and SAT could not be introduced in the same model and values are given for two separate models. Edf stands for estimated degrees of freedom and k-index tests the adequacy of basis dimension choice for each smooth (Wood, 2017).

	p-Value		Deviance explained			Edf		k-Index	
	TP	SAT	TP + SAT	TP	SAT	TP	SAT	TP	SAT
Bourget	0.043	0.043	79	76	47	4.2	1.0	1.4	1.1
Varese	0.001	0.002	63	21	22	1.0	2.6	1.0	1.4
Geneva	0.001	0.430	57	57	0	3.9		1.1	
Zürich	0.034	0.092	22	12	12	1.0	1.0	1.0	1.0
Annecy	2.8×10^{-8}	0.023		94	36	3.6	1.0	1.2	1.7
Lugano	9.9×10^{-7}	0.118		81	13	1.6		1.3	
Joux	0.107	0.188		0	0				

The GAMs explained between 22.5% and 93.9% of variability in cladoceran $\delta^{13}\text{C}$ in the lakes excluding Lake Joux for which no significant models were found (Table 2). The models displayed a good fit as shown in Supplementary material 4. For lakes Annecy, Joux and Lugano, the number of data points precluded inclusion of both predictor variables in the same model and therefore separate models were performed for TP and SAT. Overall, lowest *p*-values and highest variance explained were associated with TP with significant nutrient effect on $\delta^{13}\text{C}$ in all but Lake Joux (Fig. 4, Table 2). TP impact was primarily positive although the strength of the relationship varied considerably between the studied systems, the weakest models associated with Lake Zürich. Moreover, where TP concentrations remained below mesotrophic levels ($\sim\text{TP} < 25 \mu\text{g L}^{-1}$), the positive relationship was leveled or replaced by a reverse pattern of decreasing $\delta^{13}\text{C}$ values along the TP gradient. Accordingly, in Lake Annecy cladoceran $\delta^{13}\text{C}$ displayed a negative relationship to TP over the eutrophication period. A similar, albeit less apparent, connection was observed in lakes Geneva and Bourget during early eutrophication, replaced by a positive $\delta^{13}\text{C}$ relationship as nutrient levels rose above mesotrophic levels. Despite the overall common shape in the relationship between $\delta^{13}\text{C}$ and TP, the use of individual smoothers for each lake was deemed most appropriate based on the HGAMs. GAMs identified a significant temperature effect only in lakes Varese, Annecy and Bourget displaying a negative relationship between SAT anomalies and $\delta^{13}\text{C}$ (Fig. 4, Table 2) implying elevated CO_2 concentrations under

warming. The relationship was strongest in Lake Varese and weakest in Lake Bourget. It should be noted that the isotopic records used here do not extend over the past few years and thus do not take into account the most recent period of warming. Additionally, some uncertainty could arise from possible disparities in ages between the sediment data and modern temperature records, although the studied sediment sequences have mostly very robust chronologies (Supplementary material 2). Comparing interconnections between the model parameters and hydrogeomorphic characteristics, we observed a negative relationship between catchment to lake area ratio (drainage ratio) and the variance explained by TP, although no statistically significant correlations were found. Accordingly, the explanatory power of TP grew weaker in lakes with large catchment to lake area ratio (Fig. 5).

3.2. Decadal patterns in sediment organic content

LOI varied between 4.6 and 41.6% in the studied lakes with the highest values found in lakes Lugano and Varese (Fig. 3). In lakes Annecy and Bourget, TOC varied between 0.6 and 3.0%. The LOI and TOC measurements depicted a general trend of increasing sediment organic content in the studied lakes, initiated around the early or middle 20th century. For the most part, the initial increases occurred coincident with the early eutrophication followed by a gradual increase over the eutrophication period. In Lake Zürich, the same pattern was observed in connection to the second wave of eutrophication but not during the first, and in Lake Varese the initial rapid increase during early eutrophication was followed by a slight decline. In most of the lakes, sediment LOI and TOC content stabilized to some extent after peak eutrophication. Highest overall increases were observed in the most strongly nutrient influenced lakes Lugano and Varese, even when excluding the two conspicuously high LOI values observed during early eutrophication in Lake Varese. Despite the general connection between sediment organic content and TP, reduced nutrient inputs during reoligotrophication were not met with consistent declines in LOI/TOC, instead, the values remained stable or gradually increasing towards the surface.

4. Discussion

4.1. Effects of changing nutrient regimes on lake CO_2

Cladoceran carbon isotope values carried a strong signal of nutrient-driven perturbation to lake CO_2 over the past century in five of the seven

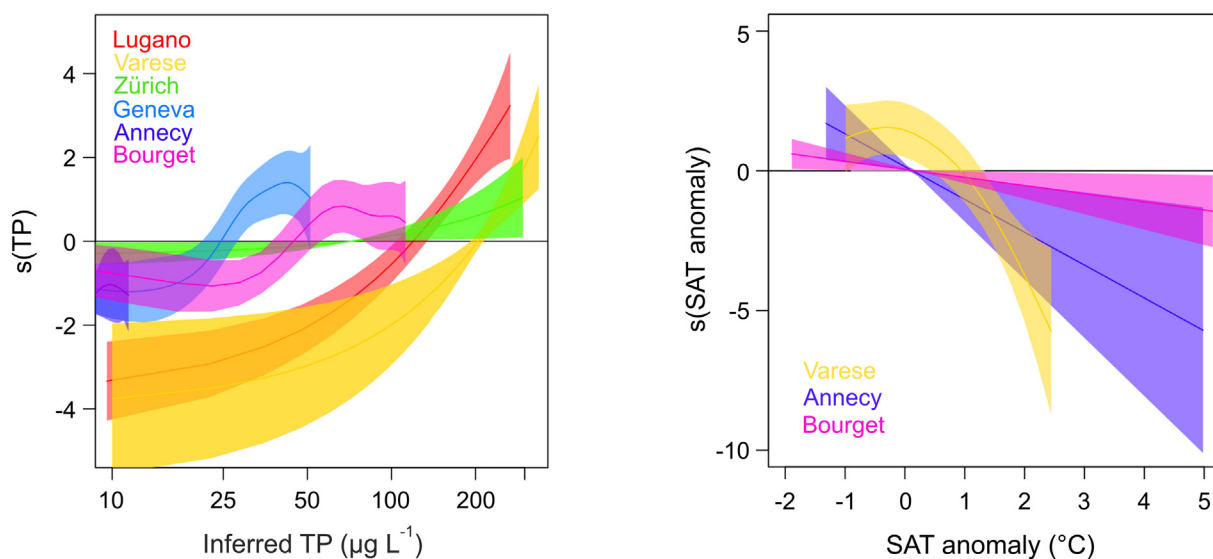


Fig. 4. Responses of cladoceran $\delta^{13}\text{C}$ to *s*(TP) (smooth term for inferred total phosphorus concentrations) and *s*(SAT) (smooth term for mean summer air temperature anomalies) in the studied perialpine lakes.

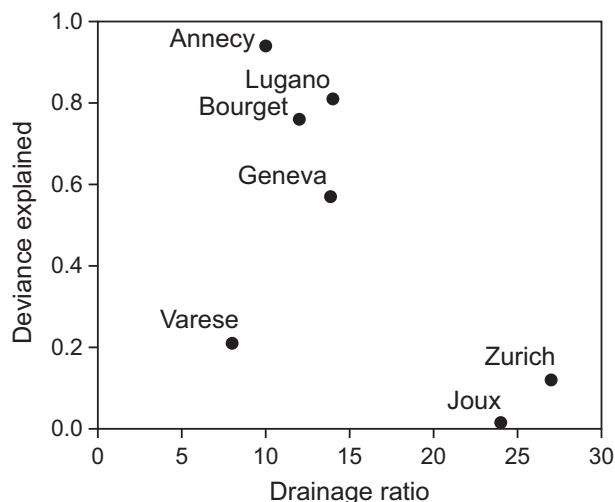


Fig. 5. Relationship between drainage ratio and the deviance explained by total phosphorus in the generalized additive models.

studied lakes. This is an unsurprising finding as trophic status imposes strong control over aquatic carbon dynamics related to nutrient regulation of lake metabolism (Elser et al., 2007) and we indeed expected to find a strong biotic response in the extensive pelagic waters. The positive relationship between cladoceran $\delta^{13}\text{C}$ and TP (Figs. 3, 4) implies enhanced photosynthetic drawdown of CO_2 under nutrient stimulation resulting in lowered summer surface CO_2 concentrations during eutrophication. Irrespective of the precise physiological mechanism underlying the relationship (Fogel and Cifuentes, 1993; Smyntek et al., 2012), depletion of the inorganic carbon pool under increased production generally results in a positive shift in $\delta^{13}\text{C}$ of the photosynthetic product. This linkage between productivity and phytoplankton $\delta^{13}\text{C}$ has been widely observed in lakes, often depicted in seasonal records of zooplankton or particulate organic matter (POM) $\delta^{13}\text{C}$ values mirroring change in CO_2 concentrations over the annual production cycle (France et al., 1997; Smyntek et al., 2012) as well as in sediment organic matter $\delta^{13}\text{C}$ tracing paleoproductivity patterns (Brenner et al., 1999; Teranes and Bernasconi, 2005; Meyers, 2006). Although a common pattern, eutrophication does not invariably lower surface CO_2 concentrations as nutrients will simultaneously promote microbial processes that could eventually set off a reverse pattern of decreasing $\delta^{13}\text{C}$ in sediment organic matter (Hollander and Smith, 2001). Prevalence of the photoautotrophic response in the studied lakes was, nevertheless, anticipated as cladoceran $\delta^{13}\text{C}$ values reflect phytoplankton $\delta^{13}\text{C}$ in surface waters over the stratification period and the influence of microbial processes should increase in the hypolimnetic waters and over the late summer and autumn (Teranes and Bernasconi, 2005). Yet, not all of the studied lakes responded to eutrophication along the expected trajectory.

The positive relationship between cladoceran $\delta^{13}\text{C}$ and phosphorus loading was most conspicuously, while not consistently, displayed in the most nutrient impacted lakes in our data set. In effect, where extensive nutrient loading left distinct traces in the isotopic records of lakes Varese and Lugano, the rapidly increasing phosphorus concentrations of the early and middle 20th century in Lake Zürich were barely reflected in $\delta^{13}\text{C}$ (Fig. 3) as also shown by the weak GAM model (Fig. 4, Table 2). We expect this discrepancy to arise from divergence in local environmental context modifying the sensitivity of lake CO_2 to nutrient enrichment (Soranno et al., 2015). Considering that the positive link between $\delta^{13}\text{C}$ and TP is principally attributable to nutrient stimulation of algal photosynthesis, we expected the connection to diminish in systems where aquatic carbon cycling is less strongly tied to pelagic metabolism. Indeed, Lake Zürich was distinguished by its larger

drainage ratio and comparatively short water residence time (Table 1, Fig. 5) that are likely to weaken the importance of internal metabolic control of lake CO_2 . Similar characteristics could contribute also to the apparent lack of TP response in Lake Joux representing the least nutrient impacted of our study sites. Specifically, shortened water residence time and reduced nutrient turnover rates combined with increased hydrological input of allochthonous carbon or alkalinity could diminish the biotic nutrient response in these two lakes. Earlier research shows that coincident catchment carbon subsidies can, in effect, altogether reverse the relationship between nutrients and lake CO_2 concentrations, whether by direct addition of dissolved inorganic carbon (DIC) (Maberly et al., 2013) or by dissolved organic carbon (DOC) fueling microbial respiration (Lapierre and Giorgio, 2012). Despite the well-established role of allochthonous DOC in driving lake CO_2 (Sobek and Tranvik, 2005; Tranvik et al., 2018), here inorganic carbon is more likely to be responsible due to the characteristic low organic carbon concentrations of the studied lakes. Deciphering the exact mechanisms is beyond the scope of this study, however, our results lend support to the notion that hydrogeomorphic features are important regulators of aquatic carbon cycling across the trophic gradient at global (DelSontro et al., 2018) and regional (Perga and Gerdeaux, 2004; Balmer and Downing, 2011) scale, although still poorly accounted for in global carbon models (Jones et al., 2018). Not all of the variability in nutrient responses was, however, manifested along natural hydrogeomorphic gradients.

Fading of the strong positive relationship between cladoceran $\delta^{13}\text{C}$ and TP at lower nutrient levels (Figs. 3, 4) may be related to a hierarchy of internal and external controls on biotic and abiotic components of the carbon cycle. For one, enhanced respiration could be counteracting the consequences of photosynthetic carbon drawdown, as suggested previously for Lake Anney (Frossard et al., 2014), by causing ^{13}C depletion of phytoplankton $\delta^{13}\text{C}$ (Perga et al., 2016; Supplementary material 1). Moreover, concomitant input of dissolved inorganic carbon from the catchment, here most probably from carbonate weathering, could well override the effect of biotic carbon uptake on lake CO_2 (Marce et al., 2015). Noticeably, all three lakes (Anney, Bourget and Geneva) that deviated from the general positive $\delta^{13}\text{C}$ nutrient response under low phosphorus loading (Fig. 4) are situated on calcareous catchments northwest of the Alps, which could imply that their distinct responses have geological origins. In these lakes, reference $\delta^{13}\text{C}$ values (prior eutrophication) were indeed generally more ^{13}C enriched (Fig. 3) suggesting larger contribution from catchment carbonates to the DIC pool of the lakes. However, all of the studied lakes contain calcareous rocks in their catchment (Tolotti et al., 2018) and have alkalinities >1 meq L^{-1} above which lake CO_2 often become strongly influenced by carbonate weathering and precipitation dynamics (Khan et al., 2020). This would suggest that catchment geology alone cannot explain the distinct temporal responses. Aside from allochthonous carbon inputs, internal biochemical processes could contribute towards a negative relationship between TP and cladoceran $\delta^{13}\text{C}$ diminished at higher trophic levels, though we cannot here ascertain the potential role of biologically initiated calcite precipitation or coprecipitation dynamics with phosphorus (Hamilton et al., 2009; Müller et al., 2016). It should also be noted that in lakes Lugano and Varese nutrient levels rose sharply above mesotrophic levels at the onset of eutrophication, which could partly contribute to their consistent positive $\delta^{13}\text{C}$ response to TP and apparent dominance of internal biotic control of surface CO_2 . Further studies on inorganic carbon dominated lakes from across different geographic regions are needed to evaluate whether these deviations along the nutrient gradient are a more widespread phenomenon, and to constrain the key underlying processes.

Nutrient dynamics were also clearly reflected in sediment organic content in all of the studied lakes, seen as increases in sediment LOI or TOC initiated coincident with the first signs of eutrophication (Fig. 3). This was expected as increases in sediment organic carbon are a common feature in lakes exposed to nutrient enrichment reflecting the

intensified production of autochthonous biomass (Anderson et al., 2014), thus also coincident with the nutrient driven shifts in cladoceran $\delta^{13}\text{C}$ values (Fig. 3). Curiously, following peak eutrophication and particularly during the reoligotrophication period, the trends in sediment organic content appeared to disconnect from the nutrient development as no conspicuous declines were observed coincident with the TP reductions. Elevated organic carbon content near the sediment surface is likely to be at least partially an artefact of postdepositional processes and the surface trends should thus be considered with caution. However, earlier research suggests that much of the effects of decomposition on organic carbon content after burial should occur over the first few years (Gälman et al., 2008) and might not be enough to explain the consistent lack of expected TP response during reoligotrophication. Similar decoupling has been observed in other eutrophic perialpine lakes, indicating sustained high organic carbon burial rates despite marked reductions in external nutrient loading (Fiskal et al., 2019). With the uncertainties related to diagenetic effects it remains uncertain whether this could be related to, for instance, remobilization of phosphorus sustaining primary production, management practices, or intensified warming over the past decades (Heathcote et al., 2015; Fiskal et al., 2019). In a similar manner, the relationships between cladoceran $\delta^{13}\text{C}$ and nutrients in the lakes remained somewhat uniform through time, except for the most recent decades.

4.2. Warming effects on lake CO_2

Over the past decades, cladoceran $\delta^{13}\text{C}$ appeared to some extent decoupled from trophic development in a few of the lakes, as diminished phosphorus load driven by nutrient abatement measures was not unambiguously mirrored in the sediment isotope records (Fig. 3). The GAMs identified significant contribution of air temperature for lakes Varese, Annecy and Bourget although the overall effect of warming remained more marginal compared to that of nutrients (Fig. 4, Table 2). Our findings have two implications pertaining to the influence of local and global human pressures on lake CO_2 in the lakes. First, despite the marked warming across the perialpine region (Auer et al., 2007) displayed particularly vividly in temperature records of the past few decades (Woolway et al., 2017), the effects of local environmental pressures on lake CO_2 appeared to dominate over global drivers even in lakes exposed to low nutrient forcing. Second, while eutrophication has the potential to reinforce warming effect on aquatic carbon fluxes (Sepulveda-Jauregui et al., 2018), here neither lake vulnerability to warming nor the strength of the isotopic response appeared related to the eutrophication history. Overall, the variable sensitivity and responses of the lakes to SAT, despite the uniform warming trend (Fig. 2), are unsurprising as air or surface water temperature trends are generally poor predictors of ensuing physical or ecological changes in lakes (Shatwell et al., 2019). As with nutrients, the impact of warming fundamentally depends on the local environmental context dictating the prevailing controls on surface CO_2 concentrations in each lake.

The negative $\delta^{13}\text{C}$ response to SAT in the three lakes displaying a significant temperature response indicates increasing CO_2 concentrations under warming temperatures. Such a relationship could emerge through a number of mechanisms, here more probably related to temperature control over internal biological (Yvon-Durocher et al., 2017), chemical (Finlay et al., 2009) and physical (Magee and Wu, 2017) processes than to catchment material fluxes (Sobek and Tranvik, 2005). Lakes Varese, Annecy and Bourget share certain hydrogeomorphic features that may partially explain their responsiveness, namely, a combination of comparatively small drainage ratio, smaller lake surface area, and shallower depths (Table 1). Shallower lakes generally warm more strongly and the effects of warming are also likely to be more pronounced in lakes with weaker hydrological connectivity. While direct temperature effects on respiration (Yvon-Durocher et al., 2017) or calcite precipitation (Homa and Chapra, 2011) could contribute towards increasing summer surface CO_2 concentrations, warming effects on

thermal characteristics are not unique to these three lakes suggesting that additional temperature-mediated mechanisms are at play. In addition to effects on biological and chemical processes, temperature controls water movement extending strong physical control over the pathways and fate of aquatic carbon. The declines in cladoceran $\delta^{13}\text{C}$ over recent decades may in part be related to deepening of the epilimnion, as observed for lakes Annecy and Bourget (Perga et al., 2016), driving enhanced vertical CO_2 transport from the hypolimnion. Deepening of the thermocline is a globally widespread phenomenon particularly prominent in shallower stratified lakes (Butcher et al., 2015; Kraemer et al., 2015). The apparent insensitivity of cladoceran $\delta^{13}\text{C}$ to warming in the larger, deeper and more connected lakes (Table 2) may to some extent reflect lower thermal vulnerability but likely also depicts the broad heterogeneity of thermal responses that tend to increase with lake size (Magee and Wu, 2017). With increasing depth and surface area, warming effects on the depth of the thermocline are likely to diminish while changes in thermal stability often become more prominent (Butcher et al., 2015; Kraemer et al., 2015). Increased thermal stability and weakened mixing, well documented for lakes Geneva (Perroud and Goyette, 2010; Perga et al., 2016) and Zürich (Livingstone, 2003), could in part explain their apparent lack of temperature response by blocking CO_2 rich waters to the hypolimnion. Rapid warming of surface waters in the southern basin of Lake Lugano is expected to have a similar effect (Lepori and Roberts, 2015). Whatever the processes, hydrogeomorphic characteristics appear important in controlling the sensitivity and responses of summer surface CO_2 to warming in the studied lakes.

4.3. Heterogeneity of lake CO_2 responses to global change

Projections of future changes in CO_2 concentrations are impaired by our limited understanding of variability in the regulation of lake CO_2 across heterogeneous landscapes and under a complexity of multiscaled and interacting human pressures. Our analysis contributed to tackling some of the uncertainties involved, specifically in the context of large and clear perialpine lakes exposed to cultural eutrophication and climate warming over the past century. Our findings support the notion that eutrophication may enhance photosynthetic carbon sequestration and lower CO_2 concentrations in surface waters (Balmer and Downing, 2011; Pacheco et al., 2013) in large lakes (DelSontro et al., 2018). The strong positive relationship between cladoceran $\delta^{13}\text{C}$ and phosphorus loading was, however, specific to lakes exposed to high nutrient loading and diminished in lakes with higher catchment connectivity, as indicated by larger drainage ratios and shorter water residence times. Our record from Lake Zürich denotes that surface CO_2 even in lakes exposed to extensive phosphorus loading may display a relatively indifferent nutrient response. The importance of nutrient driven biotic control over lake CO_2 concentrations further diminished below mesotrophic conditions whereon the relationship between cladoceran $\delta^{13}\text{C}$ and phosphorus concentrations was leveled or reversed, probably due to more prevalent influence of microbial respiration, allochthonous inorganic carbon inputs, or abiotic-biotic interactions shaping carbonate chemistry. Further research is needed to ascertain the mechanisms overwriting the photosynthetic control of CO_2 under situations of low nutrient impact and increased hydrological connection.

Our results further show that warming temperatures have contributed to shaping lake CO_2 concentrations in the perialpine region particularly after the stepwise increase in warming rates in the 1980s (Woolway et al., 2017). Despite considerable warming, reflected also in the thermal characteristics of the studied lakes, the overall effects of warming on surface CO_2 concentrations appeared comparatively small. Moreover, prior eutrophication history of the lakes was found to have little influence on temperature sensitivity in the studied lakes. The differences in the responses to temperature, regardless of the uniform warming trend, depict the diversity of physical and ecological

consequences of climate warming in lakes (Kraemer et al., 2015) and point to the importance of hydrological setting and internal hydrodynamics in controlling lake carbon responses to changing temperatures (McCullough et al., 2019). In our analysis, the effects of warming appeared more prominent in smaller and shallower lakes with weaker catchment connectivity and contributed towards increasing lake surface CO₂ concentrations. The negative relationship between cladoceran δ¹³C and SAT could indicate direct temperature effect on metabolism and carbonate chemistry, yet is likely in part related to epilimnetic expansion feeding CO₂ to surface waters. The lack of apparent temperature response in the remaining lakes denotes the frequently observed unpredictability of thermal responses in larger, deeper and more hydrologically connected lakes (Magee and Wu, 2017; Shatwell et al., 2019), while we suspect that the effects on surface CO₂ may be masked by hydrodynamic changes trapping more CO₂ in deeper waters. Overall, our results suggest that decadal patterns in surface CO₂ concentrations in the studied lakes have been to large extend driven by human activity over the past century.

CRedit authorship contribution statement

Marttiina V. Rantala: Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft, Visualization, Project administration, Funding acquisition. **Rosalie Bruel:** Software, Formal analysis, Investigation, Writing – review & editing, Visualization, Funding acquisition. **Aldo Marchetto:** Validation, Formal analysis, Investigation, Writing – review & editing. **Andrea Lami:** Validation, Formal analysis, Investigation, Writing – review & editing. **Jorge E. Spangenberg:** Validation, Formal analysis, Resources, Writing – review & editing. **Marie-Elodie Perga:** Conceptualization, Methodology, Validation, Resources, Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

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