

Carbocentric limnology: looking back, looking forward¹

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Abstract: In this perspective article, I argue that dissolved organic carbon occupies a central role in the functioning of lake ecosystems, comparable in importance to that played by nutrients. Because lakes receive so much dissolved organic carbon from the terrestrial landscape, its accumulation in water bodies usually represents the largest pool of lacustrine organic matter within the water column. The transformation of even a small fraction of this external carbon by the microbial community can alter significantly the metabolic balance of lake ecosystems, simultaneously releasing carbon dioxide to the atmosphere and burying organic carbon in lake sediments. At the landscape level, even if they occupy a small fraction of the landscape, lakes play a surprisingly important role in the regional carbon budget, particularly when considered at the appropriate temporal scale.

Résumé : Dans cet article perspective, j'avance que le carbone organique dissous joue un rôle central dans le fonctionnement des écosystèmes lacustres, comparable en importance à celui joué par les nutriments. Étant donné que les lacs reçoivent des apports tellement importants de carbone organique dissous des terres environnantes, son accumulation dans les plans d'eau représente généralement le réservoir le plus important de carbone organique lacustre de la colonne d'eau. La transformation même d'une petite fraction de ce carbone d'origine allochtone par la communauté microbienne peut altérer significativement le bilan métabolique de l'écosystème entier, libérant simultanément du dioxyde de carbone à l'atmosphère et enfouissant du carbone organique dans les sédiments lacustres. À l'échelle du paysage, même s'ils occupent une petite portion du territoire, les lacs jouent un rôle d'importance surprenante dans les bilans régionaux de carbone, particulièrement lorsqu'évalué à l'échelle de temps appropriée.

Introduction

In the last months of his life, Canadian limnologist Frank H. Rigler completed a manuscript based on a plenary lecture he gave at the second annual meeting of the Society of Canadian Limnologists. That essay (Rigler 1982) examined where limnology stood in its development as a predictive science. A quick historical analysis showed that the successes of limnological science were largely based on the application of a small set of general and repeatable principles that were, in fact, little more than statistical relationships. Although simplistic at first glance, he recognized the possibilities of extending the scope of this approach further and therefore advocated for a more empirical limnology in which greater relevance should be given to simple empirical relationships between physical, chemical, and biological state variables of ecosystems. In that framework, he considered that if limnological knowledge could be represented on an imaginary scale between 0 (we know nothing) and infinity

(we know and can predict everything perfectly well), we were at one (1) in 1982. Although he never specified to what the 1 corresponded, I speculate that it represented the notion that the limnological community had already identified one of the key limnological gradients, one main variable enabling us to understand and therefore predict so many aspects of lake function and structure. That variable is obviously phosphorus, the key driver of trophic state, at least in most temperate lakes. There are now literally hundreds of published relationships based on phosphorus concentration in lakes (Peters 1986). In turn, because it was possible to estimate lake phosphorus concentration from lake and watershed characteristics, the whole approach gave rise to one of the first comprehensive environmental management strategies that was based on quantitative science.

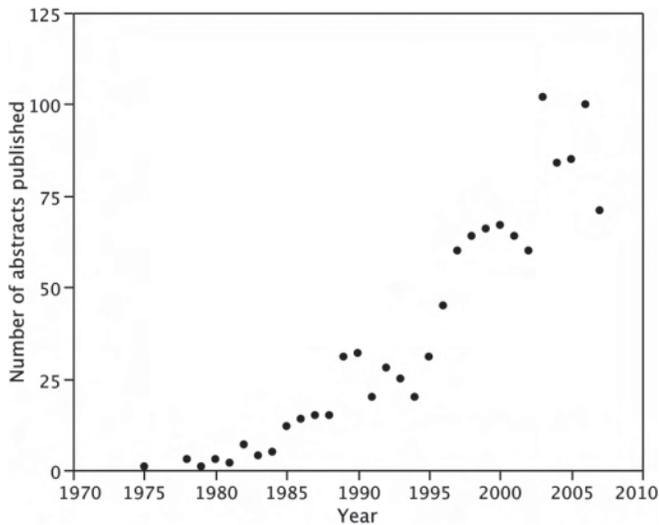
If we were to repeat this same exercise today, I venture to say that we have progressed to number 2, because the last 20 years has seen the emergence of a second main limnological gradient, dissolved organic carbon (DOC). Dissolved

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¹Based on the F.H. Rigler Lecture delivered at the annual meeting of the Society of Canadian Limnologists in January 2005.

Fig. 1. Increase in the annual number of abstracts referring to dissolved organic carbon (DOC) and lakes over the past 30 years.



organic carbon plays a somewhat different type of role than phosphorus. Whereas nutrients are analogous to the volume button on a stereo set, DOC is more akin to an equalizer whereby different components of aquatic ecosystems are filtered to different extents. DOC is the great modulator, the variable that modifies the influence of other variables.

This recognition that DOC plays such a fundamental role in lakes is reflected by the continually increasing attention we are devoting to it. Figure 1 illustrates the number of publications with the expressions “dissolved organic carbon” and “lake” in the title or abstract as a function of year of publication. This faster-than-linear increase shows that this field of research continues to be fruitful. In this paper, I wish to use the story of lake DOC research to illustrate how limnological research has important consequences, not only about the functioning of aquatic systems in general, but also about the role of lakes in their larger landscape, both at regional and global scales.

The multiple roles of DOC in freshwater systems

That DOC plays an important role should perhaps not come as a surprise. Except for the accumulated carbon buried in lake sediments over millennia, DOC represents by far the largest reservoir of organic carbon in the water column of lakes, followed by heterotrophic bacterial biomass, at the most an order of magnitude less, and the combined biomass of phytoplankton, zooplankton, and fish represent only about 2% of the total carbon mass (Table 1). Thus, the sheer magnitude of the DOC pool alone confers DOC a potentially very large role in any process that influences the metabolic activity of aquatic organisms. Consequently, even relatively small changes or alterations to that DOC pool are likely to have a greater quantitative impact on the overall carbon flux than large changes in any of the other “living” pools of organic carbon. Perhaps more overwhelming to the functioning of the lake than its sheer pool size, however, are the many constraints that DOC exerts on the physical, chemical, and biological properties of aquatic ecosystems. Although my

Table 1. Carbon pools typical of the different active organic carbon pools in lakes of southern Quebec.

| Carbon pools | Areal C content (mg C·m ⁻²) |
|--------------------------|---|
| Dissolved organic carbon | 40 000 |
| Heterotrophic bacteria | 1 000 |
| Phytoplankton | 400 |
| Zooplankton | 150 |
| Fish | 200 |

purpose is not to review them in detail, it is useful to identify the main areas of interactions.

Because of its strong light-absorbing properties, DOC largely dictates both the depth penetration (Fee et al. 1996) and the spectral properties of the light reaching aquatic organisms (Kirk 1994). Even coarse measures of water transparency in lakes, such as the all-purpose Secchi depths, are largely driven by light attenuation due to DOC and not by the photosynthetic pigments of phytoplankton. Except in highly eutrophic lakes or where DOC has been strongly photobleached, the light extinction coefficients of more than 90% of Quebec lakes that we have sampled over the past decade are due mostly (>50%) to DOC (Y. Prairie, unpublished data). Because of its particularly strong absorbance in the ultraviolet (UV) range (Laurion et al. 1997), DOC will provide natural UV protection to aquatic organisms (Schindler and Curtis 1997; Molot et al. 2004). Most of the light absorbed by the chromophoric portion of the DOC is transformed as heat and will thus largely determine the lake’s thermal regime, vertical structure, and duration of stratification. With all else being equal, lakes with highly colored DOC concentrations will typically have a much steeper thermal gradient at the thermocline and will modulate the inter-annual temperature differences owing to climate (Snucins and Gunn 2000).

The influence of DOC on the chemistry of lake waters is just as pervasive, although considerably more complex. DOC plays major roles in the transport and delivery of metals (Perdue 1998) and of organic contaminants (Haitzer et al. 1998), as well as on their bioavailability to aquatic organisms (Heekyoung Choi et al. 1998; Winch et al. 2002). Its role on the fate of nutrients, particularly phosphorus, is similar in that it modulates the extent to which they can be used by the phytoplankton (Francko and Heath 1982). In addition to modulating the fate of other elements, DOC is itself a source of highly reactive species such as hydrogen peroxide (Scully et al. 1995; Hakkinen et al. 2004) and hydroxyl radicals (Vione et al. 2006) through various light-induced interactions such as the Fenton reaction or nitrate hydrolysis. These powerful oxidants will in turn break the complex DOC molecules into simpler constituents, rendering them more available to microbial degradation (Bertilsson et al. 1999; Bertilsson and Tranvik 2000).

There is considerable research devoted to identifying and quantifying the origin of the DOC in lakes. While all living aquatic organisms can potentially release various forms of organic carbon, the bulk of the lake DOC pool is believed to be of terrestrial origin, as evidenced by its ¹³C signature of typically –28‰ (Kritzberg et al. 2006). This organic terrestrial leachate can be several centuries old (Raymond et al. 2004), which in itself may suggest a wide temporal uncou-

pling between the terrestrial and aquatic carbon transformation processes. Although this DOC remains recalcitrant while within the soil matrix, it can become much more reactive, chemically and biologically, once it reaches open aquatic environments such as streams and lakes. In this regard, the paradigm whereby allochthonous DOC is intrinsically more recalcitrant than autochthonous DOC is probably wrong, or at least not as general as currently believed.

DOC and lake metabolism

DOC, in addition to its indirect influences on the biological communities, also acts as a direct source of food for microbial growth. If it were possible to completely shade a lake from sunlight, its dark waters would still be able to support secondary production, albeit to a much reduced extent. Because most of this lake DOC is of terrestrial origin, streams and rivers feeding into lakes are not only a vehicle for nutrients and water, but are also an important energy vector, transferring and transforming land photosynthesis into lake biological productivity. Quantifying the extent to which external inputs of DOC support the lake's food web is an area of active research. Depending on the nutrients available, heterotrophic bacteria will utilize allochthonous DOC with lesser or greater efficiency (Smith and Prairie 2004) and convert it to biomass, a portion of which will eventually make its way up the food web. Recent work based on whole-lake addition of ^{13}C and ecosystem modeling suggests that in oligotrophic systems, allochthonous organic carbon can sustain 30%–40% of the biomass of higher trophic levels (Pace et al. 2004). In eutrophic systems, this fraction is considerably reduced and amounts to only a few percent (Kritzberg et al. 2005). Such experiments have shed considerable light on the pathways of carbon flow.

Some constraints on this magnitude can be estimated using a simple mass balance approach. Assuming that the passage of riverine inorganic carbon loading through a lake is essentially conservative, the carbon budget of a lake at steady-state conditions can be formulated in terms of its organic fraction as

$$\text{OC}_{\text{in}} + \text{GPP} = \text{ER} + \text{SED} + \text{OC}_{\text{out}}$$

where OC_{in} and OC_{out} are organic carbon inputs and outputs, respectively, GPP is gross primary production, ER is ecosystem respiration, and SED is net carbon sedimentation, all expressed in $\text{mg C}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$. The upper limit of the contribution of external organic carbon loads to ecosystem respiration is given by $(\text{OC}_{\text{in}} - \text{OC}_{\text{out}})/\text{ER}$, and that of in situ primary production is given by GPP/ER . For a suite of 20 oligotrophic to eutrophic lakes from southern Quebec for which we have organic carbon mass balances, as well as metabolic measurements, it is clear that external organic matter inputs is a significant but a quantitatively relatively minor source, with a potential contribution to ecosystem respiration varying between 9% and 20%.

Conversely, if it were possible to filter out the DOC from the inflowing waters before it reaches the lake, how much would the ecosystem change? In this imaginary scenario, it is unclear whether the increased light penetration would fully compensate for the eliminated terrestrial DOC – lake production shunt. Ultimately, a more fundamental challenge

is learning how light and allochthonous DOC quantitatively interact. For example, how much does the sun dictate what the fate of the organic carbon coming from the land will have in the lake? Or conversely, how much does the organic carbon from rivers affect how the phytoplankton can use the light from the sun?

The respiration of allochthonous DOC by heterotrophic bacteria will influence the equilibrium of dissolved biological gases such as oxygen and carbon dioxide. If the respiration of allochthonous DOC exceeds the portion of in situ primary production that is permanently sedimented, it will contribute to making lakes a source of CO_2 to the atmosphere, a widespread phenomenon (Cole et al. 1994). Several studies have shown that 5–6 $\text{mg DOC}\cdot\text{L}^{-1}$ represents an adequate threshold value above which lakes tend to be supersaturated in CO_2 relative to the atmosphere (Prairie et al. 2002; Hanson et al. 2003; Sobek et al. 2005), suggesting that lake DOC concentration largely reflects organic carbon loading. However, part of the noise in the relationship between DOC and pCO_2 can be attributed to the counteracting influence of in situ primary production, itself driven by nutrient conditions. In southern Quebec lakes, average surface pCO_2 is quite adequately predicted by a combination of both lake DOC and lake chlorophyll concentrations as

$$\text{pCO}_2 = -182.0 - 20.7\text{Chl } a + 131.2\text{DOC}, r^2 = 0.84$$

where pCO_2 is the CO_2 partial pressure (expressed in μatm (1 atm = 101.325 kPa)), Chl *a* is chlorophyll *a* (in $\mu\text{g}\cdot\text{L}^{-1}$), and DOC is the dissolved organic carbon (in $\text{mg}\cdot\text{L}^{-1}$). Solutions of this equation for oligotrophic (Chl *a* = 1 $\mu\text{g}\cdot\text{L}^{-1}$) and eutrophic (Chl *a* = 15 $\mu\text{g}\cdot\text{L}^{-1}$) lakes suggest that DOC thresholds for CO_2 supersaturation vary only narrowly, with values of 4.4 and 6.6 $\text{mg DOC}\cdot\text{L}^{-1}$, respectively. Standardized coefficients for the same model suggest that the relative importance of primary production and DOC in shifting the whole-system metabolic balance is nearly identical both in magnitude and in explanatory power.

One important advantage of using gas dynamics to assess lake metabolism is that it captures the net balance of all of the ecosystem's metabolic components (plankton, macrophytes, sediments). For example, previous debates concerning net heterotrophy have focused on the pelagic component alone, through measurements of primary production and respiration of bottled epilimnetic samples (del Giorgio and Peters 1994; Carignan et al. 2000). Although informative about this ecosystem component, the approach may have led to misleading inferences about the overall status of lakes because epilimnetic bottle samples do not necessarily capture the lake's respiration and primary production components to the same degree. For example, benthic primary production often represents an important fraction of the total carbon fixed by photosynthesis within the lake, particularly in small oligotrophic systems (Vadeboncoeur et al. 2001, 2003). Recent evidence suggests that primary production derived from macrophytes is often partially released as DOC in both marine (Barron et al. 2004) and freshwater (M. Demarty and Y.T. Prairie, unpublished data) systems. In clear and shallow systems, where ecosystem primary production is often dominated by benthic autotrophs, internal DOC production is likely the main source of DOC to the lake. In turn, if this organic carbon source is consumed and respired by pelagic

heterotrophic bacteria, it will shift the balance towards an apparent net heterotrophy that may be only local to the pelagic epilimnion and not necessarily appropriate as a whole-system characterization of a lake's metabolic status. In situ incubations of growing macrophytes in southern Quebec lakes showed that this DOC release occurred only during photosynthesis and can represent between 15% and 35% of the gross primary production of the plant. In the summer months of shallow lakes, where submerged macrophytes can colonize much of the lake surface, we calculate that DOC loading from aquatic plants can be nearly as important as the inputs from the watershed (M. Demarty, Université du Québec à Montréal, Département des Sciences Biologiques, C.P. 8888, Succursale Centre-Ville, Montréal, QC H3C 3P8, unpublished data). Little is known about the lability of this organic material to heterotrophic bacteria, but its rapid accumulation in in situ incubation chambers suggests that it can persist over time scales of days to weeks, long enough to be transported to the pelagic zone or even to downstream lakes.

Despite the internal generation of DOC by lake primary producers, most lakes are net sinks for organic carbon in that they export less DOC than they receive from upland areas (Dillon and Molot 1997). Whether the mechanism for this in-lake net retention is sedimentation, gas evasion (as carbon dioxide or methane), or most likely a combination of both is largely speculative and has been suggested to depend on the chemistry of the system, particularly pH (Molot and Dillon 1997). However, in southern Quebec lakes of the Eastern Townships region, gas evasion of CO₂ produced by the microbial consumption of DOC is likely the main pathway of carbon loss. In these lakes, summer net mass balance of DOC, distributed over the entire epilimnetic volume, varies between 3 and 44 µg C·L⁻¹·day⁻¹ with a mean of 19.8 µg C·L⁻¹·day⁻¹. DOC lability experiments carried out in an overlapping set of lakes where DOC consumption is measured over long incubations in the dark (2–4 weeks) showed a very similar distribution of values (range 10–37; mean 20 µg C·L⁻¹·day⁻¹), suggesting that most of the DOC loss occurs through consumption. Given generally low bacterial growth efficiency (del Giorgio and Cole 1998; Smith and Prairie 2004), the metabolized DOC is likely returned to the atmosphere as gas evasion, a situation similar to that observed in Ontario Shield lakes (Dillon and Molot 1997). Indeed, calculations based on the measured pCO₂ and gas exchange velocities appropriate to low wind conditions (Cole and Caraco 1998) suggest that gas evasion ultimately accounts for most of the organic carbon loss estimated from mass balance. This suggests that in many aquatic systems, the bulk of the allochthonous DOC utilized by the microbial community is simply burned and not transferred to the higher levels of the trophic web.

Lakes in their landscape: do they matter?

In several regions of Quebec, lakes and ponds occupy up to 15% of the landscape surface, a very high figure compared with most areas of the world. This landscape is thus particularly suitable to examine whether lakes can be important to their regional carbon budget. Although current models of carbon cycling often consider inland surface waters nearly negligible in comparison with the adjacent terrestrial

land, there are several reasons why lakes may play a disproportionate role relative to their surface area. First, lakes act as funneling receptors for all the organic materials drained from their much larger watersheds, yielding carbon processing rates that are proportionately much more intense in water than on land (Cole et al. 2007). Second, once organic matter is buried in lake sediments, it represents a much more permanent sink of carbon than that stored in the surrounding soils of its watershed. The cold and relatively constant temperature of hypolimnetic sediments of lakes, where most of the sediments are stored, provides a much less conducive environment for organic matter mineralization than the highly fluctuating temperature and humidity conditions of soils, particularly in regions where periodic forest fires can destroy much of the accumulated soil organic carbon. As a result, soil organic carbon is rarely older than a few hundred years, whereas lake sediment organic carbon can remain stable for millennia, as shown in the organic carbon profile of long sediment cores. Lastly, because lakes occupy local low points within the surrounding topography, they provide natural delivery points where subsurface water highly supersaturated in CO₂ derived from soil respiration is ultimately liberated to the atmosphere and therefore constitute landscape chimneys. In short, lakes can play a much larger role in carbon cycling than their modest occupation in the landscape may suggest.

This view is not shared by the larger scientific community, however. Whether they are forests, wetlands, or land converted to agricultural purposes, terrestrial ecosystems are thought to represent much greater sinks for carbon than the lakes spotting the landscape. For example, net ecosystem exchange (NEE) measured by eddy-covariance towers in several temperate forests suggests that they accumulate between 60 and 240 g C·m⁻²·year⁻¹ (Barr et al. 2002). Similar values have been obtained for other forested ecosystems throughout the world. Considering that the average watershed to lake area ratio is around 8–10, lakes would have to process carbon at areal rates nearly one order of magnitude greater to be regionally on par with the terrestrial landscape. This indeed would be at odds with measured rates of carbon efflux (as CO₂ + CH₄ evasion) or carbon storage, both only amounting to a few grams C·m⁻²·year⁻¹. However, I argue that in addition to the known technical difficulties associated with measuring terrestrial NEE from eddy covariance towers, the approach suffers from a deeper conceptual mismatch in the time scales that are appropriate for a comparison of terrestrial and lacustrine carbon processes. On land, once a forest ecosystem has reached its maturity, long-term carbon storage can only be in the form of soil carbon accumulation. Yet, soil carbon inventories in Quebec (Tremblay et al. 2002) and elsewhere (Kortelainen et al. 2004) are small (about 12 kg organic C·m⁻² for southeastern Quebec), and they correspond to net annual carbon accumulation rates integrated over the Holocene that are much smaller than their instantaneous rates of sequestration (by about two orders of magnitude), presumably because soils are periodically burned and (or) have much higher decay rates. Thus, I suggest that the measured instantaneous carbon assimilation rates of terrestrial systems largely reflect the state of our forests, i.e., that they are still growing in biomass following their harvest during the past century. However, these rates

are nearly irrelevant as a measure of their long-term role in the carbon budget of the landscape and do not represent the appropriate time scale with which to compare the carbon storage capacity of lakes. In several regions where it has been measured, there is more organic carbon buried in the bottom of lakes than there is in the surrounding soils of their catchments.

Carbon gas evasion also plays a surprisingly large role in the carbon balance of the landscape. The most striking example is the work of Richey and coworkers on the carbon balance of the Amazon region (Richey et al. 2002). When only the terrestrial component is considered, the region is considered an important net sink for carbon. However, when emissions of CO₂ and CH₄ from the floodplains are accounted for, the whole ecosystem is close to neutral equilibrium. Thus, carbon limnological processes are highly relevant even at the spatial scale of whole landscapes. Recent work on the global role of lakes is making that point even more forcefully (Cole et al. 2007).

Lessons from carbocentric limnology

There is no sacrosanct way of advancing limnology, yet it is not useful to continue working within a given framework without ever questioning its relevance to the greater progress of our discipline. Indeed, one of Frank Rigler's greatest legacies to our scientific community is the example he made through his own research career. After two decades of highly regarded research on the details of phosphorus dynamics, he had the courage and exceptional intellectual honesty to reassess whether the way in which he was conducting his own research would eventually lead to what he would himself consider progress. His ensuing discontent led to a complete reorientation of his research approach (Rigler 1975). He felt that to be mired in a reductionistic approach, where ecosystem components are studied in ever smaller pieces, did not and could not deliver the primary level of understanding that a whole-ecosystem approach could. The problem is obvious and just as relevant today as it was three decades ago. I think of it as the scientific version of the Humpty Dumpty rhyme: once the ecosystem is broken into small pieces, "all of the (limnological) horses and all of the (limnology) men couldn't put (the lake) together again". I wonder why we teach it to our children if we do not apply it to our own science. The story of carbocentric limnology teaches us the same lesson. More and more effort is currently devoted to deconstructing the DOC box into smaller compartments. Although all information acquired about these compartments constitutes a positive knowledge gain, I suggest that it is ultimately necessary that it be tested at the ecosystem level where its true importance can be rightfully assessed.

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