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Long-term trends in carbon and color signal uneven browning and terrestrialization of northern lakes

Bianca M. Rodríguez-Cardona[1,2✉], Daniel Houle[3], Suzanne Couture[3], Jean-François Lapierre[2,4] & Paul A. del Giorgio[1,2]

The widespread browning of northern lakes has been associated with long-term increases in dissolved organic carbon and color and should be linked to changes in surface water carbon dioxide, yet the long-term covariation in these three key carbon components of lake functioning remains to be assessed. We present long-term trends in dissolved organic carbon, color, and carbon dioxide from lakes, with generally positive but highly variable trends in organic carbon and a large degree of uncoupling with color and carbon dioxide. The highest rates of change in color and carbon dioxide were in lakes with greatest increasing dissolved organic carbon trends. Lakes with the lowest water retention times had greater increases and stronger coupling between all three parameters, coinciding with dominance of terrestrially derived carbon. These results suggest an uneven terrestrialization of northern lakes, where the increases and coupling in the three carbon components depends on hydrology and watershed connectivity.

[1] Université du Québec à Montréal, Montréal, Canada. [2] Groupe de Recherche Interuniversitaire en Limnologie (GRIL), Montréal, Canada. [3] Environment and Climate Change Canada, Montréal, Canada. [4] Université de Montréal, Montréal, Canada. ✉email: rodriguez.cardona.bm@gmail.com

Terrestrial carbon transport to aquatic networks has changed over the past decades leading to a general increase in dissolved organic carbon (DOC) concentrations in lakes and rivers of Europe, UK, Canada, and northeast USA[1–4]. Different hypotheses have been advocated to explain these trends, but the consensus is that the decline in atmospheric acid deposition[4,5], as well as a changing climate (i.e., increased precipitation and temperature)[2,6], have both played a major role. The observed changes in aquatic DOC imply increases in the export of terrestrial organic matter, which is typically rich in highly chromophoric aromatic, humic, and fulvic compounds[7,8]. Not surprisingly, along with the increases in DOC concentrations, there have been reports of increases in water color in lakes and rivers[9,10], often measured as colored dissolved organic matter (CDOM), a trend referred to as freshwater browning[11]. Although DOC and CDOM in surface waters tend to be tightly linked, their relationship can vary greatly spatially along the landscape and between ecosystem types[12], and at different temporal scales[13,14], due to changes in the sources and therefore the intrinsic properties of DOC and its processing in the aquatic network. Although very few studies have analyzed long-term trends in both CDOM and DOC, there is now evidence that decadal trends in lake DOC are not always coupled to long-term trends in CDOM[13–16], such that DOC increases are not always associated with freshwater browning. However, the factors underlying these differential patterns are not well understood.

The long-term trends in DOC and CDOM should in theory be further reflected in other aspects of the C dynamics of these systems, and in particular, patterns in surface water CO_2 concentrations. DOC and CO_2 have been found to be positively, albeit weakly, correlated in temperate[17] and boreal lakes[18,19]. This relationship has been hypothesized to reflect both the abiotic and biological processing of terrestrially derived DOC to produce CO_2 within aquatic systems, and the co-transport of terrestrial DOC with soil-derived CO_2 by groundwater[20]. The relationship between DOC and surface water CO_2 partial pressure (pCO_2) varies greatly between lakes in different regions, reflecting watershed scale differences in both DOC and CO_2 export[21,22], but little is known regarding the temporal variability in this relationship. Based on evidence from boreal lakes, it has been hypothesized that increases in terrestrially derived colored DOC should result in increases in ambient lake pCO_2 in northern lakes due to greater photodegradation and processing of carbon, but there have been few empirical tests of this hypothesis[23]. A positive long-term trend in surface water pCO_2 has been observed in some Swedish lakes[24], although there was only a weak relationship with long-term trends in either DOC or CDOM[24,25]. Conversely, a positive coupling between long-term trends in lake pCO_2 and DOC in Ontario has been reported, but this coupling emerged only above a certain threshold of DOC concentration and rate of change[26]. These apparently contrasting results may be in fact linked to differences in the inherent complexity and reactivity of the organic carbon (C) pools, and in the local hydrologic regimes such as regional runoff and lake water retention time (WRT), which are major modulators of C delivery and processing[27,28] that can subsequently influence DOC, CDOM, and pCO_2 as well as the coupling amongst parameters[12].

Numerous studies have focused on either long-term trends in DOC or CDOM but more rarely in CO_2. These three parameters, DOC, CDOM, and CO_2, are key facets of the terrestrial influence on northern lakes. Increased concentrations of DOC, increases in colored DOM, as well as over saturation in CO_2 are all indicative of terrestrial inputs to lakes[29,30], yet it remains unclear if and how strongly DOC, CDOM, and CO_2 tend to co-vary over long-term time scales, and what may modulate this co-variation. Collectively, the above evidence suggests that although long-term changes in DOC, CDOM, and pCO_2 in northern lakes should be connected, these relationships are complex and dynamic and should ideally be assessed over broad environmental, hydrologic, and climatic gradients that also capture a wide range of lake and watershed types. Our hypothesis is that all three parameters are positively correlated such that as DOC concentrations increase with concomitant increases in color, then pCO_2 should also increase as this is mostly driven by terrestrial inputs[23] from soil derived CO_2 reflecting a stronger terrestrial-aquatic connection. In order to test this hypothesis, we determined long-term trends (of up to 34 years) of mean annual DOC, water color (hereafter referred to as CDOM), and reconstructed surface pCO_2 (based on DIC and pH) for 92 lakes across eastern Canada (Fig. S1) with a broad range in catchment feature, climate, and hydrologic regimes. The reconstructed pCO_2 takes into account pH corrections from Liu et al.[31], and follows the same approach as Couturier et al. 2022[26], where they demonstrated that analytically measured and reconstructed pCO_2 based on DIC and pH agreed well for Northern lakes with similar ranges of pH, alkalinity, and DOC as those encountered here. Collectively, we assessed the degree of coupling and synchrony within the three C forms and linked these to hydrologic properties such as lake WRT and contemporary DOM composition to better understand the factors that modulate the long-term trends in these key C forms and their coupling on Northern lakes. We report that DOC, CDOM, and pCO_2 long-term trends are generally positive but highly variable and DOC and CDOM are decoupled for a large number of lakes. However, lake WRT plays an important role in modulating the degree of coupling between DOC, CDOM, and pCO_2, where low WRT lakes had overall greater increases and stronger coupling among all three parameters. This can be attributed to a tighter hydrologic connectivity within the catchment that provides greater proportions of DOC from terrestrial origin and reflects a strong connection to the landscape. These results suggest that the rates of change and coupling of DOC, CDOM, and CO_2 depend on hydrology and watershed connectivity that dictates different, but not totally independent facets of the terrestrialization of northern lakes.

Results and discussion

Long-term trends in lake DOC, CDOM, and pCO_2: patterns across lakes. To better understand the connections between DOC, CDOM, and pCO_2 trends, we grouped lakes based on their temporal trends in DOC, CDOM, and surface pCO_2 (using k-means clustering based on tau values) with no a-priori selection or sorting. Three groups resulted (Fig. 1A, Data S1), each composed of lakes having the greatest similarity in their long-term patterns of change in all three C variables; these clusters therefore represent categories of lake and watershed functioning that exist across the landscape. The clustering did not show any clear regional pattern, with lakes from all three regions present in the three clusters, although cluster one was dominated by Québec lakes (Fig. 2). Generally, lakes showed positive trends (+ tau) in DOC, CDOM, and pCO_2 across all three groups except for cluster one that showed declining (- tau) pCO_2 trends (Fig. 1B). The lakes in these three clusters also showed differences in watershed and hydrologic properties. Lakes in cluster one had higher median watershed slope, lowest median runoff, longest median WRT, and highest median elevation (Fig. 1B). Lakes in clusters two and three had lower median watershed slopes, lower median WRT, higher median runoff, and lower median elevation. There was no clear distinction in hydrologic or morphological properties between clusters two and three (Fig. 1B), although depth is slightly greater in clusters two and three (Fig. S3). We compared multiple lake properties (watershed slope, lake perimeter, and

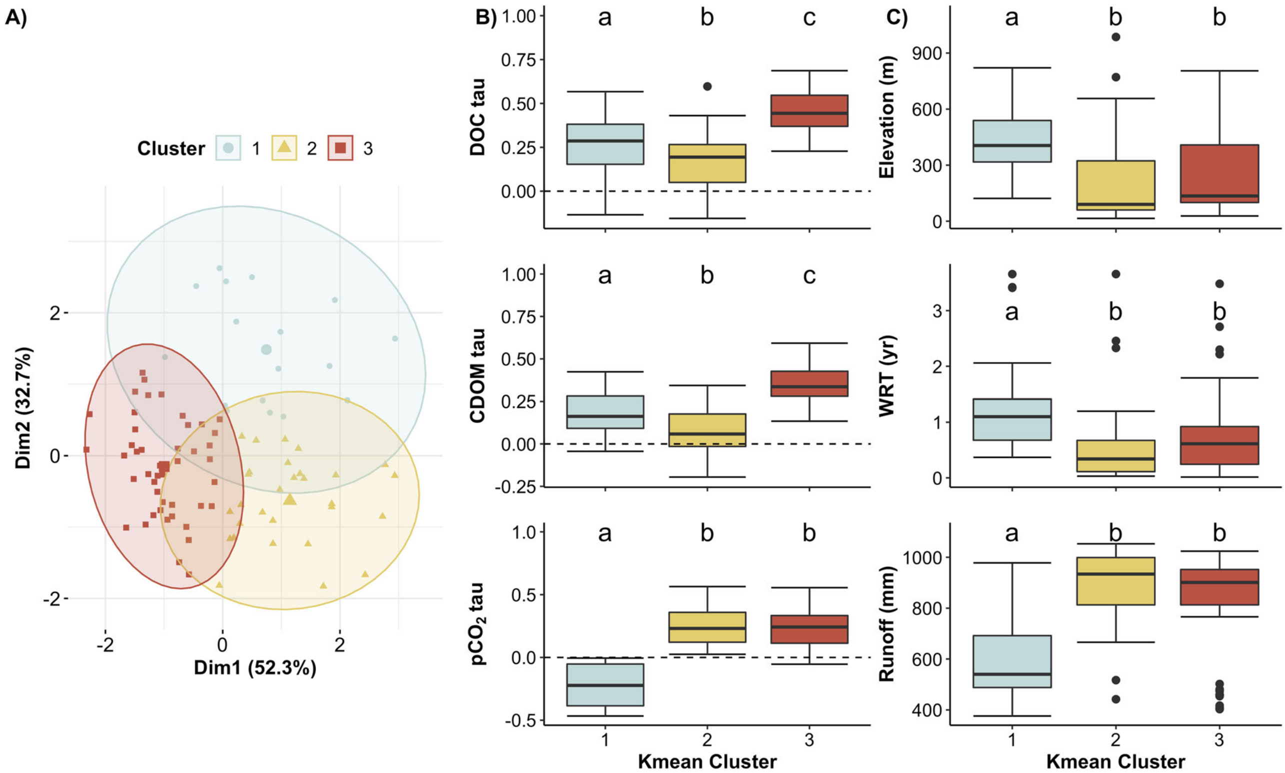

Fig. 1 Lake clustering based on long-term trends in DOC, CDOM, and pCO_2 and corresponding hydrological and morphological properties. A Visual representation of the Kmeans clusters for all lakes ($n = 92$) based on tau values of DOC, CDOM, and pCO_2 creating three clusters: one (blue), two (yellow), and three (orange), where each point is an individual lake. The explained variation of these representative axes are respectively included in parentheses. **B** Boxplots of DOC ($p = 2.75 \times 10^{-10}$), CDOM ($p = 9.86 \times 10^{-12}$), and pCO_2 ($p = 1.76 \times 10^{-9}$) tau values for lakes within each cluster (one: $n = 17$, two: $n = 29$, three: $n = 46$). **C** Boxplots of mean lake elevation ($p = 0.001$), water retention time (WRT) ($p = 0.006$), and surface runoff ($p = 7.40 \times 10^{-5}$) for lakes within each cluster (one: $n = 17$, two: $n = 29$, three: $n = 46$). Boxes represent interquartile range with the median value as the bold line, whiskers represent 1.5 interquartile range, and points are possible outliers. Parenthetical p-values in figure description above and lowercase letters above boxplots denote statistically significant differences ($\alpha = 0.05$) across clusters based on Kruskal-Wallis test for nonparametric variables. Dashed horizontal lines mark 0 to facilitate differentiation between positive and negative values.

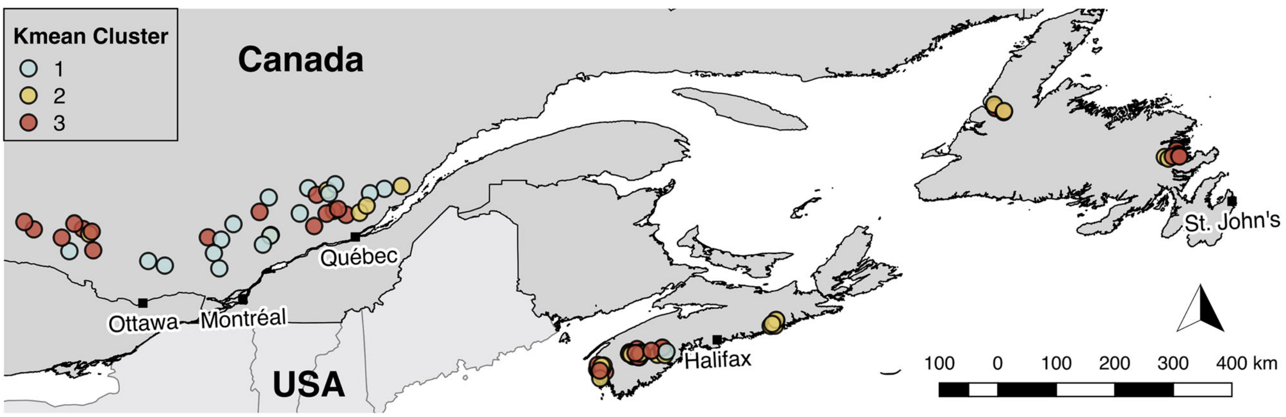

Fig. 2 Lakes across study in eastern Canada. Each point is a lake and colored by the corresponding Kmean cluster.

lake area) as well as lake chemistry (mean concentrations of NO_3^-, SO_4^{-2}, Ca^{+2}, and Mg^{+2}) and found no clear distinction between groups two and three (Fig. S2). The major difference between clusters 2 and 3 are DOC and CDOM trends, where both are greater in cluster 3 than in cluster 2, reflecting that lakes that are similar in morphology and chemistry can have very different long-term carbon trends. However, there may be watershed features that we have not captured in our data that determine these differences in long-term DOC, CDOM, and pCO_2 dynamics, and that these should be further explored.

Sen slopes were calculated for DOC, CDOM, and surface pCO_2 for each lake to describe the magnitude and direction of change over time. DOC Sen slopes ranged from -0.11 to $0.15\ \mathrm{mg\ L^{-1}\ y^{-1}}$, but values were generally positive (Fig. S3A) and within the range of DOC long-term rates of change of -0.4 to $0.8\ \mathrm{mg\ L^{-1}\ y^{-1}}$ [2,4,6] that have been reported for northern lakes. In particular, the median Sen slope in our study ($0.05\ \mathrm{mg\ L^{-1}\ y^{-1}}$) agrees very well with the median rate of change reported for lakes in Québec[1] and Ontario[3], both also in the order of $0.05\ \mathrm{mg\ L^{-1}\ y^{-1}}$ as well as a recent literature synthesis reporting a median rate of change of

0.04 mg L^{-1} y^{-1}, for lakes across Europe and North America[2]. CDOM Sen slopes in our study varied between −0.023 and 0.17 m^{-1} y^{-1} (Fig. S3B), with only 19% (18 out of 92) of lakes with negative trends or no clear trend, and an overall positive trend with a median of 0.02 m^{-1} y^{-1}, which translates into a median increase of around 1.1% y^{-1}. Other studies have reported rather contrasting results, for example, no change in water color across Finnish lakes and rivers from 1947 to 2014[13], and no clear trends in CDOM at the daily or annual scale for the Mississippi River from 1917 to 2010[14]. Conversely, a strong overall increase in color of Swedish lakes was observed from 1985 to 2015, in the order of 1.6% per year[32]. The patterns of change in surface water pCO_2 were less consistent than those of DOC and CDOM, with a range of −33.2 to 64.9 ppmV yr^{-1} and a higher proportion (20%) of negative Sen slopes relative to DOC (Fig. S3C). It should be noted that surface water pCO_2 is strongly influenced by the seasonal patterns of lake stratification, and therefore the uneven inclusion of stratified and non-stratified periods in the database likely adds noise to the long-term CO_2 patterns. Regardless, our overall median pCO_2 change was 9.5 ppmV y^{-1}, which is lower than the median value of 32.1 µatm yr^{-1} for lakes in the Adirondacks Region, USA[33], but within the range reported for Ontario lakes for the same period (8 to 11 µatm yr^{-1})[26]. Although yearly changes in DOC, CDOM, and pCO_2 were generally in line with studies that have studied them individually, or more rarely, in pairs, the degree of coupling of these three parameters across broad geographic gradients has not been explored previously.

Linking long-term trends in DOC, CDOM, and pCO_2. The relationships between DOC, CDOM, and surface pCO_2 Sen slopes were generally positive but highly variable (Fig. 3A–C). It was generally in lakes where DOC increased the most that the highest increases in CDOM and pCO_2 were measured; as DOC Sen slope increased, CDOM Sen slopes also increased, and pCO_2 Sen slopes tended to also peak (Fig. 3A). This same pattern persisted between DOC and pCO_2 Sen slopes (Fig. 3B) and CDOM and pCO_2 Sen slopes (Fig. 3C) although the relationships were noisier. Although other studies have reported that there is no consistent relationship between long-term trends in DOC and pCO_2[24], our results suggest that DOC, CDOM, and pCO_2 tend to covary in our northern lakes as a whole, albeit with greatly varying degrees of coupling between them[18,19,21].

To better understand the relationships among DOC, CDOM, and pCO_2 trends (Fig. 3A–C), we assessed how the strength (as r^2) and slope of the linear regressions between Sen slopes varied across the three different cluster groups defined in Fig. 1. For DOC and CDOM trends, both the slope of the regression and the % variability explained in CDOM Sen slopes by DOC Sen slope increased from cluster one to three, with lakes in cluster three having the greatest increases in both DOC and CDOM (Fig. 3D). The regressions between DOC and pCO_2 Sen slopes were inconsistent across the three clusters and only lakes in cluster three showed a clear positive relationship between the two (Fig. 3E). CDOM and pCO_2 Sen slopes had a similar pattern, with the only clear positive regression for lakes in cluster three (Fig. 3F). In addition, there was an overall positive relationship between Sen slopes with the respective average DOC, CDOM and CO_2 lake concentrations (Fig. S4A–C), but this relationship differed between clusters, it was non-existent in cluster one, which had the overall lowest Sen slopes and ambient concentrations (Fig. S4D), and was strongest for cluster three, which had the highest average concentrations of all C forms and the highest Sen slopes (Fig. S4F). The fact that the strongest regressions between Sen slopes were found in cluster three, where the highest average DOC concentrations and Sen slopes were observed,

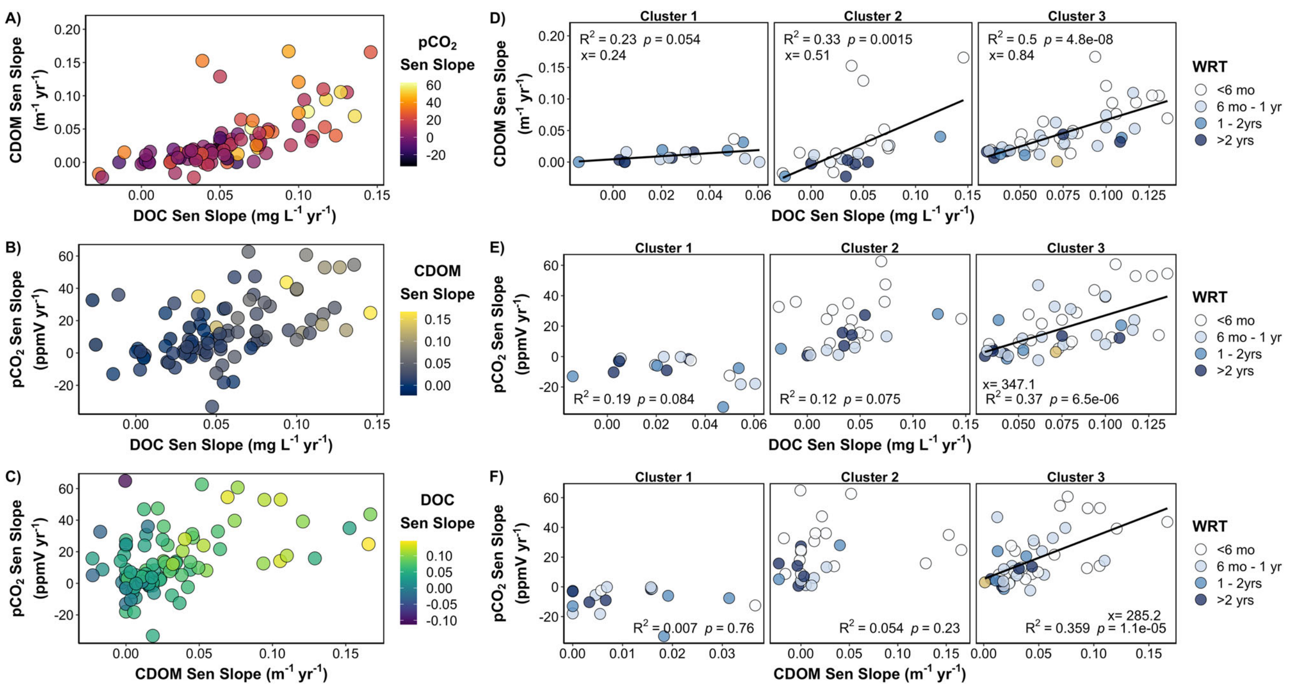

Fig. 3 Different iterations of the C triangle demonstrating variable relationships between DOC, CDOM, and pCO_2 that differed along a gradient in water retention time (WRT). Relating (**A**) DOC and CDOM Sen slopes with a color ramp of pCO_2 Sen slopes, (**B**) DOC and pCO_2 Sen slopes with a color ramp of CDOM Sen slopes, and (**C**) CDOM and pCO_2 Sen slopes with a color ramp of DOC Sen slopes for all lakes. Regressions between (**D**) DOC and CDOM Sen slopes per cluster, (**E**) DOC and pCO_2 Sen slopes per cluster, and (**F**) CDOM and pCO_2 Sen slopes per cluster with color describing the water retention time (WRT, years) for each lake; yellow point is lake where WRT was not available. In all figures, each point corresponds to an individual lake ($n = 92$) and n-values per cluster group: one: $n = 17$, two: $n = 29$, three: $n = 46$. Lines and regression slope (x) were only included for statistically significant relationships ($p < 0.05$).

points to the existence of a potential threshold of DOC concentration and magnitude of long-term change below which little or no discernible coupling between DOC, CDOM, and CO_2 is apparent. For example, Fig. 3A, B would suggest that there is no consistent long-term change in CDOM or pCO_2 relative to changes in DOC in lakes with DOC Sen slopes below 0.05 mg C L^{-1} y^{-1}, and these generally correspond to lakes with DOC concentrations below 5–6 mg L^{-1} (Fig. S4). This agrees with a previous study of Ontario lakes[26] where coupling between long-term trends in CO_2 and DOC was only observed above a threshold of 5 mg C L^{-1}, and with other studies that have also pointed to this same range of DOC as a threshold of change for important lake functions, such as metabolic balance[20] and primary production[34].

The factors that could regulate the trends and relationships within DOC, CDOM, and pCO_2 include watershed features such as runoff, topography, forest and soil types, and human activities, which influence the export of water and carbon forms to lakes[35]. Lake characteristics such as morphometry and WRT further influence the processing and transformation of carbon within lakes[21,28,36], where shorter WRT implies tighter hydrologic connectivity within the watershed and a higher C turnover as a result of both increased renewal and processing of C pools[27]. Within each cluster, lakes with lower WRT tended to have the highest long-term increases in DOC, CDOM, and pCO_2 (Fig. 3D–F). Our results suggest that local hydrology, and in particular, WRT appears to modulate these watershed drivers of long-term DOC change in individual lakes even within the same region, and therefore, also the coupling of DOC, CDOM, and pCO_2. In particular, short WRT is associated with continuous flushing and replenishment of both terrestrial DOC, which can be mineralized within the lake to CO_2, and soil derived CO_2[27,28,37]. This high connectivity with the landscape in turn allows lakes to reflect the shifts in biogeochemical signatures that may occur in watersheds due to climate or environmental change. In contrast, longer WRT tends to disconnect lakes from watershed processes by enhancing processing and removal of terrestrially derived C within lakes[37] leading to overall low Sen slopes of DOC and increases in the relative importance of autochthonous production of DOC, which further decouples DOC from CDOM and CO_2. This implies that WRT does not itself drive the long-term shifts in C loading to lakes or rates of change, which are likely driven by a combination of climatic and landscape level alterations. Rather, WRT modulates the expression of these watershed level signals by moderating the inputs, influencing the relationships and degree of coupling between DOC, CDOM, and pCO_2 within lakes, where greater WRT will lead to a divergence in the long-term trends in the three carbon forms.

To further explore the watershed or climate drivers potentially underlying the long-term trends in DOC, CDOM, and pCO_2, we related trends in all C forms to climate variables, lake hydrology and morphology, and lake chemistry variables. We found no clear patterns between DOC, CDOM, and pCO_2 Sen slopes and mean annual air temperature (Fig. S5) and none to very weak relationships with Sen slopes of mean annual air temperature but in some cases, there were weak negative relationships between CDOM and pCO_2 Sen slopes and temperature trends in Nova Scotia lakes and with DOC trends in Quebec lakes (Fig. S6). There were also no clear patterns between DOC, CDOM, and pCO_2 Sen slopes and total precipitation (Fig. S7) or Sen slopes of total precipitation (Fig. S8) per region. The lack of patterns are similar to Houle et al. 2020[35] and Hall et al. 2021[3] who also found no relationships between DOC change and mean annual air temperature or precipitation and suggests that there are local forces rather than regional factors influencing long-term patterns in the different C forms in lakes. We found weak positive relationships between CDOM and pCO_2 trends and lake median TN and TP concentrations (for a subset of lakes where available, Fig. S9, 10), suggesting cotransport of terrestrially derived nutrients. We also related the long-term trends in DOC, CDOM, and pCO_2 with TN Sen slopes (for a shorter time period, 1995–2008 and a subset of lakes where TN was available) and found no clear relationships with any of the C trends, despite a regional increasing long-term trend in TN (Fig. S11). Despite increasing trends in TN, most of these northern lakes remain mostly oligotrophic with TP below 20 μg L^{-1}, TN below 0.25 mg L^{-1}, suggesting that the patterns in DOC are not linked to eutrophication.

Assessing interannual synchrony in DOC and color within lakes. The degree of synchrony between monthly variation in the long-term time series in DOC and CDOM concentrations in each lake was characterized using mutual information (MI) as it describes the mutual dependence of two time series[38,39]. MI can measure how similar or different two vectors are over time by comparing two values per time point for the length of a time series. The temporal patterns between DOC and CDOM concentrations were generally highly decoupled in our study lakes, despite a strong positive correlation between average DOC and CDOM concentrations (Fig. S12). Most lakes (73 of 92) had low MI values (< 0.5), whereas only 21% of lakes had MI values closer to one (> 0.5) (Fig. 4A), suggesting that the temporal dynamics of DOC and CDOM concentrations are synchronized in only a small portion of lakes. This temporal decoupling between DOC and CDOM concentrations suggests that the quantity of OC and its optical properties are not always consistently linked. Lakes with high MI values tended to have the highest average concentrations and the highest DOC and CDOM Sen slopes (Fig. S13), suggesting that the coupling between these two aspects is strongest in scenarios of both high DOC and CDOM concentrations as well as the greatest long-term DOC and CDOM increases.

Lakes where DOC and CDOM concentrations were more synchronous, as reflected by high MI values, were also characterized by the highest average surface pCO_2 Sen slopes (Fig. 4A), and highest average pCO_2 (Fig. S5), confirming that under conditions when DOC and CDOM are temporally highly correlated, then all three parameters are more likely to be coupled and undergo the highest degree of long-term change. Scenarios where DOC and CDOM are highly coupled suggest a higher degree of connectivity to the surrounding landscape[13,15]. Higher input and turnover of terrestrial organic matter should be associated with higher pCO_2, due to both the injection of soil derived CO_2, and through the mineralization of fresh, soil derived organic matter[28]. Our own data confirm these hypotheses. For a subset of the lakes evaluated here, we obtained contemporary qualitative properties of the DOM, including optical components derived from excitation/emissions spectra and PARAFAC modeling; components 1 and 2 (C1 and C2) in particular, are highly aromatic compounds of terrestrial origin and highly photoreactive[40]. Lakes with the highest DOC, CDOM, and pCO_2 Sen slopes, and highest MI, were the ones with the highest contribution of C1 and C2 components to the total optical signature (Fig. 4B), suggesting that the DOM pool in these lakes is overwhelmingly dominated by terrestrial organic matter. The highest contribution of C1 and C2 tends to peak in lakes with the shortest WRT (Fig. S14), which further demonstrates the role of WRT as the mediator of lake response to changes in the watershed and climate. These low WRT lakes therefore have undergone a clear process of *terrestrialization*, i.e., increasing overall terrestrial influence, reflected in the convergence of the

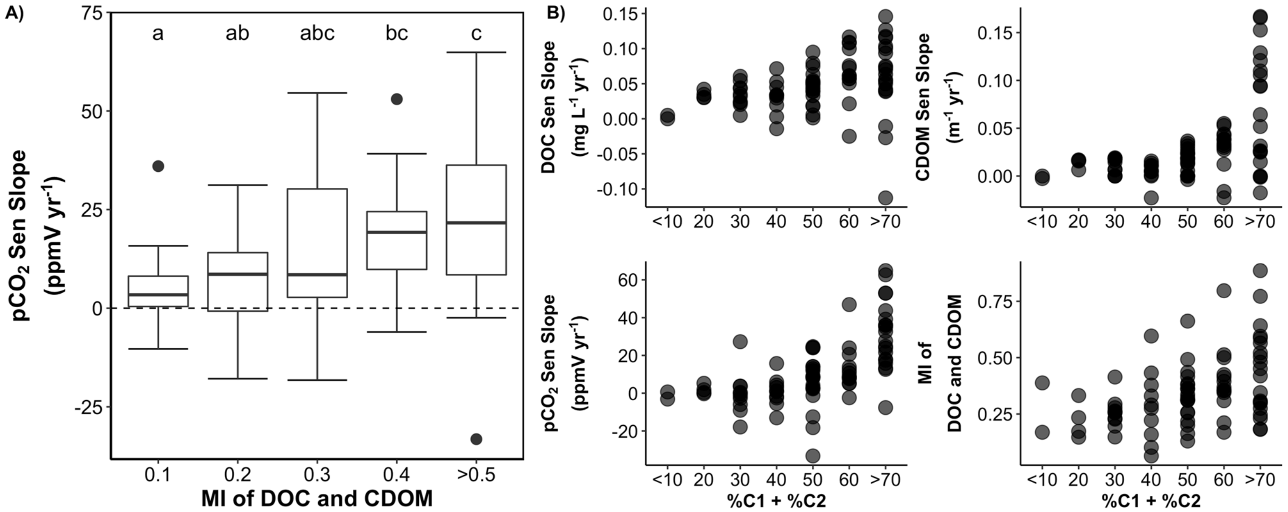

Fig. 4 pCO_2 increases in lakes where DOC and CDOM are highly synchronized reflecting DOM that is dominated by humic- and fulvic-like DOM of terrestrial origin. A Boxplots of pCO_2 Sen Slopes for binned mutual information (MI) values from DOC and CDOM for each lake ($n = 92$). MI group of 0.1 ($n = 14$) contain lakes with MI values < 0.2; the 0.2 group ($n = 23$) with MI values between 0.2 and 0.3; the 0.3 group ($n = 26$) values between 0.3 and 04; the 0.4 group ($n = 10$) values between 0.4 and 0.5; and the > 0.5 ($n = 19$) are lake MI values greater than 0.5. Lowercase letters denote statistically significant differences ($\alpha = 0.05$) across MI groups tested using Kruskal-Wallis test for nonparametric variables ($p = 0.02$). Boxes represent interquartile range with the median value as the bold line, whiskers represent 1.5 interquartile range, and points are possible outliers. Dashed horizontal line marks 0 to facilitate differentiation. **B** Relating the PARAFAC model components 1 and 2 (C1 and C2) with the Sen slopes of DOC, CDOM, CO_2, and MI of DOC and CDOM for each lake where each point is a lake with available PARAFAC data.

long-term dynamics of the three C forms. Terrestrialization in turn impacts multiple aspects of the functioning of the lakes, including metabolism, gas dynamics, physical structure, chemical composition, and biology[36,37,41,42].

The need for new framework in carbon trends. The varying degrees of temporal coupling between DOC, CDOM, and surface pCO_2 that we report here for northern lakes suggests that although these parameters are undoubtedly biogeochemically linked, they cannot be assumed to follow similar long-term trends, or act as proxies of each other or of the same watershed processes. Long-term increases in lake DOC concentrations, particularly in low DOC systems, are not always associated with concomitant trends in CDOM or pCO_2. Likewise, lakes that have experienced relatively large long-term shifts in CDOM do not always express significant changes in DOC concentration, suggesting qualitative changes in the incoming OM rather than shifts in the loading of DOC[16]. Therefore, we argue that the current nomenclature on long-term trends in lake carbon may have to be revised to accommodate this diversity of scenarios. The term *browning* has been used rather interchangeably for increasing DOC concentrations and color (CDOM)[4,9], yet these processes are in no way analogous, as we and others before have demonstrated[16]. The term *browning* should be restricted to long-term increases in water color due to CDOM, since increases in water color and CDOM are not always linked to changes in the quantity of DOC. We propose the term *organification* to describe long-term increasing trends in DOC concentrations, regardless of water color. While terrestrial inputs of DOC can be associated with increases in N or P, the term organification should adhere only to increases in DOC concentrations. Finally, we propose the term *carbonation* to describe increasing long-term trends in surface water pCO_2. Our results suggest that most lakes in eastern Canada show evidence of some degree of organification, yet only a fraction show distinct signs of browning or carbonation. Our own results further show that lakes that have experienced high degrees of organification will typically have also undergone both browning and carbonation, the convergence of the three processes resulting in a clear *terrestrialization of these northern lakes* (Fig. 5), which is likely driven by long-term changes at the watershed level. This convergence, which can be conceptualized as an equilateral C triangle (Fig. 5), tends to be expressed mostly in lakes with low WRT. The degree of coupling between DOC, CDOM, and pCO_2 relaxes, however, along a gradient of increasing WRT, therefore obscuring the terrestrialization signal[37], which can be expressed as C triangles of widely varying shapes and sizes (Fig. 5). Using adequate terminology to distinguish these processes is therefore important as they have very different consequences, and different underlying mechanisms. The drivers of browning may in some scenarios not be the same as those underlying organification, even if the two appear to be coupled, and although carbonation also partly reflects C export from watersheds that is common to browning and organification, it further integrates other lake and watershed mechanisms that render this process particularly complex.

Local hydrology is an integral regulator of the coupling within the C triangle across northern lakes. Over the past three decades for which we have reconstructed lake carbon trends, the average annual surface runoff of Québec and the Maritime regions has been consistently increasing (Fig. S15). As precipitation and surface runoff have increased regionally (on average between 0.3 and 0.4 $mm\,yr^{-1}$), terrestrial C export to lakes likely increased, WRT within aquatic networks may have declined, and therefore the terrestrial-aquatic linkage may have strengthened over the past decades. These patterns may underlie in part the widespread organification we have observed across these northern lakes. Should these climatic and hydrologic trends continue in the future, northern lakes in general would tend to converge towards a pattern of increased terrestrialization (Fig. 5), where shorter WRT allows the expression of the accelerating inputs of DOC, CDOM, and pCO_2, and where the temporal trends of these three C pools would be increasingly synchronous leading to regional shifts in the shapes and sizes of the carbon triangle.

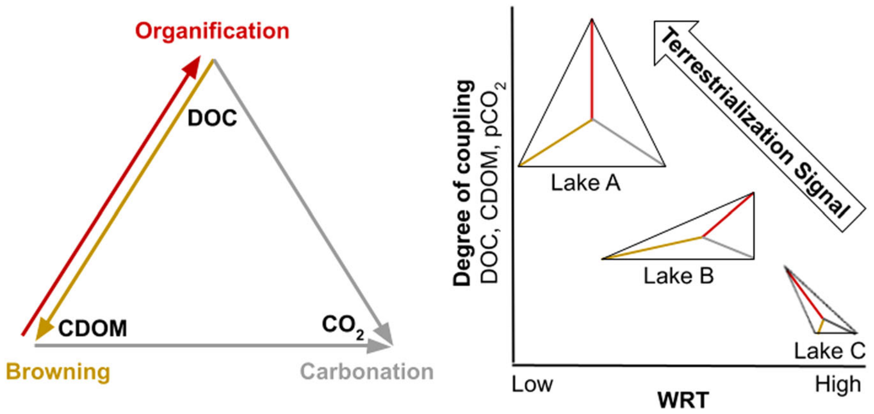

Fig. 5 The carbon triangle, long-term trends in DOC, CDOM, and pCO_2. Inter-relationships among the three constituents of the carbon triangle, with increasing DOC leading to organification, increasing CDOM leading to browning, and increasing CO_2 leading to carbonation. These three processes tend to be expressed in an increasingly strong and coupled way in lakes with low water retention times (WRT), which is depicted in the top-left triangle of the right panel (the red, orange, and gray lines are proportional to the strength of the organification, browning, and carbonation trends of a theoretical lake, respectively). The size and shape of the triangle will vary along a gradient of WRT as well as the rates of change and coupling of DOC, CDOM, and CO_2. The size or length of edges denotes magnitude of the rate of change over time, where low WRT lakes would exhibit greater rates of change than high WRT lakes. Additionally, as WRT declines with increasing trends and coupling of DOC, CDOM, and CO_2, then the terrestrialization signal increases.

Material and methods

Data set compilation. We compiled data for 92 lakes across Québec (QC), and the Maritime region (Newfoundland (NF) and Nova Scotia (NS) in Canada. Lakes in QC and NS were sampled by helicopter and collected at the center of the lake while lakes in NF were sampled from the edge. All samples were kept cool and sent to Environment and Climate Change Canada (ECCC) laboratories within 24–36 h. For each lake we obtained lake color, pH, conductivity, and concentrations of DOC and dissolved inorganic carbon (DIC) to obtain annual averages for each parameter based on data from May to September, as these were consistently available across all lakes and years and generally the ice-free period. Lake water pH and conductivity were measured potentiometrically using respectively pH-meter (Accumet 50) and conductivity meters (Accumet model AB30). Lake water temperature was not available for all dates so we used air temperature as a close approximation obtained from BioSIM[43,44].

Samples collected in QC lakes were filtered with 0.45 µm filters prior to analyses and DIC and DOC were measured using oxidation with persulfate-ultraviolet radiation and detection by infrared spectrometry until 2013, then thermal oxidation technique since 2014. Samples collected from NS and NF lakes were not filtered and TOC and TIC were determined by infrared analysis. Based on in-house laboratory studies, particulate organic matter is not often a problem in Atlantic Canada and pre-filtering is rarely done in regional studies[45].

Given that our lakes tend to be rich in organic matter (1–13 mg L^{-1}) and acidic (pH 4.5–7.6) pH was corrected for ionic strength (IS)[31]:

$$IS = 1.3 \times 10^{-5} \text{ x conductance} \quad (1)$$

$$\Delta \text{pH} = 0.3 + 0.5 \text{ x} \log_{10}(\text{IS}) \quad (2)$$

$$\text{pH}_{\text{Corr}} = \text{pH}_{\text{raw}} - \Delta \text{pH} \quad (3)$$

where IS (Eq. 1) is obtained from lake conductance measured in situ and applied to Eq. 2 to obtain a delta pH (Δ pH). The final corrected pH (Eq. 3) is the difference between pH_{raw}, the pH from the lake, and (Δ pH).

We reconstructed pCO_2 based on DIC concentrations[46,47] as Couturier et al. 2022[26], showed that calculated pCO_2 based on DIC and pH agrees better with the measured pCO_2 (headspace sampling analyzed on a Picarro G2201-i) than that calculated pCO_2 based on alkalinity and pH (even when correcting for DOC influence on alkalinity). Additionally, they also showed that the pH correction proposed by Liu et al. 2020[31] improved the calculated CO_2 based on the DIC method and reduced the % error in pCO_2 calculations.

For QC, true color measurements were obtained by spectrophotometric technique while in NS and NF lakes, apparent color was determined by platinum-cobalt standard; all color measurements are expressed in Hazen units. To express these in more contemporary metrics used for CDOM, we converted Hazen units to absorbance at 440 nm[48] (Eq. 4):

$$CDOM\,[m^{-1}] = \frac{Color[Hu] + 0.209}{18.216} \quad (4)$$

Water samples were also analyzed for nitrate (NO_3^-) and sulfate (SO_4^{-2}) by colorimetric analysis until 2014 and by ion chromatography since them. Concentrations of calcium (Ca^{+2}) and magnesium (Mg^{+2}) were determined by atomic absorption and after 1999 by inductively coupled plasma mass spectrometry (ICP-MS). Total nitrogen (TN) was determined spectrophotometrically at 520 nm by flow injection analysis and TP was determined by autoclave digestion with a LACHAT-FIA. Both TN and TP were determined from unfiltered samples. ECCC laboratory participates every year in national interlaboratory comparisons and is accredited by the Canadian Association for Laboratory Accreditation (CALA, http://www.cala.ca).

Time series and trend analyses. Time series are based on the annual averages of CDOM and DOC concentrations and reconstructed pCO_2 up to 34 years in length starting in 1983 for Quebec lakes and 1995 for Maritime lakes extending to 2019 for most lakes (Data S1). Time series were used to determine tau values for DOC, CDOM, and pCO_2 using the seasonal Mann-Kendall trend test from the *Kendall R*-package[49]. Tau values are unitless and between −1 and 1 to describe the monotonicity of a trend where closer to −1 describes strong negative monotonic trends and closer to 1 are strong positive monotonic trends. We used the tau values as a general descriptor of DOC, CDOM, and pCO_2 directional trends for clustering analysis purposes given that k-means clustering is sensitive to scaling. We also obtained Sen slopes[50] with the *trend* R-package[51] for DOC, CDOM, and

pCO_2. Sen slope is a non-parametric approach that provides a slope (median change over time), similar to a regression but not heavily influenced by outliers and estimates the magnitude of the trend. Long-term trends for TN concentrations for a subset of lakes in Nova Scotia and Newfoundland where TN was available (55 of 92 lakes) were determined the same way described above but time series were shorter, between 1995 and 2008.

Time series from each lake were also used to determine the synchrony between DOC and CDOM concentrations in each lake using mutual information (MI) with the *muti* R-package[52]. Mutual information characterizes the mutual dependence of two time series in a non-parametric approach[38,39]. MI provides values between 0 and 1 where values closer to 1 indicate a strong synchrony between DOC and CDOM and MI values closer to 0 describe little covariance between the temporal dynamics of DOC and CDOM concentrations.

Clustering analysis. Lake clustering was based on DOC, CDOM, and pCO_2 tau values by k-means partitioning method from the *stats* R-package (R Core Team 2019). The number of clusters was determined a-priori with the elbow method with the fviz_nbclust function from the *factoextra* R-package[53], targeting the smallest possible total within-cluster sum of square (WSS) using Euclidean distance.

Lake morphology. Lake area, elevation, perimeter, and watershed slope were obtained using ArcGIS (Arcmap 10.6.10) from hydrological layers obtained from *Données Québec* and hydrographic features (Lakes, Rivers and Glaciers in Canada - CanVec Series) and digital elevation model layers (Canadian Digital Elevation Model, 1945–2011) from *Open Government Portal*. Lake depth was measured at the sampling site with a Hawkeye DT1H handheld sonar system. Climatic variables used to calculate runoff were obtained from BioSIM[43,44]. Lake WRT was calculated as the ratio of estimated lake volume to mean annual runoff.

Regional surface runoff. Regional long-term surface runoff for lakes in QC, N, and NF were obtained from the ERA5 model[54] from the European Center for Medium-Range Weather Forecasts. Trends in surface runoff were obtained as described above.

PARAFAC model. Fluorescent DOM (FDOM) was measured for a subset of 78 lakes with a Cary Eclipse Fluorescence spectrofluorometer (Agilent Technologies) in 1 cm quartz cuvettes across excitation and emission wavelengths of 230 to 450 (5 nm increments) and 240 to 600 (2 nm increments). FDOM emission and excitation matrices (EEMs) were corrected (inner filter effect, conversion to Raman Unit, removal of scattering) using the *paRafac.correction* R-package[55]. EEMs were then analyzed using the parallel factor analysis (PARAFAC) model[56] in MATLAB 8.2 (MathWorks, Natick, MA, USA) with the DOMFluor toolbox[57]. We obtained a 4-component model with components widely corresponding to previously published models; in particular, C1 is comparable to C3 in[40] for hundreds of Quebec boreal lakes, rivers and wetlands, which was very photosensitive and tended to be more relatively abundant in high DOC and nutrient sites with high terrestrial influence. C2 is similar to the C2 reported in the same study, which was also particularly abundant in lakes with high terrestrial influence and with high concentrations of colored DOC of terrestrial origin.

Statistical analysis. Differences across tau values, MI values, and hydrologic properties were determined with a Kruskal-Wallis rank sum test in the *stats* R-package (R Core Team 2019)[58], due to uneven sample size between clusters. Where significant differences were detected, we used a *post-hoc* Wilcoxon test in the *stats* R-package to compare cluster levels. Relationships between DOC, CDOM, and pCO_2 across clusters were determined by linear regressions. All data and statistical analyses were conducted in R (R Core Team 2019) using RStudio (version 1.4.1106 RStudio, Inc. 2019) except for PARAFAC modeling that was done in MATLAB.

Data availability

All data are publicly available and can be accessed through the *metaGRIL* hosted on Borealis, the Canadian Dataverse Repository: https://borealisdata.ca/dataset.xhtml?persistentId=doi:10.5683/SP3/GAZNGK.

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Author contributions
B.R.C., Pd.G., and D.H. conceived and designed the study, B.R.C. conducted all data and statistical analyses with assistance from Pd.G. and D.H., D.H. and S.C. provided and curated the data set, and J.F.L. conducted analyses on qualitative properties of DOM; B.R.C. wrote the manuscript with significant assistance and comments from Pd.G., D.H., and J.F.L.; B.R.C., Pd.G., and J.F.L. created the conceptual figure. All authors read, contributed, and approved the final manuscript.

Competing interests
The authors declare no competing interests.

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Correspondence and requests for materials should be addressed to Bianca M. Rodríguez-Cardona.

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