

## Terrestrial dominance of organic matter in north temperate lakes

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[1] Aquatic ecosystems are hotspots of decomposition and sources of carbon dioxide to the atmosphere that are globally significant. Carbon exported from land (allochthonous) also supplements the carbon fixed by photosynthesis in aquatic ecosystems (autochthonous), contributing to the organic matter (OM) that supports aquatic consumers. Although the presence of terrestrial compounds in aquatic OM is well known, the contribution of terrestrial versus aquatic sources to the composition of OM has been quantified for only a handful of systems. Here we use stable isotopes of hydrogen and carbon to demonstrate that the terrestrial contribution ( $\Phi_{\text{Terr}}$ ) to particulate organic matter (POM) is as large or larger (mean = 54.6% terrestrial) than the algal contribution in 39 lakes of the northern highlands region of Wisconsin and Michigan. Further, the largest carbon pool, dissolved organic matter (DOM), is strongly dominated by allochthonous material (mean for the same set of lakes approximately 100% terrestrial). Among lakes, increases in terrestrial contribution to POM are significantly correlated with more acidic pH. Extrapolating this relationship using a survey of pH in 1692 lakes in the region reveals that, with the exception of eutrophic lakes, most of the OM in lakes is of terrestrial origin. These results are consistent with the growing evidence that lakes are significant conduits for returning degraded terrestrial carbon to the atmosphere.

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### 1. Introduction

[2] Resolving the contribution of terrestrial material to organic matter (OM) pools in lakes is significant for understanding carbon cycling at the regional and global scale as well as for understanding food web subsidies. Models of carbon accumulation based on terrestrial biomes significantly overestimate terrestrial C sequestration when these models exclude surface waters in lake-rich regions [Christensen *et al.*, 2007; Buffam *et al.*, 2011]. At the global scale, excluding inland waters leads to an overestimate of terrestrial sequestration by up to 60% [Cole *et al.*, 2007; Battin *et al.*, 2009; Tranvik *et al.*, 2009].

[3] The amount and form of allochthonous material exported to lakes has large impacts on ecosystem metabolism, resilience, and food web structure [Polis *et al.*, 1997; Loreau and Holt, 2004; Power, 2001]. Additionally, differences in OM composition within the water column may be important for supporting consumers such as zooplankton that migrate daily through the water column [Matthews and Mazumder, 2006; Francis *et al.*, 2011]. However, the relative contribution of allochthonous material

to OM pools in lakes varies within the landscape, and the heterogeneity in terrestrial loading among lakes is not well quantified. Regional estimates of particulate organic matter (POM) and dissolved organic matter (DOM) composition in lakes are largely derived from case studies as there have been few comparative estimates of the variation in lake OM composition [Pace *et al.*, 2007].

[4] Chemical and spectral approaches frequently identify terrestrial compounds in DOM [Karlsson *et al.*, 2003; Cory and McKnight, 2005; Bade *et al.*, 2007; Pace *et al.*, 2007; Caraco *et al.*, 2010; Stets *et al.*, 2010; Tank *et al.*, 2011], but neither spectral approaches (which are not generally applicable to POM) nor methods based on carbon isotopes have produced robust, quantitative estimates of the terrestrial contribution ( $\Phi_{\text{Terr}}$ ) to aquatic DOM and POM. The carbon isotope approach often yields uncertain composition estimates due to the small difference between terrestrial and algal isotope ratios and uncertain estimates of algal photosynthetic fractionation ( $\epsilon_c$ ) [Bade *et al.*, 2006]. One study was able to avoid these limitations by only comparing the carbon isotope values of POM in lakes primarily dominated by algae [Mohamed and Taylor, 2009]. Others have estimated  $\Phi_{\text{Terr}}$  of POM in a small number of lakes through extensive carbon isotope sampling and found the pool dominated by allochthonous material [Karlsson *et al.*, 2003; Jones *et al.*, 1998] or composed equally of allochthonous and autochthonous material [Taipale *et al.*, 2008]. Enrichment of aquatic inorganic  $^{13}\text{C}$  provides an approach to overcome the small difference between source

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isotope values, whereby the isotope dynamics of the POM pool are modeled to fit the dynamics of changing  $^{13}\text{C}$  composition [Pace *et al.*, 2007]. This method provides stronger contrasts than ambient isotope methods but is expensive, labor intensive, and thereby limited in application.

[5] Recently, the stable isotope of hydrogen, deuterium ( $^2\text{H}$ ), has been used successfully in studies of aquatic food web subsidies [Doucett *et al.*, 2007; Caraco *et al.*, 2010; Finlay *et al.*, 2010; Babler *et al.*, 2011; Cole *et al.*, 2011; Solomon *et al.*, 2011; Batt *et al.*, 2012] due to the large ambient separation between terrestrial and aquatic material [Smith and Zeigler, 1990] allowing for well-constrained estimates of source OM signatures. Using  $\delta^2\text{H}$  and  $\delta^{13}\text{C}$  values of OM in lakes and algebraic mixing models that assumed this OM had two sources (terrestrial and algal), we compared the terrestrial contribution to OM pools in 39 lakes in order to quantify the heterogeneity of terrestrial contribution to OM pools among systems. By developing relationships between our estimates in the 39 lakes with commonly measured limnetic variables, we were able to extrapolate the variance in terrestrial contribution to OM pools in lakes regionally.

## 2. Methods

### 2.1. Study Area

[6] The survey lakes (Table 1), located in the Northern Highland Lake District of Wisconsin and Michigan (USA), were sampled once over a period of 65 days between midMay and August of 2011. Because the pattern of allochthonous contributions to OM may vary seasonally within a given lake, this study is a point estimate of the conditions in a single season. This region is characterized by numerous glacial kettle lakes surrounded by forest and wetland with modest or no human development [Magnuson *et al.*, 2006]. The lakes were selected as representative of a gradient in the ratio of water color (absorbance at 440 nm) to chlorophyll-*a* concentration.

### 2.2. Isotope Samples and End Members

[7] OM samples were collected at a depth of 0.5 m in each lake. POM samples were concentrated on 40-mm MicroSep Cellulosic filters (nominal pore size = 0.8  $\mu\text{m}$ ) through vacuum filtration. The collected particles were gently back-washed from the filters into slightly acidic deionized water (to remove inorganic C) and then dried and ground to a fine powder for isotope analysis. The filtrate was acidified with 1  $\mu\text{L}$  of 1 N HCl per 1 L sample water to lower the pH to approximately 3 to remove inorganic C without altering the OM. The water was evaporated in glass dishes, and the previously dissolved organic material remaining in the dish was used for DOM isotope analysis. Filtered water was used for  $\delta^2\text{H}_2\text{O}$  and dissolved inorganic carbon isotope analysis ( $\delta^{13}\text{C}$ -DIC).

[8] The terrestrial isotope values used in this study were from Solomon *et al.* (2011) in which 81 samples of live terrestrial vegetation collected over the course of a season from the watersheds of lakes also sampled in this study were analyzed for  $\delta^2\text{H}$  and  $\delta^{13}\text{C}$ . The mean ( $\pm\text{SD}$ ) value of terrestrial  $\delta^2\text{H}$  for these samples is  $-129.5\text{‰} \pm 15.2$  and the mean ( $\pm\text{SD}$ ) value of terrestrial  $\delta^{13}\text{C}$  is  $-29.2\text{‰} \pm 1.5$ . The mean hydrogen fractionation ( $\epsilon_{\text{H}}$ ) between lake water and algae ( $-160.9\text{‰} \pm 17.0$ ) was determined by analyzing algal samples collected by net tow (mesh = 80  $\mu\text{m}$ ) from lakes in

this study visited during blooms ( $n=11$ ). Algal samples were visually inspected under a microscope to remove non-algal material (e.g., zooplankton and any leaf material or stem fragments). The  $\epsilon_{\text{H}}$  values from these samples were pooled with values derived from algal regrowth experiments ( $n=4$ ) in which pure algal cultures were grown under controlled conditions [see Caraco *et al.*, 2010; Solomon *et al.*, 2011]. The  $\epsilon_{\text{H}}$  values were used with water isotope samples from each lake to calculate the mean and standard deviation of the algal-end member in each system. The aqueous  $\delta^{13}\text{CO}_2$  for each lake was calculated from the  $\delta^{13}\text{C}$  of the DIC measured in each lake along with pH and temperature [Zhang, Quay, & Wilbur, 1995].

### 2.3. Isotope Analyses

[9] All samples were sent for  $\delta^2\text{H}$  and  $\delta^{13}\text{C}$  isotope analysis to the Colorado Plateau Stable Isotope Laboratory (CPSIL) at Northern Arizona University (Flagstaff, AZ). Following the methods described in Doucett *et al.*, (2007) for obtaining the isotopic signature of the nonexchangeable H fraction, the samples for  $\delta^2\text{H}$  analysis were corrected for exchange of H atoms between samples and ambient water vapor using the bench top equilibration method.  $\delta^2\text{H}$  samples were pyrolyzed to  $\text{H}_2$  gas following the procedures of Doucett *et al.*, (2007) and Finlay *et al.*, (2010) and analyzed on Thermo-Finnigan TC/EA and DeltaPLUS-XL (Thermo Electron Corporation, Bremen, Germany). Cavity ring-down laser spectroscopy was used to analyze water samples for  $\delta^2\text{H}$  using a Los Gatos Research Off-Axis Integrated Cavity Output (Los Gatos Research, Mountain View, CA). Samples for  $\delta^{13}\text{C}$  followed standard procedures for the CPSIL lab. The analytical precision for replicate samples at CPSIL are 0.1‰ for  $\delta^{13}\text{C}$  and 2‰ for  $\delta^2\text{H}$  (M. Caron, unpublished data, 2012). All isotope values are reported in per mil (‰) notation and in relation to Vienna PeeDee Belemnite ( $\delta^{13}\text{C}$ ) or Vienna Standard Mean Ocean Water ( $\delta^2\text{H}$ ).

### 2.4. Water Chemistry Samples and Analysis

[10] In addition to the isotope data collected at each lake, further measurements were made to characterize lake conditions and to use as predictors in regression analysis to explain the variation in OM pool composition among lakes. Water was collected at 0.5 m depth in each lake and analyzed for chlorophyll- $\alpha$  concentration, water color (absorbance at 440 nm), dissolved organic carbon (DOC), total nitrogen (TN), total phosphorus (TP), and pH. Dissolved oxygen profiles were measured in each lake using an optical probe [YSI Incorporated, Yellow Springs, OH]. Of the 39 lakes, 23 did not have mid- or deep-water oxygen peaks; 16 lakes had heterograde dissolved oxygen profiles at the time of sampling, indicating possible deep primary production. In these 16 lakes, POM and DOM samples were taken at the oxygen maximum as well using a peristaltic pump to determine the composition of this potentially distinct OM pool. Water samples from the depth of the dissolved oxygen maximum were also analyzed for chlorophyll- $\alpha$  concentration, water color, and DOC.

[11] Water stored and transported in a glass bottle sealed to prevent carbon dioxide evasion was used to measure pH. We used an Ag/AgCl electrode pH probe and the long equilibration method of Stauffer (1990), which is required for accurate pH measurements in soft waters. Chlorophyll- $\alpha$  samples were filtered onto Whatman 47 mm GF/F filters,

**Table 1.** Morphological, Chemical, and Biological Characteristics of the 39 Lakes Used in This Study

Lake Name	SA <sup>a</sup> (ha)	CA (ha)	Z <sub>max</sub> (Z <sub>mean</sub> ) (m)	pH	DOC (mg L <sup>-1</sup> )	Color (m <sup>-1</sup> )	Chl- $\alpha$ ( $\mu\text{g L}^{-1}$ )	DIC ( $\mu\text{mol L}^{-1}$ )	TN ( $\mu\text{g L}^{-1}$ )	TP ( $\mu\text{g L}^{-1}$ )
Allequash	102.5	3643.2	7.3 (3.1)	8.2	5.2	1.4	6.0	876.8	324.8	81.1
Bay	64.7	216.4	12.2	7.0	9.4	1.4	3.1	39.3	353.5	20.9
Big	3215.4	9511.8	9.1 (4.0)	8.4	8.3	1.3	7.6	864.1	440.7	77.5
Big Muskellunge	359.2	2118.5	21.3 (7.9)	8.1	3.3	0.3	1.9	474.7	404.5	28.3
Bogpot	1.4	17.4	2.0	5.7	4.0	8.3	11.2	149.3	757.5	56.2
Brandy	43.0	1766.1	13.4	8.6	5.1	0.6	14.6	959.9	480.1	41.8
Brown	28.3	434.3	4.9 (2.8)	8.3	5.9	2.5	11.3	1361.3	607.9	98.6
Crampton	25.2	54.3	15.2 (4.9)	5.9	4.6	1.1	2.3	46.9	362.3	26.5
Cranberry	2.9	29.2	7.3 (4.3)	4.1	18.2	11.7	8.5	45.4	565.9	31.1
Crystal Bog	1.2	2.1	2.5 (1.7)	4.9	8.9	8.1	7.4	33.2	663.6	46.5
Deadwood	8.7	24.1	8.8	6.7	8.6	3.2	3.3	38.1	509.2	23.0
Forest Service Bog	0.1	0.1	4.9	5.2	10.4	2.4	2.7	58.5	288.1	23.6
Found	134.9	1411.7	6.4 (3.4)	8.0	7.2	1.6	11.4	505.3	457.6	68.0
Hummingbird	1.1	11.1	7.6 (3.7)	5.4	24.4	20.9	16.2	81.5	833.1	49.0
Indian	22.8	232.0	11.9	7.3	4.6	0.7	9.7	108.6	611.3	30.4
Inkpot	6.8	232.0	5.2 (2.9)	7.8	13.3	3.2	6.9	927.0	497.8	50.5
Kickapoo	13.6	588.4	2.7	7.3	10.5	6.6	28.0	1011.7	807.7	107.2
Lac du Lune	167.5	1091.5	20.7 (7.3)	7.4	2.6	0.4	3.0	88.5	194.5	23.7
Little Arbor Vitae	207.2	4790.9	9.8 (3.4)	9.6	2.9	0.6	32.4	934.6	835.8	66.1
Morris	5.8	120.0	6.7 (2.6)	7.8	16.3	10.6	23.9	896.6	881.9	66.4
North Sparkling Bog	0.8	2.5	4.5 (2.5)	5.1	11.8	6.1	5.2	34.4	425.5	31.8
Northgate	0.8	1.0	8.0	4.7	25.6	19.1	1.8	108.8	674.4	35.9
Palmer	257.8	5017.8	4.0 (2.4)	7.8	8.7	4.5	7.3	931.5	615.4	71.9
Paul	1.5	9.2	12.0 (3.7)	7.2	4.3	1.1	2.3	116.0	408.3	28.0
Peter	2.4	15.7	18.0 (5.7)	7.7	5.2	1.9	4.4	120.1	494.0	20.3
Presque Isle	445.4	3582.9	24.4	8.3	3.8	0.3	2.3	1393.5	325.4	48.1
Raspberry	3.6	11.3	6.1 (3.1)	6.5	6.9	3.0	5.5	41.7	639.2	28.4
Reddington	1.8	28.8	16.0	6.8	22.0	16.7	9.1	222.2	860.4	68.7
Roach	32.0	103.6	10.0 (4.2)	6.5	2.9	0.7	2.9	34.7	328.1	36.3
Sparkling	59.8	345.1	19.5	8.3	3.7	0.2	1.6	724.1	183.1	43.3
Tender Bog	0.4	0.5	10.1	4.4	27.0	17.1	2.1	268.2	840.8	35.1
Tenderfoot	180.7	5839.8	10.1 (5.1)	8.4	8.3	2.9	14.0	1008.4	558.4	67.5
Towanda	51.2	244.3	8.2 (3.1)	7.6	3.8	0.7	11.9	125.6	626.3	34.7
Trout	1568.2	12245.6	35.7 (14.9)	9.0	6.4	0.2	1.1	965.2	150.5	39.5
Tuesday	2.4	2.7	15.0 (6.9)	6.7	10.3	4.7	8.0	65.5	521.6	32.2
Ward	2.2	57.6	8.2 (2.7)	6.6	13.1	8.0	11.9	1461.5	1121.8	77.1
West Long	3.6	14.1	14.0 (2.1)	6.0	7.8	4.6	4.4	71.9	655.6	41.9
Why Not? Bog	0.9	14.3	6.5	6.3	6.9	3.2	2.5	38.0	386.0	29.0
Wildcat	122.8	722.4	11.6 (3.7)	7.9	5.8	0.9	9.4	1508.0	423.8	72.3

<sup>a</sup>SA, lake surface area; CA, catchment area, Z<sub>max</sub> (Z<sub>mean</sub>), maximum depth and mean depth when available, DOC, dissolved organic carbon; DIC, dissolved inorganic carbon; TN, total nitrogen; TP, total phosphorus.

frozen for 24 hours, extracted in methanol, and analyzed fluorometrically [Holm-Hansen and Riemann, 1978]. The filtrate from the chlorophyll- $\alpha$  analysis was analyzed for water color by measuring light absorbance at 440 nm on a UV-visible spectrophotometer [Cuthbert and del Giorgio, 1992]. Filtrate was also preserved through acidification to pH  $\sim$ 3 with dilute ultrapure H<sub>2</sub>SO<sub>4</sub> and analyzed for DOC. Filtered water was also frozen for DIN analysis. Unfiltered water samples preserved through acidification (same as above) were analyzed for TN and TP by persulfate digestion. DOC, TN, and TP were all analyzed on a Lachat QuikChem 8000 (Hach Corporation, Loveland, CO) flow injection analyzer.

## 2.5. Data Analysis

### 2.5.1. Graphical Analysis of POM and DOM

[12] Both the  $\delta^2\text{H}$  and  $\delta^{13}\text{C}$  data were analyzed with a graphical, gradient-based mixing model similar to the approach used by Mohamed and Taylor (2009) for  $\delta^{13}\text{C}$  variation in Ontario lakes and Rasmussen (2010) for a river. This approach makes use of the natural variation in either  $\delta^{13}\text{C}$  or  $\delta^2\text{H}_2\text{O}$  among lakes. If OM were derived entirely

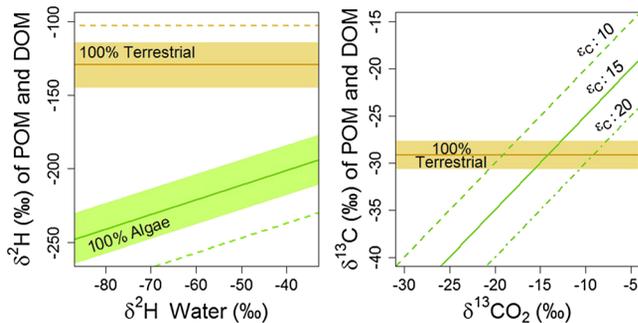
from terrestrial inputs, its C and H isotopic ratios would not vary with either  $\delta^{13}\text{CO}_2$  or  $\delta^2\text{H}_2\text{O}$  among lakes. A plot of either DOM or POM versus aqueous  $\delta^{13}\text{CO}_2$  or  $\delta^2\text{H}_2\text{O}$  among lakes would yield a flat-line pattern with a slope of zero and the y-intercept value at the mean for the terrestrial values of  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$ . Conversely, if DOM or POM were derived entirely from algal photosynthesis, DOM and POM would vary systematically with both aqueous  $\delta^{13}\text{CO}_2$  and  $\delta^2\text{H}_2\text{O}$  and would deviate from a perfect regression, due only to variations in photosynthetic fraction values among lakes (Figure 1). Because there is little consensus on the value of  $\epsilon_C$  among lakes, algal values based on the reported range of  $\epsilon_C$  in lakes were included [Bade et al., 2006; Mohamed and Taylor, 2009].

### 2.5.2. Algebraic Mixing Model

[13] In addition, an algebraic mixing model was used to determine the contribution of OM sources to the mixture (POM or DOM) using the deuterium isotope values of each variable:

$$\delta^2H_{\text{POM or DOM}} = (\delta^2H_{\text{Algae}} * \Phi_{\text{Algae}}) + (\delta^2H_{\text{Terrestrial}} * \Phi_{\text{Terr}}) \quad (1)$$

$$\Phi_{\text{Algae}} + \Phi_{\text{Terr}} = 1 \quad (2)$$



**Figure 1.** Conceptual diagram of the gradient-based mixing model approach for (a)  $\delta^2\text{H}$  and (b)  $\delta^{13}\text{C}$ . In (a) the solid brown line is the mean  $\delta^2\text{H}$  terrestrial value and the solid green line is the algal value. The shaded regions are the standard deviations of the source  $\delta^2\text{H}$  and  $\delta^{13}\text{C}$  value distribution. The dashed lines are the most extreme terrestrial and algal isotope values sampled, indicating the maximum range of source  $\delta^2\text{H}$  values. In (b) the solid brown line is the mean  $\delta^{13}\text{C}$  terrestrial value and the diagonal green lines are the possible algal  $\delta^{13}\text{C}$  value assuming either  $\epsilon_c$  is 10, 15 or 20.

where  $\Phi$  is the fractional portion of algal or terrestrial material in the POM or DOM pool. In order to calculate the possible range of  $\Phi_{\text{Terr}}$  in each lake, the standard deviation values of the terrestrial end member samples ( $n=81$ ) and the algal end member estimation ( $n=14$ ) and algal material applied to each lake were also used in equation (1) as well.

[14] These calculations were made assuming that only two sources were contributing to the mixture: terrestrial material and algae. Macrophytes, another potential source of OM, were excluded from the sources due to the generally low abundance of macrophytes in most of the sampled lakes. This assumption was tested by also examining the  $\delta^{13}\text{C}$  data for POM and DOM as the  $\delta^{13}\text{C}$  of macrophytes is greatly enriched, compared to the  $\delta^{13}\text{C}$  of terrestrial and algal material.

[15] To examine if there are differences in OM composition between the epilimnion and metalimnion for systems with heterograde oxygen profiles, epilimnetic POM, and metalimnetic POM  $\Phi_{\text{Terr}}$  values calculated for each lake were plotted against one another. The same was done for epilimnetic and metalimnetic DOM  $\Phi_{\text{Terr}}$  values. The data were assessed against a 1:1 line representing equivalent terrestrial contribution to the OM pool at both depths within a lake and visually evaluated for deviation from the 1:1 line.

### 2.5.3. Regression and Regional Analysis

[16] In order to estimate the distribution of OM composition for a greater number of lakes, we used commonly measured water chemistry variables that are available for many lakes to model the variation in terrestrial contribution to OM pools. The POM and DOM  $\Phi_{\text{Terr}}$  calculated using mean algal and terrestrial  $\delta\text{H}$  values in equation (1) was used for regression analysis with other log transformed, nonisotope variables. All combinations of variables were run to test for the most parsimonious model to explain the variation in terrestrial contribution to POM and DOM among lakes. Models were evaluated using the Akaike information criterion (AIC) corrected for small sample size ( $\text{AIC}_c$ ) and ranked using  $\Delta\text{AIC}_c$  and Akaike weights [Burnham and

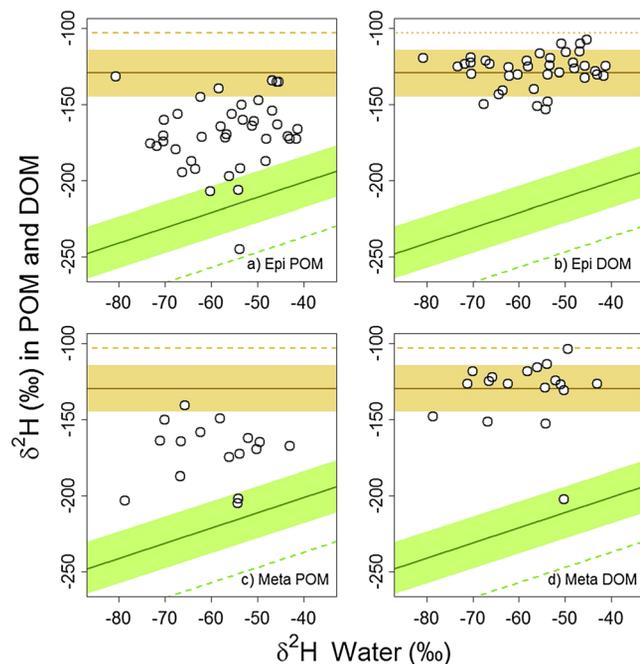
Anderson, 2002]. Candidate models with a  $\Delta\text{AIC}_c$  greater than 10 were discarded as very unlikely given the data. The model that best described the variation in terrestrial contribution to POM was then used to calculate the terrestrial contribution to POM in lakes for the entire NHLD region, using data from a survey of more than 1600 lakes in the region [Overton *et al.*, 1986].

## 3. Results

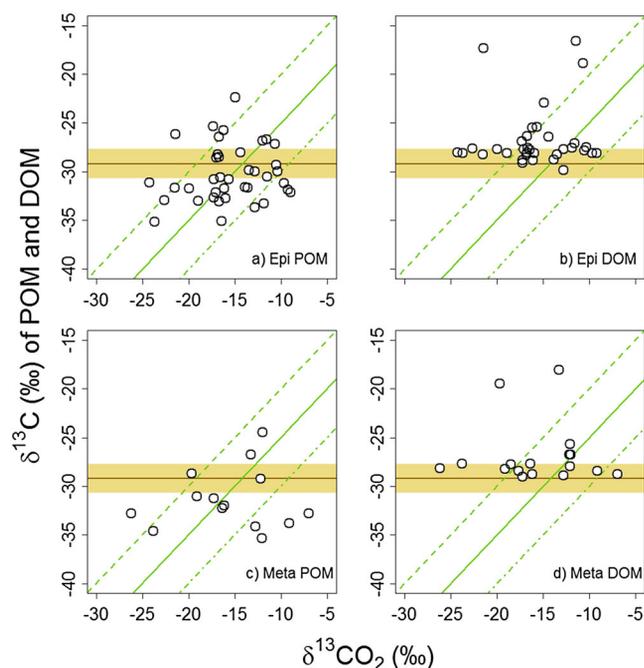
### 3.1. Graphical Analysis

[17] There is a large variation in the  $\delta^2\text{H}$  values of OM in both the epilimnion and metalimnion among lakes. The  $\delta^2\text{H}$  of neither POM nor DOM varies systematically with  $\delta^2\text{H}_2\text{O}$  (Figure 2). The  $\delta^2\text{H}$  values of DOM in the epilimnion and metalimnion have a narrow range and all values lie close to the  $\delta^2\text{H}$  of terrestrial material from the lake's catchments (Figures 2b and 2d). To a first approximation the  $\delta^2\text{H}$  results suggest that DOM is entirely of terrestrial origin and that POM is derived from a mixture of algal and terrestrial sources. It is noteworthy that a few POM and DOM  $\delta^2\text{H}$  values lie outside the average terrestrial (solid line, Figure 1) and algal source values (solid diagonal line, Figure 2); however, all of the OM samples fall within the source constraints represented by upper and lower standard deviation of the sources (dotted lines, Figure 2).

[18] Similarly, the  $\delta^{13}\text{C}$  values of POM and DOM do not vary linearly with aqueous  $\delta^{13}\text{CO}_2$  by following the trajectory of any of the  $\epsilon_c$  lines in Figure 3. The slopes of linear regressions of either POM (Figures 3a and 3c) or DOM (Figures 3b and 3d)  $\delta^{13}\text{C}$  versus aqueous  $\delta^{13}\text{CO}_2$  among the lakes are not significantly different from zero (*t*-test,



**Figure 2.** Hydrogen isotope values for (a) epilimnion POM, (b) epilimnion DOM, (c) metalimnion POM, and (d) metalimnion DOM versus  $\delta^2\text{H}_2\text{O}$  in each lake plotted with the terrestrial and algal isotope values for comparison. See Figure 1 for more information regarding the different lines in this figure.

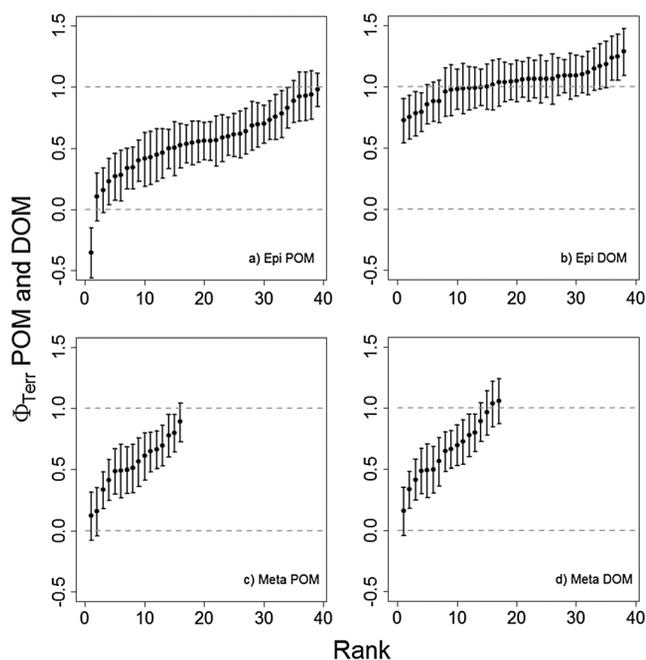


**Figure 3.** Carbon isotope values of POM and DOM in each lake plotted with the terrestrial and possible algal isotope values for comparison. If the OM pools are dominated by algal material, the POM or DOM  $\delta^{13}\text{C}$  value would change linearly with (a) aqueous  $\delta^{13}\text{CO}_2$ , (b) epilimnion POM, (c) epilimnion DOM, (d) metalimnion POM, and (e) metalimnion DOM versus aqueous  $\delta^{13}\text{CO}_2$ . The solid gray line is the average terrestrial  $\delta^{13}\text{C}$  value. The shaded region is the standard deviation of the terrestrial  $\delta^{13}\text{C}$  distribution.

$p$ -value for POM = 0.37 [ $n = 39$ ], for DOM = 0.58 [ $n = 38$ ]. Additionally, the  $\delta^{13}\text{C}$  of POM and DOM in each lake indicates that macrophytes likely did not contribute significantly to the pools because the values are not greatly enriched above the mean terrestrial  $\delta^{13}\text{C}$ . The pattern in DOM  $\delta^2\text{H}$  values is mirrored in the DOM  $\delta^{13}\text{C}$  values (Figure 3b) that do not follow the change in algal  $\delta^{13}\text{C}$  with  $\delta^{13}\text{CO}_2$  but instead align with the terrestrial  $\delta^{13}\text{C}$  end member. To a first approximation the  $\delta^{13}\text{C}$  results also suggest that DOM is nearly entirely derived from terrestrial sources and that POM is derived from a mixture of algal and terrestrial sources.

### 3.2. Mixing Model Results

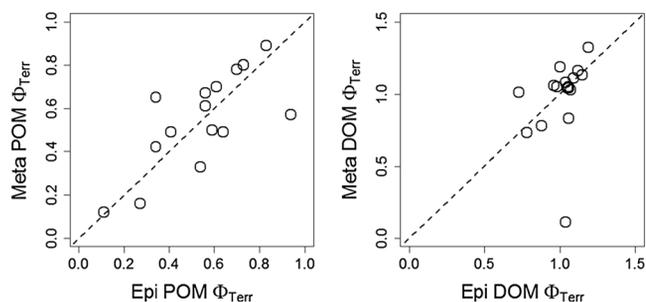
[19] Estimates of epilimnetic POM  $\Phi_{\text{Terr}}$  based on  $\delta^2\text{H}$  in the individual lakes ranges from 0.0–0.98 with a mean  $\Phi_{\text{Terr}}$  among lakes of  $0.54 (\pm 0.26)$  (Figure 4a). The POM value in one lake (Little Arbor Vitae) fell outside of the bounds of the source mean values and was more enriched than the most depleted algal isotope value, yielding a negative, or effectively 0.0 terrestrial contribution. Similarly, some epilimnion DOM values were more enriched than the terrestrial source average yet still more depleted than the most enriched terrestrial source value. The  $\delta^2\text{H}$  calculations for these lakes yielded estimates of terrestrial contribution greater than, yet effectively equivalent to, 100%. The epilimnion DOM pool is dominated by terrestrial material in all lakes, ranging



**Figure 4.** The 39 survey lakes ranked by the fraction of the POM and DOM that is terrestrial in origin calculated using  $\delta^2\text{H}$ . Black diamonds are the mean  $\Phi_{\text{Terr}}$  in each lake calculated using the mean terrestrial and algal isotope values (Figure 1). The error bars are the minimum and maximum  $\Phi_{\text{Terr}}$  in each lake calculated using the isotope values of one standard deviation around the end member mean: (a) epilimnion POM, (b) epilimnion DOM, (c) metalimnion POM, and (d) metalimnion DOM.

from 0.73–1.29 for  $\Phi_{\text{Terr}}$  with a mean  $\Phi_{\text{Terr}}$  of 1.02 ( $\pm 0.13\%$ ), not significantly different from 1.0 (Figure 3c).

[20] Similar to epilimnetic POM composition, there is a large range (0.12–0.88) of  $\Phi_{\text{Terr}}$  for metalimnetic POM pools (mean = 0.53, Figure 4b). Metalimnetic DOM  $\Phi_{\text{Terr}}$  also was largely terrestrial (mean = 0.66, Figure 4d) similar to the upper mixed layer, with the notable exception of one lake (Sparkling Lake) in which aquatic contribution was high. This one lake increased the range in DOM  $\Phi_{\text{Terr}}$  to 0.15–1.0. There was no clear pattern of  $\Phi_{\text{Terr}}$  increasing or decreasing with depth in either the POM or DOM pools among lakes (Figure 5).



**Figure 5.** Evaluation of the composition of OM pools at different depths in the lake: (a) comparison of epilimnion and metalimnion POM  $\Phi_{\text{Terr}}$  and (b) comparison of epilimnion and metalimnion DOM  $\Phi_{\text{Terr}}$ . The dashed lines indicate no change in  $\Phi_{\text{Terr}}$  over depth within the lake.

### 3.3. Terrestrial Contribution and Water Chemical Properties

[21] There were nine significant ( $p$ -value  $< 0.01$ ) relationships with a  $\Delta AIC_C < 10$  between epilimnion POM  $\Phi_{Terr}$  and other limnetic variables (Table 2). The variable that best described the variation in epilimnion POM  $\Phi_{Terr}$  among the surveyed lakes was pH (Figure 6a). By extrapolating the relationship between pH and epilimnion POM  $\Phi_{Terr}$  to a regional lake survey [Overton *et al.*, 1986] of 1692 lakes, we estimate that the majority of lakes are dominated by terrestrial material (mean = 0.63 terrestrial, Figure 6b). There are also nine significant relationships with a  $\Delta AIC_C < 10$  between epilimnion DOM  $\Phi_{Terr}$  and other limnetic variables. Compared to the variability in POM  $\Phi_{Terr}$  among lakes however, the range in epilimnion DOM  $\Phi_{Terr}$  is small and at a minimum is overwhelmingly terrestrial at DOM  $\Phi_{Terr} = 0.73$ . There were significant correlations between metalimnion POM  $\Phi_{Terr}$  and pH and the color to TP ratio. There were no significant correlations between metalimnion DOM and any other variable.

## 4. Discussion

[22] From the graphical gradient analysis (Figures 2 and 3), there is a clear pattern of terrestrial dominance of both POM and DOM pools in lakes. The same pattern exists if the analysis is based on  $\delta^2H$  or  $\delta^{13}C$ . DOM is nearly entirely

derived from terrestrial inputs in all but the most eutrophic lakes. POM has mixed algal and terrestrial sources, and this mixture varies among lakes. There is a greater variability (vertical range in Figures 2a and 2c and Figures 3a and 3c) in the terrestrial contribution to POM pools in both the epilimnion and metalimnion compared to DOM pools, although the average terrestrial contribution to POM among lakes was still greater than 50%. The small vertical range in epilimnetic DOM clustered around the terrestrial isotope values for both  $\delta^2H$  and  $\delta^{13}C$  (Figures 2b and 2d and Figures 3b and 3d) indicates little variation in the terrestrial dominance of the DOM pool. The pattern is similar for metalimnetic DOM except for the Sparkling Lake with a largely algal DOM pool. Sparkling Lake was experiencing a metalimnetic algal bloom at the time of sampling, and it is likely that the highly algal signature of the pool was due to extracellular release of DOM by the algae in that layer [Baines and Pace, 1991]. This observation of DOM derived from algae is a significant indicator that the isotope analysis detects autochthonous dominance when present.

[23] Although  $\delta^{13}C$  values of POM and DOM show a clear pattern of terrestrial dominance as discussed (Figure 3), the difficulty in calculating the terrestrial contribution encountered by other investigators is illustrated by the low resolution of OM source  $\delta^{13}C$  values relative to the spread of the POM and DOM data. However, the clear separation in the sources'  $\delta^2H$  values and position of the data between

**Table 2.** Regression Analysis of Epilimnetic and Metalimnetic POM and DOM Fraction Terrestrial and Independent Variables

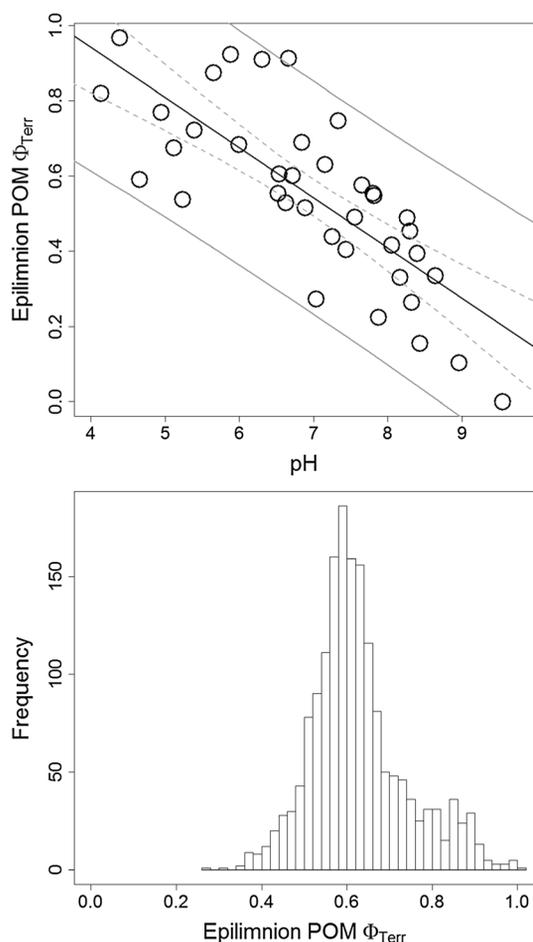
Dependent	Independent(s)	Adjusted $R^2$	AICc	Akaike Weight	$\Delta AIC$	Equation
Surface POM $\Phi_{Terrestrial}$	pH	0.59	-29.61	0.7	0	1.47 - (0.13 * pH)
	Color: TP <sup>a</sup> , pH	0.6	-25.57	0.09	4.04	1.13 + (0.05 * log <sub>10</sub> (Color: TP)) - (0.09 * pH)
	SA, pH	0.59	-24.82	0.06	4.8	1.29 - (0.03 * log <sub>10</sub> (SA)) - (0.10 * pH)
	Color: TP	0.52	-24.63	0.06	4.98	0.48 + (0.13 * log <sub>10</sub> (Color: TP))
	Color: Chl- $\alpha$ <sup>b</sup> , pH	0.57	-22.84	0.02	6.77	1.37 + (0.02 * log <sub>10</sub> (Color: Chl- $\alpha$ )) - (1.12 * pH)
	pH, DIC <sup>c</sup>	0.57	-22.38	0.02	7.23	1.48 - ((0.13 * pH) - (0.01 * log <sub>10</sub> (DIC))
	DIC, Color: TP	0.57	-22.23	0.02	7.39	0.73 - (0.05 * log <sub>10</sub> (DIC)) + (0.10 * log <sub>10</sub> (Color: TP))
	SA <sup>d</sup>	0.47	-21.15	0.01	8.46	0.71 - (0.06 * log <sub>10</sub> (SA))
	Color: TP, SA	0.54	-19.64	0	9.97	0.57 + (0.08 * log <sub>10</sub> (Color: TP)) - (0.03 * log <sub>10</sub> (SA))
Surface DOM $\Phi_{Terrestrial}$	DIC	0.37	-57.86	0.69	0	1.34 - (0.06 * log <sub>10</sub> (DIC))
	DIC, Color: Chl- $\alpha$	0.4	-53.37	0.07	4.49	1.31 - (0.05 * log <sub>10</sub> (DIC)) + (0.03 * log <sub>10</sub> (Color: Chl- $\alpha$ ))
	pH	0.29	-53.12	0.06	4.74	1.40 - (0.05 * pH)
	DIC, Color: TP	0.39	-52.74	0.05	5.12	1.27 - (0.05 * log <sub>10</sub> (DIC)) + (0.02 * log <sub>10</sub> (Color: TP))
	DIC, SA	0.39	-52.25	0.04	5.6	1.31 - (0.05 * log <sub>10</sub> (DIC)) - (0.01 * log <sub>10</sub> (SA))
	DIC, pH	0.38	-52.2	0.04	5.65	1.41 - (0.04 * log <sub>10</sub> (DIC)) - (0.02 * pH)
	SA	0.21	-49.07	0.01	8.79	1.09 - (0.03 * log <sub>10</sub> (SA))
	Color: TP	0.21	-48.93	0.01	8.93	1.00 + (0.05 * log <sub>10</sub> (Color: TP))
	Color: Chl- $\alpha$	0.2	-48.3	0.01	9.56	1.07 + (0.05 * log <sub>10</sub> (Color: Chl- $\alpha$ ))
	Color: TP	0.24	0.93	0.52	0	0.51 + (0.08 * log <sub>10</sub> (Color: TP))
Deep POM $\Phi_{Terrestrial}$	pH	0.23	1.06	0.48	0.13	1.17 - (0.09 * pH)

<sup>a</sup>TP = total phosphorus

<sup>b</sup>Chl- $\alpha$  = chlorophyll- $\alpha$  concentration

<sup>c</sup>DIC = dissolved inorganic carbon concentration

<sup>d</sup>SA = surface area (ha)



**Figure 6.** Epilimnion POM  $\Phi_{Terr}$  plotted against the pH in each lake. (a) The black line is the linear regression model ( $y = 1.47 - (0.13 * pH)$ , adjusted  $R^2 = 0.59$ ,  $p$ -value  $< 0.01$ ), the gray dotted line is the 95% confidence interval and the solid gray line is the 95% prediction interval. (b) Histogram of the POM  $\Phi_{Terr}$  in 1692 lakes in Northern Highlands Lake District based on the pH model described above.

terrestrial and algal sources (Figure 2) allowed for a simple, algebraic estimation of the terrestrial contribution to POM and DOM in the surveyed lakes (Figure 4). If the same algebraic model in equation (1) is used for the  $\delta^{13}C$  and  $\epsilon_c = 10$ , mean epilimnion POM  $\Phi_{Terr}$  is 0.56, although it is impossible to estimate a range using the  $\delta^{13}C$  data. Without a well-constrained estimate of the terrestrial contribution, a quantification and regional extrapolation of the variation between lakes would be impossible.

[24] For this analysis we made simplifying assumptions about seasonality and the smaller fractionation processes affecting the end member isotope values. First, the seasonal change in the dominant form of terrestrial subsidies may change the isotope signature of terrestrial material entering the lake. We have partially tested this assumption by comparing the isotope signature of groundwater DOM to that of leaf litter (fresh and decomposed) and found that there was no significant difference in the isotope signatures [Solomon *et al.*, 2011]. The terrestrial end member value was also calculated from samples taken throughout the growing season. There could also be systematic differences

in isotope values related to POM and DOM concentration that were unaccounted for. Evaporation can also cause a systematic isotopic enrichment of  $\delta^2H$  surface waters. In lakes in the Northern Highland Lake District, seasonal surface water isotope changes have been observed to be  $\sim 5\%$  [Krabbenhoft, Bowser, Anderson, & Valley, 1990], which is much smaller than the range in the algal end member isotope value used in this study. Furthermore, Cole *et al.* (2011) found little difference in the isotope signature of water from the epilimnion and hypolimnion of two lakes, indicating that evaporative fractionation is likely minimal for these systems. Additionally, photodegradation chemically transforms DOM and can cause the isotope signature of DOM to change with exposure to UV radiation. To our knowledge, the photodegradation effect on OM  $\delta^2H$  has not been quantified, so it is unclear how that might impact our estimates here. However, the few samples of groundwater DOM that have been collected are isotopically similar to DOM samples that have been exposed to UV radiation in the water column.

[25] Dietary water contribution to the POM pool was not accounted for in this study but could impact the estimate of  $\Phi_{Terr}$  of POM. Dietary (or environmental) water is the contribution of hydrogen to consumer biomass  $\delta^2H$  from water consumed via diet or diffusion [Solomon *et al.*, 2009]. In the strictest sense, POM is not a consumer and does not have dietary water. However, POM could be influenced by the dietary water of microbes (bacterial and protozoa) in the POM pool. There are two reasons that dietary water in microbes in POM has minimal effect on estimates of  $\Phi_{Terr}$ . First, bacterial and protozoan biomass on POM is a small fraction of the POM pool (approximately 10%, Cole *et al.*, 1993; Pace *et al.*, 1998). Second, the  $^{13}C$  estimate of the terrestrial contribution to POM (which is not affected by dietary water) yields the same answer as the  $\delta^2H$  estimate. Although the dietary water use for microbial consumers is not well quantified, if a value of 0.2 for freshwater primary consumers is used to calculate the potential impact of dietary water use on estimates of POM  $\Phi_{Terr}$  [Solomon *et al.*, 2009], the estimate is only decreased by 0.03. This is well within the range of error considered for each estimate in this study (Figure 4).

[26] As demonstrated by a series of experiments in six small lakes in the NHL, the ratio of color to chlorophyll-*a* (as indicative of allochthonous to autochthonous resources) was a reasonable predictor of terrestrial support of aquatic consumers [Pace *et al.*, 2007; Batt *et al.*, 2012; Solomon *et al.*, 2011]. Our larger study of 39 lakes found that whereas this ratio explained a significant fraction of the variability in POM  $\Phi_{Terr}$  (adjusted  $R^2 = 0.41$ ,  $p$ -value  $< 0.01$ ) color to chlorophyll was not as strong a predictor in comparison to other models using  $\Delta AIC$  as a criterion (Table 2). The ratio of color to TP, however, was better (yet still not the strongest) predictor of POM allochthony. The pool of autochthonous material may be redistributed through grazing by zooplankton and therefore would not be well represented by chlorophyll measurements alone. TP may be a better predictor of the autochthonous portion of the POM pool as it integrates the effects of grazing and redistribution of autochthonous material to other forms in the POM pool [Jones and Bachmann, 1976].

[27] Several water chemistry variables (and combinations of variables) explained more than 50% of the discrepancy in the terrestrial contribution to POM. Among these, epilimnetic pH performed the best (Table 2 and Figure 6a). The lakes in this region have low mineral content [Cook *et al.*, 1987], and the pH of these lakes is significantly influenced by ecosystem metabolism [Cole, Pace, Carpenter, & Kitchell, 2000]. Additionally, low pH tends to occur in lakes that also have high color and DOC, so pH may integrate both a metabolic signal and terrestrial DOC loading. In fact, for the lakes in this study, pH and the color to TP ratio are significantly correlated ( $\text{pH} = -0.80 * \log(\text{Color: TP}) + 6.15$ ; adjusted  $R^2 = 0.65$ ,  $p$ -value  $< 0.001$ ), supporting the hypothesis that pH is an integrative indicator of allochthonous and autochthonous material as previously discussed. Extrapolating the pH-terrestrial contribution relationship to the whole region, the majority of lakes are dominated by terrestrial material in the POM pool (Figure 6b). Combining this regional estimate with the DOM results, lake OM is overwhelmingly terrestrial throughout the landscape.

[28] Lakes emit a significant amount of carbon dioxide into the atmosphere [Cole *et al.*, 1994; Battin *et al.*, 2009; Tranvik *et al.*, 2009]. Most researchers have found that this is due to net heterotrophy [Cole *et al.*, 1994; Ask *et al.*, 2012; Karlsson *et al.*, 2012; McCallister and del Giorgio, 2012], that is, an excess of respiration over gross primary production. From a mass balance perspective, the excess respiration would have to be supported by exogenous material [Karlsson *et al.*, 2012; McCallister and del Giorgio, 2012]. Our results, showing that DOM is largely of terrestrial origin and that POM in most lakes is dominated by terrestrial material, support the idea that the excess respiration in lakes that produces carbon dioxide emissions is sustained by the oxidation of terrestrially derived OM. Our results highlight the importance of accounting for the flux and subsequent return of terrestrial carbon to the atmosphere when estimating terrestrial carbon sequestration.

[29] Globally, the loading of terrestrial material to surface waters continues to be altered due to changes in climate, land use, and pollution deposition chemistry, all of which impact aquatic carbon cycling and ecosystem structure and function [Evans *et al.*, 2005; Monteith *et al.*, 2007]. Constrained estimates of terrestrial contribution to aquatic OM pools and statistical models quantifying heterogeneity within a region such as we have provided here offer a powerful tool for monitoring change as well as identifying hotspots of carbon cycling.

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