

Evidence for the respiration of ancient terrestrial organic C in northern temperate lakes and streams

S. Leigh McCallister^{a,1} and Paul A. del Giorgio^b

^aDepartment of Biology and Environmental Studies, Virginia Commonwealth University, Richmond, VA 23284; and ^bGroupe de Recherche Interuniversitaire en Limnologie (GRIL), Dépt. des sciences biologiques, Université du Québec à Montréal, Montréal, QC, Canada H3C 3P8

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Northern rivers and lakes process large quantities of organic and inorganic carbon from the surrounding terrestrial ecosystems. These external carbon inputs fuel widespread CO₂ supersaturation in continental waters, and the resulting CO₂ emissions from lakes and rivers are now recognized as a globally significant loss of terrestrial production to the atmosphere. Whereas the magnitude of emissions has received much attention, the pathways of C delivery and processing that generate these emissions are still not well-understood. CO₂ outgassing in aquatic systems has been unequivocally linked to microbial degradation and respiration of terrestrial organic carbon (OC), but the nature (i.e., age and source) of this OC respired in surface waters is largely unknown. We present direct radiocarbon measurements of OC respired by bacteria in freshwater aquatic systems, specifically temperate lakes and streams in Québec. Terrestrial OC fuels much of the respiration in these systems, and our results show that a significant fraction of the respired terrestrial OC is old (in the range of 1,000–3,000 y B.P.). Because the bulk OC pools in these lakes is relatively young, our results also suggest selective removal of an old but highly bioreactive terrestrial OC pool and its conversion to CO₂ by bacteria. The respiration of ancient ¹⁴C-depleted terrestrial C in northern lakes and rivers provides a biological link between contemporary aquatic carbon biogeochemistry and paleo-conditions in the watershed, and it implies the aquatic-mediated return to the atmosphere of C putatively considered permanently stored, thus challenging current models of long-term C storage in terrestrial reservoirs.

aquatic respiration | priming effect | source and age of labile OC | aquatic CO₂ emissions | aquatic carbon cycle

Historically, the exchange of C between land and atmosphere was considered to primarily occur through the removal of atmospheric CO₂ by photosynthesis and its subsequent evasion from the terrestrial biosphere through plant and soil respiration and biomass burning. Lately, an unrecognized pathway gaining quantitative significance in the exchange of C between land and atmosphere, particularly in northern landscapes, is the emission of terrestrially derived C from inland aquatic systems (1). In this regard, lakes and rivers serve a dual biogeochemical role, acting as both vents for the degassing of soil-generated CO₂ and reactors for transforming and mineralizing organic carbon (OC) that leaches out of terrestrial systems (1–6). These processes lead to widespread supersaturation of CO₂ in surface waters of northern rivers and lakes (7–9) and significant fluxes of CO₂ to the atmosphere (9–11).

Current evidence suggests that aquatic bacterial decomposition of terrestrial OC is one of the major pathways that fuels these CO₂ emissions from lakes to the atmosphere (2, 3, 12). This latter process is quantitatively important at the regional scale (1, 9–11), and it represents a net loss of terrestrial OC that is generally unaccounted for in current terrestrial models (for example, not considered by the Intergovernmental Panel on Climate Change) (1, 5, 9–11). Despite its relevance to terrestrial C budgets, little is known of the nature of the terrestrial OC decomposed and ultimately respired in aquatic systems (13). In particular, we do not know if this pathway returns OC that was recently fixed to the

atmosphere or if it involves older OC stored in deeper soil layers. The biogeochemical implications of these two scenarios are fundamentally different, because the former represents a contemporary C loop, whereas the latter would imply an uncoupling between contemporary primary production and the emission of C from the landscape (13, 14).

The terrestrial C cycling community has long recognized the significance of determining not only the amount of C returned from soils to the atmosphere but also its age (15). To date, there has been no comparable direct empirical determination of the age of C respired in any aquatic or marine environment. Furthermore, the paradigm of age as an a priori proxy for its microbial bioavailability has been recently challenged in both terrestrial and aquatic systems (13–15). The data presented herein provide fundamental evidence that a paradigm shift is essential to accurately depict the uncoupling of OC stability and age and its chemical recalcitrance.

Results and Discussion

^Δ¹⁴C of OC Respired by Aquatic Bacterioplankton. We present here direct determinations of the age of the OC respired in aquatic systems. We measured the ^Δ¹⁴C of bacterial respiratory CO₂ recovered from short-term incubations of natural lake and river water to determine the age of OC respired in five temperate lakes and two streams in southern Québec (Canada). The ^Δ¹⁴C of lake respiratory CO₂ varied widely, ranging from +94‰ to –172‰ (Table 1), showing that the consumption of OC can be in excess of 1,000 y of age. Aquatic bacteria consume and respire, at any given time, a wide range of available organic substrates, and the respiratory ^Δ¹⁴CO₂ integrates the signature of OC substrates respired across a continuum of molecular composition, source, and radiocarbon ages (15). The respiratory CO₂ was more depleted in ¹⁴C than the bulk particulate C (POC) and dissolved organic C (DOC) pools in the same lakes (Table 1). Given that the ambient OC pools are dominated by relatively modern C, it is likely that respiration is also fueled by these younger substrates, and therefore, the ancient endmember respired must be considerably older than the average values recorded for the bulk respiratory CO₂.

Respiration of Ancient Terrestrial OC. The fact that the old component of respired C is of terrestrial origin is suggested by the strong negative relationship between the radiocarbon age of the respiratory CO₂ and the proportion of this C that is of terrestrial origin (Fig. 1), previously determined on the basis of the ^δ¹³C signature of this respiratory CO₂ (3). Extrapolation of our own results shown in Fig. 1 (100% respired terrestrial OC) places the old endmember at approximately –300‰ ^Δ¹⁴C, well within the

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¹To whom correspondence should be addressed. E-mail: slmcalliste@vcu.edu.

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Table 1. Biogeochemical characteristics of sampled water bodies

Water body (sampling date)	Chl a ($\mu\text{g L}^{-1}$)	Total phosphorus ($\mu\text{g L}^{-1}$)	DOC (mg L^{-1})	Respiration $\text{CO}_2 \Delta^{14}\text{C}$ (‰)	Respiration CO_2 ^{14}C -age* (y B.P.)	POC $\Delta^{14}\text{C}$ (‰)	DOC $\Delta^{14}\text{C}$ (‰)	DIC $\Delta^{14}\text{C}$ (‰)	BR_{Total} ($\mu\text{g C L}^{-1}\text{d}^{-1}$)	BR_{Terr} ($\mu\text{g C L}^{-1}\text{d}^{-1}$)	Residence time (y)
Bran de Scie (9/1)	5.1	16.7	7.5	87 ± 3	>Modern	115 ± 4	14 ± 5	37 ± 3	113	16	0.03
Bran de Scie (9/1)				3 ± 4	>Modern						
Des Monts (9/8)	2.5	12.3	7.4	94 ± 3	>Modern	111 ± 4	73 ± 4	52 ± 3	77	40	0.01
Des Monts (9/8)				74 ± 6	>Modern						
Stukely (9/15)	2.5	6.5	5.0	-94 ± 3	740	179 ± 4	93 ± 4	37 ± 4	66	28	4.00
Bowker (9/15)	2.0	5.8	2.8	-48 ± 4	345	73 ± 3	76 ± 4	-0.4 ± 3	48	16	8.96
Fraser (9/28)	1.5	11.2	6.9	-172 ± 4	1,470	106 ± 4	101 ± 4	-91 ± 3	45	25	0.36
Bran de Scie (9/22)	—	10.6	4.9	-116 ± 3	935	126 ± 4	50 ± 4	19 ± 5	48	42	—
Fraser (9/22)	—	21.1	6.1	-21 ± 3	115	— [†]	110 ± 6	-36 ± 4	65	54	—

*Determined with ReCReS (*SI Methods*).

[†]Lost at graphitization.

range of signatures of ancient bioreactive OC determined in a variety of soil types (-200‰ to -400‰ $\Delta^{14}\text{C}$ or $\sim 1,800\text{--}4,100$ y B.P.) (15–18) and streams and riparian zones ($\sim 4,000\text{--}16,663$ y B.P.) (13, 19).

The respiratory CO_2 becomes less ^{14}C -depleted (more modern) as total planktonic respiration increases (Fig. 2A), the latter having been determined in parallel for the same samples (3). Because algal OC mirrors the $\Delta^{14}\text{C}$ of the bulk dissolved inorganic carbon (DIC) pool (3, 20), the $\Delta^{14}\text{C}$ of algal production in these lakes should be in the same range as the $\Delta^{14}\text{C}$ of DIC ($+2\text{‰}$ to $\pm 50\text{‰}$) (Table 1), considerably more enriched in ^{14}C than the respiratory CO_2 . Because total plankton respiration is a function of primary production in these lakes (3), this pattern suggests a dilution of an ancient terrestrial respiratory OC component with CO_2 derived from the respiration of younger OC, most likely of autochthonous origin. Interestingly, there was a significant positive relationship between the $\Delta^{14}\text{C}$ of the respiratory CO_2 and the $\Delta^{14}\text{C}$ of the bulk DIC pool (Fig. 2B), suggesting that CO_2 generated through bacterial respiration of ancient terrestrial OC influences the bulk lake DIC signature, which had been previously hypothesized but to date, never empirically ascertained (21). Our results also suggest a strong selective removal of specific age fractions of the ambient OC pool, which has been reported for other systems (18, 19), and therefore, the age of the C respired cannot a priori be derived from the age of the bulk OC (Table 1).

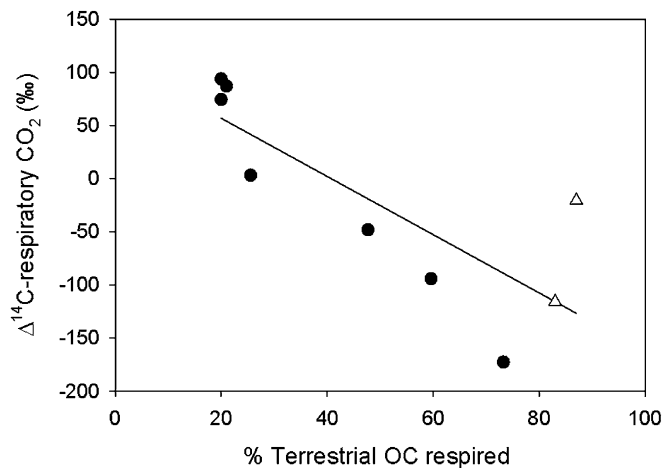


Fig. 1. The $\Delta^{14}\text{C}$ of bacterial respiratory CO_2 as a function of the relative contribution of terrigenous DOC to bacterial respiration ($r^2 = 0.65$; $P < 0.005$; $y = 111.5 - 2.7 \times x$). Open triangles denote the two streams sampled.

Uncoupling of Age and Lability in Terrestrial and Aquatic Systems.

Our results agree with recent studies that have shown that age and reactivity of OC are uncoupled in both aquatic (13, 14, 22) and terrestrial (15, 16, 18, 23) environments. The traditional view that the long-term persistence of OM in soils is the direct result of its recalcitrance has been recently challenged (15, 16, 18, 23–25) and replaced by the notion that OC persistence in soils is regulated by a combination of intrinsic factors (related to substrate quality and chemical composition) and extrinsic factors (such as soil physical structure, formation of organo-mineral complexes, and bioenergetic constraints of the soil microbiota) (18, 23). An important corollary of this changing paradigm is that OC persistence in soils is not necessarily a function of its recalcitrance but rather, its stabilization in what has been termed partial refuges (23). Our results clearly suggest that, when this old, mineral-associated OC is transported from soils to the aquatic system, these refugia are lost, and the OC can be readily mineralized, which was reported in the work by Gurwicz et al. (13) for the riparian zone. Furthermore, after desorption, the physical movement of OC from nutrient-poor soils to aquatic systems with fresh inputs of nutrients and labile OC in addition to light and various chemical factors may prime the metabolism of previously unreactive OC through the microbial priming effect and/or photosensitization (14, 16, 18, 23–25). It has previously been suggested that bacterial incorporation of preaged terrestrial OC may be facilitated, in part, by the cleavage of photoreactive DOC and the subsequent release and metabolism of low-molecular weight compounds (22, 26, 27). Moreover, exposure of old ($>6,000$ y B.P.) presumably recalcitrant oceanic DOC to UV light has been shown to enhance its bioavailability to the microbial consortium (28, 29). We suggest an analogous process operating at the aquatic–terrestrial interface, where soil organic matter that has been sequestered from UV light for decades to millennia may be phototransformed and metabolized by aquatic bacteria.

Ancient Terrestrial OC Supports Contemporary Aquatic Respiration.

Presumably, this ancient bioreactive OC is delivered to lakes through ground and surface water inputs. Although the former is most likely the carrier of old OC leached from deep soil horizons (30), our own results as well as the results in the work by Tipping et al. (31) show that inflowing streams may also transfer old bioreactive OC. Our measurements on samples from inflowing headwater streams taken close to the inlet of two of the study lakes showed that the OC respired was also, on average, old (up to 1,000 y B.P.) (Table 1). This stream OC is overwhelmingly terrestrial (3), suggesting that streams in this region deliver to lakes, among other pools, a fraction of ancient but highly reactive terrestrial OC, which is in agreement with previous studies (13, 19, 30, 32).

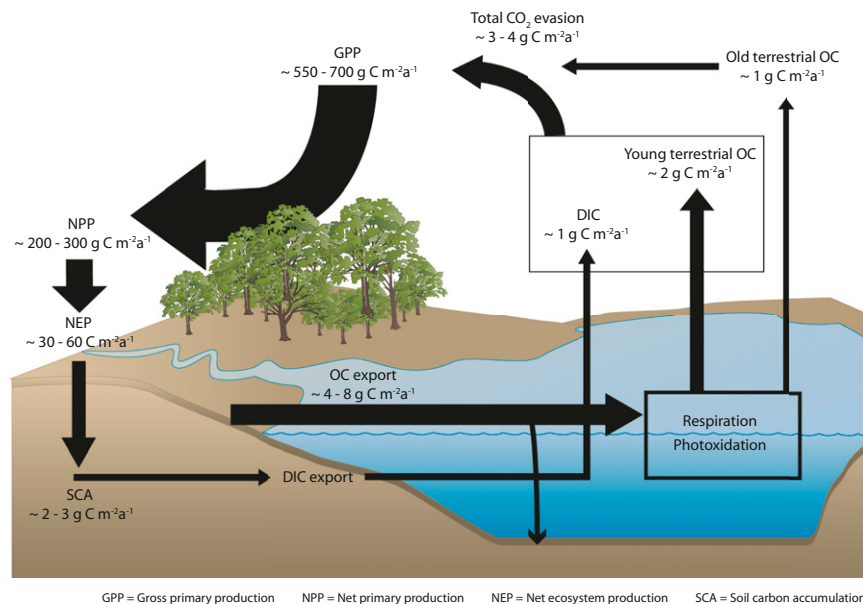


Fig. 3. The inclusion of bacterially mediated CO_2 emission from lakes and rivers in a simplified watershed C budget. The conceptual depiction distinguishes lake C emissions that originate from direct DIC injection to lakes from the bacterial respiration of both recent and ancient terrestrial OC. The model combines published ranges for the main fluxes for northern temperate landscapes (34–38), our own previous estimates of C emissions for these lakes (3), and average estimates of CO_2 fluxes originating from bacterial respiration of recent and old terrestrial OC as described in *Methods*. All rates are expressed per meter² of total landscape and thus, are comparable.

For comparative purposes, the current estimates of global lake CO_2 emissions are in the order of $1.4\text{--}1.6 \text{ pg a}^{-1}$ (1, 9), and a large fraction of these global emissions originate from northern temperate and boreal lakes (7, 9), similar to those emissions that we have studied here. It is premature to extrapolate our results at the regional or global scale, because we still do not know how the delivery and subsequent degradation in lakes of ancient terrestrial OC vary across the major northern landscape types; however, we can safely assume that our results are not simply a localized feature. The study watershed is representative in many ways of large portions of the temperate and subboreal landscapes of North America and Euroasia. If, indeed, our results were to apply to northern lakes and rivers in general, this finding would imply a flux of ancient C to the atmosphere of potentially the same order of magnitude as the loss of C from thawing permafrost (42) and thus, global significance.

Currently, we do not know how this microbially mediated flux of ancient CO_2 from temperate/subboreal lakes has varied over time. Conceivably, the export of old terrestrial OC from soils and its respiration in the aquatic system may have been occurring for millennia, and as such, it is not necessarily a consequence of anthropogenic climate change. In this regard, there is evidence that both the DOC-induced color of water and the actual DOC concentrations have been increasing in many northern landscapes (43–45), including boreal Québec (46). The magnitude and regulation of this browning phenomenon are the focus of intense research and debate but likely involve shifts in the pathways of delivery of terrestrial C to rivers and lakes (43). Whether this browning of inland waters results in positive or negative feedbacks on the mobilization and efflux of ancient C to the atmosphere has not been established.

To summarize, our results suggest an unforeseen role of northern aquatic systems in the landscape: the role of reaction sites for the mineralization of ancient terrestrial OC. This function is critical; whereas the respiration of young terrestrial carbon reinforces a tight land–atmosphere C loop, the release of old OC represents loss of C that was considered removed from atmospheric circulation. There is clearly still much to be learned concerning the interactions between terrestrial and continental aquatic systems in northern landscapes,

but our results suggest that lakes must be viewed as an integral part of the landscape C storage/decomposition system, because key reactions in the OC cycle may only occur in surface waters. Our understanding of the terrestrial C cycle and regional OC sources and sinks is, thus, incomplete without the inclusion of aquatic processes, particularly in water-rich northern landscapes.

Methods

Study Site and Sample Collection. Five lakes and two streams from the Eastern Townships region of southern Québec, Canada (45.50° N , 73.58° W) were sampled during the summer of 2004. The lakes span a large range in morphometry (mean depth = 5–27 m), residence time (0.9–8 y), and trophic status (Table 1 and Table S2). Land cover data obtained from geographic information systems using ArcView were used to characterize the watersheds of the Eastern Township lakes into three primary land use classifications: forested, wetland, and pasture. Overall, the watersheds were dominated primarily by forested land cover, ranging from a maximum of 96% for both Stukely and Bowker to a minimum of 49% in Bran de Scie. In contrast, pastureland was greatest for Bran de Scie and lowest for Stukely and Bowker (3.4% and 4.3%, respectively). Des Monts was characterized by a mix of forest (76%) and pastureland (18%). Only Bran de Scie and Fraser contained a wetland component (0.7% and 0.5%, respectively).

Sample water was collected with a diaphragm pump connected to an acid-rinsed (10% HCl) plastic hose at a depth of 1.0 m to avoid any potential contamination with the surface film and stored in cooled acid-washed containers until processing in the laboratory within 3 h of collection. In the laboratory, a portion of the water was set aside for chlorophyll and nutrient analyses as well as total plankton respiration measurements (see below). The remainder of the water sample was pumped using a peristaltic pump through combusted (525° C for 4 h) Millipore AE glass fiber filter (1.0-mm nominal pore size) to concentrate particles for radiocarbon analysis. The 1.0-mm filtrate was subsequently passed through an inline (0.2 mm) Gelman filter capsule to remove bacteria, and the filtrate was collected for DOC, DIC (poisoned with HgCl_2) radiocarbon analysis, and respiratory CO_2 incubations (*SI Methods*). Samples for POC, DOC, DIC, and respiratory CO_2 were subsequently analyzed for natural abundance ($\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$) isotopic analysis (*SI Methods*). All sample manipulations and incubations were carried out in an ultraclean dedicated laboratory, and we performed regular wipe checks to assess background ^{13}C and ^{14}C levels.

Determination of Total and Bacterial Respiration. Short-term measurements of total planktonic respiration were carried out in parallel to the Respiratory Carbon Recovery System (ReCreS) experiments and have been reported elsewhere (3). In brief, plankton respiration was determined as O₂ consumption in short-term, dark incubations of unfiltered water; O₂ concentrations were measured at several time points during the 24 h incubations using membrane inlet spectrometry, and rates were converted to C production using a respiratory quotient of one. We have estimated bacterial respiration from the measured total planktonic rates by calculating the contribution of nonbacterial components and subtracting it from the total. Algal respiration was first calculated by estimating the average rates of primary production for each lake based on the average Chl a concentrations using the empirical model provided in the work by del Giorgio et al. (47) for these same northern temperate lakes and assuming an average algal respiration 25% of primary production. Algal respiration generally ranges from 5% to 10% of photosynthetic biomass maximum (the maximum rate of biomass-specific photosynthesis) (48), and therefore, the above assumption yields a generous estimate of algal respiration (R). We also assumed that metazoan and microzooplankton respiration was equivalent to the respiration of algae, and therefore, the total nonbacterial respiration was estimated as 2x algal respiration. The nonbacterial respiration was subtracted from the total measured R to derive total bacterial respiration (BR). The work by del Giorgio et al. (48) showed that this approach yields realistic estimates of BR based on independent approaches

Proportion of Modern and Preaged Terrigenous and Algal OC Supporting Bacterial Respiration. The proportion of terrestrial DOC respired by bacteria in these samples had been previously determined in the work by McCallister and del Giorgio (3). In brief, we used the algal endpoint derived from the zooplankton δ¹³C signature with a terrigenous OC endmember of -27‰ to determine the relative contributions of algal and terrigenous-derived OC sources to BR using a δ¹³C isotopic, two-source mixing model. The series of two equations and two unknowns is (Eq. 1)

$$\delta^{13}\text{C}_{\text{CO}_2} = f_1 \bullet \delta^{13}\text{C}_{\text{Terr}} + f_2 \bullet \delta^{13}\text{C}_{\text{Algal}} \quad [1]$$

and (Eq. 2)

$$f_1 + f_2 = 1, \quad [2]$$

where CO₂ δ¹³C values are measured from the ReCreS and f₁ and f₂ are the relative contributions of terrigenous (C_{Terr}) and algal (C_{Algal}) sources to the CO₂ signature, respectively. We note one exception to this two-endmember model. Des Mont is a shallow lake dominated by submersed aquatic macrophytes, which release significant amounts of highly labile DOC (49) of similar isotopic signature as terrigenous sources (-27.2‰) (3). In this instance, our mass balance most likely overestimates the proportion of terrigenous OC respired in this lake because of the overlap between the terrigenous and aquatic macrophytes and the greater relative lability of macrophyte-derived OC (*SI Methods*). To correct for this potential overestimate of terrestrially derived OC respired in Des Monts, we calculated the algal contribution to the respiratory ¹³C-CO₂ signature (detailed above in Eqs. 1 and 2). We then partitioned the balance of respiratory CO₂ between terrestrially (soil and litter) and macrophyte-derived OC based on their respective labilities (*SI Methods*).

The radiocarbon values of respiratory CO₂ derived were then apportioned between contemporary and preaged terrigenous and algal-derived radiocarbon signatures (Eqs. 3, 4, and 5) for each lake independently. As a first-order approach, the terrestrial OC respired (15, 23) was assumed to include two pools, one modern (Δ¹⁴C of 90‰; representative of recent forest litter and surficial soils) and one preaged fraction (Δ¹⁴C signature ranges from -200‰ to -400‰), which represents an ancient but nevertheless labile component. The algal signature is equivalent to Δ¹⁴C (3, 20, 22), and we used the relative proportion of algal vs. total terrestrial OC respired that had been calculated previously from δ¹³C-respiratory CO₂ (3), thus allowing the Δ¹⁴C of the total terrigenous component (Δ¹⁴C_{Bulk terrigenous}) to be solved according to the formula (Eq. 3)

$$\Delta^{14}\text{C}_{\text{CO}_2} = \Delta^{14}\text{C}_{\text{Bulk terrigenous}} (\% \text{ terrigenous}) + \Delta^{14}\text{C}_{\text{algal}} (\% \text{ algal}). \quad [3]$$

The Δ¹⁴C of the total terrigenous C respired was partitioned between a modern and preaged (-200‰ to -400‰) component with the equations (Eq. 4)

$$\begin{aligned} \Delta^{14}\text{C}_{\text{CO}_2} &= +90(f_{\text{modern}}) + -200(f_{\text{pre-aged}}) \text{ OR} \\ \Delta^{14}\text{C}_{\text{CO}_2} &= +90(f_{\text{modern}}) + -400(f_{\text{pre-aged}}) \end{aligned} \quad [4]$$

and (Eq. 5)

$$f_{\text{modern}} + f_{\text{pre-aged}} = 1. \quad [5]$$

To summarize, we first calculate the radiocarbon signature (Δ¹⁴C_{Bulk terrigenous}) of the total (modern + preaged) terrestrial C pool respired using Eq. 3 for each lake independently. This radiocarbon signature is then parsed into the percentage of preaged OC on a modern terrestrial OC signature of +90‰ and a preaged endmember of either -200‰ or -400‰. Based on these end-member signatures, we calculate that an average of 30% of the respiration of terrestrial OC is attributable to the preaged component when the younger (-200‰) endmember is selected and 20% when an older endmember (-400‰) is applied.

Determination of Water Column Bacterial Respiration Fueled by Old and Young Terrigenous DOC and Resulting Water-Air CO₂ Fluxes. We also partitioned the terrestrially derived component of water column bacterial respiration into a fraction based on old terrestrial C and a fraction based on young terrestrial C by expressing bacterial respiration rates of terrigenous C (Table 1) per meter⁻² of drainage basin for each lake and combining these rates with the results of the isotopic mass balance described above (Eqs. 3, 4, and 5). The contributions of modern and old OC to the terrestrially supported component of bacterial respiration derived from the mass balance averaged 30%, and we used these average values for all five lakes (Fig. 3). We then integrated the resulting bacterial respiration rates over the depth of the epilimnia of each lake to derive the potential areal CO₂ efflux rates generated by the respiration of terrigenous OC and more specifically, the respiration of old terrestrial OC, and we express these CO₂ fluxes as grams C per meter⁻² of drainage basin per year (assuming 210 ice-free days); therefore, the rates are comparable with other components of the regional terrestrial C budget.

Watershed C Balance. Terrestrial primary production has been modeled in detail for our entire study watershed using an adapted version of the TRIPLEX model (50) as part of an ongoing collaborative research project. This spatially explicit model is based on vegetation type, climate, and soils, and it yielded estimates of gross and net primary production and net ecosystem production that are in good agreement with regional-scale models of primary production (34, 40). DOC export from comparable northern temperate and boreal regions has been reported to range from 4 to 8 g C m⁻² a⁻¹ (36-38). Previous studies in this watershed also reported an annual average C evasion from these lakes of ~4 g C m⁻² (of watershed) a⁻¹ (3) and suggested that up to 75% of this total flux (or up to 3 g C m⁻² a⁻¹) could be generated by the biological or photochemical degradation of DOC, the remaining caused by direct injection of DIC (CO₂) to the lake. We combined these estimates with the estimate of CO₂ generated by the respiration of old terrestrial OC to derive an approximate contribution of the latter pathway to total lake CO₂ evasion at the watershed scale (Fig. 3).

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