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Sources and fates of dissolved organic carbon in lakes as determined by whole-lake carbon isotope additions

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Abstract Four whole-lake inorganic ^{13}C addition experiments were conducted in lakes of differing trophic status. Inorganic ^{13}C addition enriched algal carbon in ^{13}C and changed the $\delta^{13}C$-DOC by +1.5‰ to +9.5‰, depending on the specific lake. This change in $\delta^{13}C$-DOC represented a significant input of algal DOC that was not completely consumed by bacteria. We modeled the dynamics in $\delta^{13}C$-DOC to estimate the fluxes of algal and terrestrial carbon to and from the DOC pool, and determine the composition of the standing stock. Two experiments in lightly stained, oligotrophic lakes indicated that algal production was the source of about 20% of the DOC pool. In the following year, the experiment was repeated in one of these lakes under conditions of nutrient enrichment, and in a third, more humic lake. Algal contributions to the DOC pool were 40% in the nutrient enriched lake and 5% in the more humic lake. Spectroscopic and elemental analyses corroborated the presence of increased algal DOC in the nutrient enriched lake. Natural abundance measurements of the $\delta^{13}C$ of DOC in 32 lakes also revealed the dual contributions of both terrestrial and algal carbon to DOC. From these results, we suggest an approach for inferring the contribution of algal and terrestrial DOC using easily measurable parameters.

Keywords Allochthonous · Autochthonous · Carbon stable isotopes · Dissolved organic carbon

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Introduction

Dissolved organic carbon (DOC) influences a number of properties in lake ecosystems (Williamson et al. 1999). For example, DOC can limit productivity (Jackson and Hecky 1980; Carpenter et al. 1998) and affect epilimnetic (Hanson et al. 2003) and hypolimnetic respiration (Houser et al. 2003). Incorporation of DOC into bacterial bio-

mass and its subsequent uptake by grazers is a mechanism that links terrestrial subsidies to higher levels of the aquatic food web (Tranvik 1992). Colored DOC may also play a critical role in protecting aquatic plants and animals from the deleterious effects of ultraviolet (UV) radiation exposure (Schindler and Curtis 1997).

Two major sources of DOC are generally considered in lake ecosystems, allochthonous inputs of terrestrial material (Aitkenhead-Peterson et al. 2003) and within-lake (autochthonous) production by phytoplankton, benthic algae, and aquatic macrophytes (Bertilsson and Jones 2003). Since terrestrial DOC has been extensively processed in the soil before entering an aquatic system, this terrestrial DOC is expected to be relatively recalcitrant to further decomposition (Schiff et al. 1997). The large input and relatively slow decomposition rate of terrestrial DOC creates the expectation that the standing stock of DOC in lakes should be dominated by terrestrial sources (Wetzel 2001). This terrestrial dominance of DOC is consistent with predictive models that relate the standing stock of lake DOC to characteristics of the lake's watershed, including relative area of wetlands (Kortelainen 1993; Gergel et al. 1999; Xenopoulos et al. 2003). Further, carbon budgets of lakes indicate external loading often dominates over internal production (Canham et al. 2004; Caraco and Cole 2004). While there is strong conceptual support for the dominance of terrestrial sources in the standing stock of lake DOC, direct evidence is rare and a number of factors indicate that the situation is complex. For example, terrestrial derived DOC may be made more labile in lakes by photolysis or photobleaching (Lindell et al. 1995; Wetzel et al. 1995; Reche et al. 1998). In addition, use of allochthonous DOC supplies energy fueling lake metabolism and aquatic food webs (Sundh and Bell 1992; Tranvik 1992; del Giorgio and Peters 1994).

Numerous studies have investigated the production of autochthonous carbon in a variety of aquatic habitats (Baines and Pace 1991; Norrman et al. 1995; Biddanda and Benner 1997). Production of DOC from planktonic algae can enter the water column through extracellular release by living cells, cell death and lysis, or herbivore grazing (Bertilsson and Jones 2003). The DOC of algal origin is usually considered to be of high quality for bacterial use, as suggested by the pattern of increased bacterial production with increased primary production (Cole et al. 1988). Autochthonous DOC is generally also considered to be relatively labile (Kirchman et al. 1991; Søndergaard et al. 1995). However, autochthonously derived DOC may be rendered more refractory and become persistent over time (Fry et al. 1996; Tranvik 1998).

Despite numerous studies on various aspects of DOC, determination of the proportions of algal and terrestrial DOC standing stock in the total pool has been difficult (Cole et al. 1984). Detailed budgets accounting for each source are rare (Likens 1985). Newer techniques analyzing trace organic moieties and optical properties unique to each source could potentially determine these proportions directly (Hood et al. 2003; McKnight et al. 2003; Boyd and Osburn 2004; Waiser and Robarts 2004). Whole-lake tracer experiments are another potentially informative way to assess sources, but studies to date have not focused specifically on determining the relative proportions of algal and terrestrial DOC (Hesslein et al. 1980; Bower et al. 1987; Schindler et al. 1992; Cole et al. 2002).

Meili (1992) examined the potential contribution of autochthonous and allochthonous sources of organic matter in lakes. Starting from empirical relations, he posed the hypothesis that the percentage of autochthonous carbon in DOC should vary with water color and phosphorus (surrogates for terrestrial carbon loading and primary productivity, respectively). However beyond this theoretical treatment, tests have been lacking that encompass the production, decomposition and standing stock of DOC at an ecosystem scale. Our study is a rare attempt to simultaneously quantify the various contributions to the DOC pool, the standing stock, and losses. Specifically, we are interested in the relative contribution of algal and terrestrial DOC in lakes that differ in trophic status and therefore potentially differ in algal and terrestrial contributions to DOC.

We used three approaches to determine whether the proportion of each source of carbon

varies among lakes. First, we conducted four whole-lake additions of ^{13}C-labeled dissolved inorganic carbon to trace algal sources of carbon. Despite the presumably labile nature of algal DOC, we observed accumulation and persistence of ^{13}C labeled algal carbon in the DOC pool. Modeling the isotope results, we were able to calculate the proportion of terrestrial and algal carbon, and provide estimates of production and losses. Second, the results from two of the ^{13}C labeling experiments were compared with spectroscopic and elemental properties of the dissolved organic matter from those lakes to corroborate conclusions from the models. Finally, we compared the variation in natural abundance of $\delta^{13}C$-DOC among 32 lakes to examine patterns of autochthonous and allochthonous contributions to DOC for a broader range of systems. All three approaches indicate algal derived carbon becomes an increasingly important source of DOC as primary productivity increases. Although this result may seem intuitive, we use our empirical data to explore, for the first time, where different lakes lie along this gradient based on easily measurable indicators.

Methods

Isotope addition experiment

We added inorganic ^{13}C to the epilimnia of three lakes (Peter, Paul and Tuesday) located at the University of Notre Dame Environmental Research Center in Michigan, USA. These lakes have been the site of numerous whole ecosystem studies and are described in detail elsewhere (Carpenter and Kitchell 1993; Carpenter et al. 2001; Pace et al. 2004). Briefly, the lakes are small, deep, dimictic, and surrounded by mixed coniferous and hardwood forest and varying amounts of *Sphagnum* bog. Paul and Peter are oligo- to mesotrophic in nutrient status and only slightly stained. Tuesday Lake is completely surrounded by *Sphagnum* bog and is more colored.

In 2001, Paul and Peter lakes received 20 and 30 g, respectively, of $NaH^{13}CO_3$ d^{-1} for 42 consecutive days, starting 11 June and ending 22 July. In 2002, the addition period was 35 days from 17 June to 21 July. In that year Peter and Tuesday lakes received 50 and 21 g $NaH^{13}CO_3$ d^{-1}, respectively. The addition amounts were based on epilimnion volume, lake DIC concentration and estimated loss of isotope *via* uptake and gas evasion. The goal was to increase isotope signatures of dissolved inorganic carbon ($\delta^{13}C$-DIC) well above +20‰ in order to label major carbon pools and food web constituents (Pace et al. 2004).

The ^{13}C was added daily to the epilimnion of each lake in the early morning. A preweighed amount of $NaH^{13}CO_3$ (>98% ^{13}C; Isotec) was dissolved in lake water in a 20 l carboy. The solution was injected from a moving boat into the epilimnion at a depth of 1 m using a peristaltic pump. The boat was rowed around the midsection of the lake while the solution was being injected to distribute the isotope and promote faster mixing throughout the epilimnion.

Additionally, Peter Lake received nutrient amendments to increase primary productivity in 2002. Initially we added 1.25 l 85% H_3PO_4 and 22.7 kg NH_4NO_3 on 3 June and then continued with daily additions of 0.2 l 85% H_3PO_4 and 3.2 kg NH_4NO_3 from 10 June to 25 August. Nitrogen was added well in excess of P to ensure that P remained the limiting nutrient. Nutrients were dissolved in lake water and poured slowly over the transom of a moving boat in the central area of the lake.

Limnological parameters measured weekly included Chlorophyll *a* (Chl. *a*), DOC and color. Chl. *a* was determined fluorometrically from material captured on Whatman GF/F filters that had been frozen and extracted with methanol. Filtration was done at low vacuum (<200 mmHg). DOC and color samples were collected as the filtrate of epilimnetic water. DOC samples were preserved by acidifying with 2 N H_2SO_4 to pH <2. DOC was analyzed on a Shimadzu model 5050 high temperature TOC analyzer. Color samples were refrigerated and within a few days of Collection and absorbance was measured on a spectrophotometer at 440 nm in a 10-cm cuvette. Color is expressed as a wavelength-specific absorption coefficient (a_{440}; m^{-1}).

We measured productivity and respiration in each lake using Yellow Spring Instruments sondes equipped with rapid-pulsed oxygen-temperature electrodes. O_2 measured at 5-min intervals throughout a majority of the summer stratified season was used to determine ecosystem gross primary production (GPP) and respiration (R) according to Cole et al. (2000). We also determined respiration weekly based on 24 h oxygen consumption in dark bottles using the Winkler method, detailed in Pace and Cole (2000).

Isotope ratios were determined for dissolved inorganic carbon (DIC), particulate organic carbon (POC) and DOC. Dissolved inorganic carbon was collected in 60-ml serum vials, acidified to pH <2 with 10 N H_2SO_4, and sealed with butyl rubber septa and aluminum crimp caps. Isotope ratios of DIC were analyzed using a Micromass Isochrome GC-C-IRMS at the University of Waterloo, Environmental Isotope Laboratory. Particulate organic carbon was collected on precombusted GF/F filters at low vacumm (<200 mmHg), dried for at least 48 h at 55–60 °C, and stored in a desiccator prior to analysis. Particulate organic carbon samples were acid fumed immediately prior to analysis to remove residual inorganic carbon. Samples for isotopic analysis of DOC were collected by evaporating ~900 ml of GF/F filtrate water. The water was acidified with 1 N HCl to pH <2 to prevent microbial activity during the period of evaporation, and to drive off any inorganic carbon. The water was evaporated in acid washed glass petri dishes in a food dehydrator. The residue remaining after evaporation was scraped from the petri dish with a razor blade and stored in a desiccator until isotopic analysis. Isotopic analysis of organic material was conducted using a Carlo Erba Elemental Analyzer, a Finnigan MAT Conflo II/III interface with a Delta+ mass spectrometer at the University of Alaska-Fairbanks, Stable Isotope Facility.

On 23 and 24 July 2002, approximately 120 l of water was collected from Peter and Tuesday lakes for fulvic acid isolation. Samples were collected in 20 l plastic cubitainers and shipped on ice to INSTAAR for processing. The water samples were filtered through 0.25 and 0.45 μm glass fiber filters housed in stainless steel filter towers (Balston Filters, Parker-Hannefin). After filtration, samples were acidified to pH 2 with concentrated hydrochloric acid (trace metal grade) prior to fulvic acid isolation. The fulvic acids were isolated using XAD8 chromatography (Thurman 1985). Aliquots of the filtered, unacidified water were saved for DOC, fluorescence, and UV/VIS absorbance analyses.

Fulvic acid solutions for UV/VIS and fluorescence were prepared by dissolving the freeze-dried solid in MilliQ water and stirring for 24 h. After stirring, samples were pH adjusted to 6–7 using 0.1 N HCl or NaOH. DOC concentrations of the fulvic acid solutions ranged from 3 to 5 mg C l^{-1} to minimize self-absorption error during fluorescence measurements. UV/VIS absorbance data for specific ultraviolet absorbance at 254 nm (SUVA-254; Traina et al. 1990) were collected on the whole water and fulvic acid solutions with an Agilent UV/VIS spectrophotometer in a 1-cm quartz cuvette. Fluorescence measurements were made on a Fluoromax-2 fluorometer (Jobin-Yvon) for both the whole water and fulvic acid samples in a 1-cm quartz cuvette. The fluorescence index (FI; McKnight et al. 2001) was obtained after verifying the presence of the FI peak (Cory et al. in preparation) at an excitation of 370 nm. Because the emission scan used to determine the FI was corrected for instrument variation using the instrument manufactured correction files (Cory et al. in preparation), the FI was calculated as a ratio of emission intensities at 470 over 520 nm.

Freeze dried fulvic acid samples were analyzed for C, H, N, O, S and ash content on an elemental analyzer by Huffman Laboratories. Elemental analysis data, including molar ratios, were calculated after correcting for ash content.

Isotope modeling

In order to understand the isotopic response of DOC to the addition and to partition the sources of DOC, we constructed a model of ^{13}C dynamics. Conceptually the model considers two sources of DOC, terrestrial inputs and pelagic algal production. Losses of DOC include respiration, flushing and photo-oxidation. Total DOC concentration was assumed to be at steady state throughout the summer so that

inputs balanced losses. The parameters estimated by the model were the total amount of DOC derived from primary production within the lake (PP) and heterotrophic respiration (R) of the DOC pool. Terrestrial inputs (T_{in}) were then calculated by difference, assuming steady state. Water residence time in the epilimnia of these lakes is roughly 400 days (Cole and Pace 1998) and photooxidation was assumed to be 1% d^{-1} (Granéli et al. 1996). Therefore, flushing and photooxidation removed 1.25% of the DOC pool per day.

The differential equation defining the ^{13}C-DOC dynamics is as follows:

$$\frac{d[DO^{13}C]}{dt} = PP^{13} + T_{in}^{13} - R^{13} - L_{fp}^{13}. \quad (1)$$

The input of primary production (PP^{13}) is equal to

$$PP^{13} = PP \times propalgal \quad (2)$$

where PP is the total input of DOC from primary production, and propalgal is the proportion of algal DOC that is ^{13}C based on carbon isotope signatures. Respiration, R, is

$$R^{13} = R \times propdoc \quad (3)$$

the total bacterial respiration (R), which is multiplied by the proportion of the DOC pool that is ^{13}C (propdoc). L^{13}_{fp}, the daily loss of ^{13}C to flushing and photo-oxidation is

$$L_{fp}^{13} = 0.0125 \times [DO^{13}C]. \quad (4)$$

T^{13}_{in}, the input of terrestrial material, is determined as the difference between all losses and total algal input, such that

$$T_{in}^{13} = (R + L_{fp} - PP) \times propterr, \quad (5)$$

where the loss of total DOC to flushing and photo-oxidation (L_{fp}) is,

$$L_{fp} = 0.0125 \times [DOC], \quad (6)$$

and propterr is the proportion of total terrestrial DOC that is ^{13}C, based on the isotopic value assumed for terrestrial material. A small, albeit potentially important isotopic fractionation that occurs with photo-oxidation (Opsahl and Zepp 2001; Osburn et al. 2001) was not included in the model because of uncertainty in the fractionation over longer time periods (Opsahl and Zepp 2001). In a marine system, little overall fractionation was observed for the general degradation of DOC (Fry et al. 1998).

To calculate the proportion of ^{13}C in the above equations, the ratio (r) of ^{13}C to ^{12}C is determined by rearranging the standard equation used for del notation:

$$r = 0.0112372 \times (1 + (\delta^{13}C \times 1000)). \quad (7)$$

The proportion of ^{13}C is then $r/(1+r)$.

Observed changes in the algal isotope signature due to the isotope addition created the dynamics in the model. For the 2001 experiments, the algal isotope signature was calculated from δ^{13}C-CO_2 and a photosynthetic isotopic fractionation of –11.5‰ and−11.4‰ for Paul Lake and Peter Lake, respectively (Pace et al. 2004). Similarly in Tuesday Lake a photosynthetic fractionation factor of−8.5‰ was applied (Bade et al. 2006). In Peter Lake 2002, δ^{13}C-POC was used for the algal isotope signature, because under nutrient enrichment the POC was essentially all algal material (Carpenter et al. 2005; Bade et al. 2006). Algal isotope signatures were linearly interpolated to give daily inputs values. Terrestrial DOC was assumed to have a signature of−28‰ (Lajtha and Michener 1994). The $DO^{13}C$ signature was set to the initial observed value and the parameters (PP, T_{in}, and R) were fitted simultaneously to the remaining δ^{13}C-DOC data using the differential equation above (Equation (1)). A least squares minimization routine in Matlab 6.5 was used for parameter estimation. Parameter uncertainty was estimated by bootstrapping model residuals (Efron and Tibshirani 1993).

Comparative study

Isotope samples of DOC and particulate organic carbon (POC) were collected from 32 lakes in the Northern Highland Lake District in northern Wisconsin and the Upper Peninsula of Michigan during the summer of 2000. The selection of the lakes was designed so that a broad range of total

phosphorus and DOC concentrations were represented, and so that these two variables would be roughly orthogonal for statistical purposes. The details of isotope sample collection are the same as above. All other limnological methods in the comparative study were described previously (Hanson et al. 2003; Bade 2004; Bade et al. 2004), and are similar to the isotope addition experiments. We made no attempt to calculate the relative contribution of algal and terrestrial DOC using isotope mixing models because of uncertainty in the algal isotope signature. Although δ^{13}C-POC was measured in all these lakes, it is not an accurate estimate of the algal end-member because of contribution of terrestrial detritus and other material (Bade et al. 2006).

Results

Isotope addition experiment

The four ^{13}C isotope addition experiments exhibited differences in the concentration and patterns of DOC and Chl. *a* (Table 1 and Figure 1). Tuesday Lake (2002) had the highest DOC concentration and water color, while Chl. *a* concentrations were notably high in Peter Lake (2002) due to the nutrient addition (Table 1). Peter Lake (2002) also had the highest level of GPP and Tuesday Lake had the highest levels of R (Table 1). The δ^{13}C-DOC changed in each lake as a result of the addition of inorganic ^{13}C, but the magnitude of the response was unique in each lake (Figure 2). The increase in δ^{13}C-DOC was least in Tuesday Lake (+1.5‰) and greatest in Peter Lake 2002 (+9.5‰). In 2001, the responses in Peter and Paul lakes (+3‰ and +5‰, respectively) were intermediate to those observed in 2002.

Model-predicted δ^{13}C-DOC compared well with observations in all lakes (Figure 2). The model simulation indicated that the contribution of algal DOC varied among lakes. The model estimate of the input of DOC from primary production (PP) was greatest in Peter Lake (2002) and least in Tuesday Lake (Table 2). Terrestrial inputs of DOC (T_{in}) were fairly similar in all lakes except Tuesday Lake, which had nearly double the amount of terrestrial input compared with the other lakes. Loss of DOC to respiration (R) was highest in Tuesday Lake, and increased slightly in Peter Lake (2002). Losses of DOC to photo-oxidation and flushing (L_{fp}) were nearly equal to respiration in Peter Lake both years. In Tuesday and Paul lakes, R exceeded L_{fp}. The sum of all the daily losses of DOC was approximately 2.7% of the total DOC pool in all lakes. Based on *PP*, between 5 and 13% of measured GPP accumulated as DOC in these lakes (Table 2). The percentage of algal contribution to the total DOC pool ranged from 5% in Tuesday Lake to 40% in Peter Lake (2002) (Table 2).

The percentage of algal DOC was related to the ratio of color:GPP, such that as GPP decreased or color increased the percentage of algal DOC decreased (Figure 3). Since the linear equation would result in negative algal contribution above a color:GPP ratio of about 0.16, some other mathematical expression seems more likely for this relationship (e.g., an exponential equation). A similar relationship was also evident using Chl. *a* instead of GPP. The exponential equation fit to the color:Chl. *a* data is (R^2=0.83):

$$\%\text{algal DOC} = 56.36 \times \exp(-3.73 \times [\text{color:GPP}]). \quad (8)$$

Table 1 Average summer limnological and metabolic conditions of the experimental lakes

Lake	Year	Chl. *a* (μg l^{-1})	DOC (mg l^{-1})	Color (a_{440}; m^{-1})	GPP	R (mmols O_2 m^{-3} d^{-1})	Bottle *R*
Paul	2001	4.2 (1.3)	3.7 (0.4)	1.5 (0.2)	20.5 (9.7)	23.7 (9.2)	6.2 (3.1)
Peter	2001	3.6 (1.7)	4.5 (0.2)	1.3 (0.1)	12.3 (8.1)	12.5 (9.5)	6.1 (1.4)
Peter	2002	42.1 (30.6)	5.8 (0.8)	1.7 (0.2)	44.2 (25.4)	22.6 (18.1)	21.2 (6.8)
Tuesday	2002	6.8 (3.2)	8.4 (1.1)	3.5 (0.3)	24.0 (13.0)	24.2 (12.2)	18.3 (11.7)

Standard deviations in parentheses

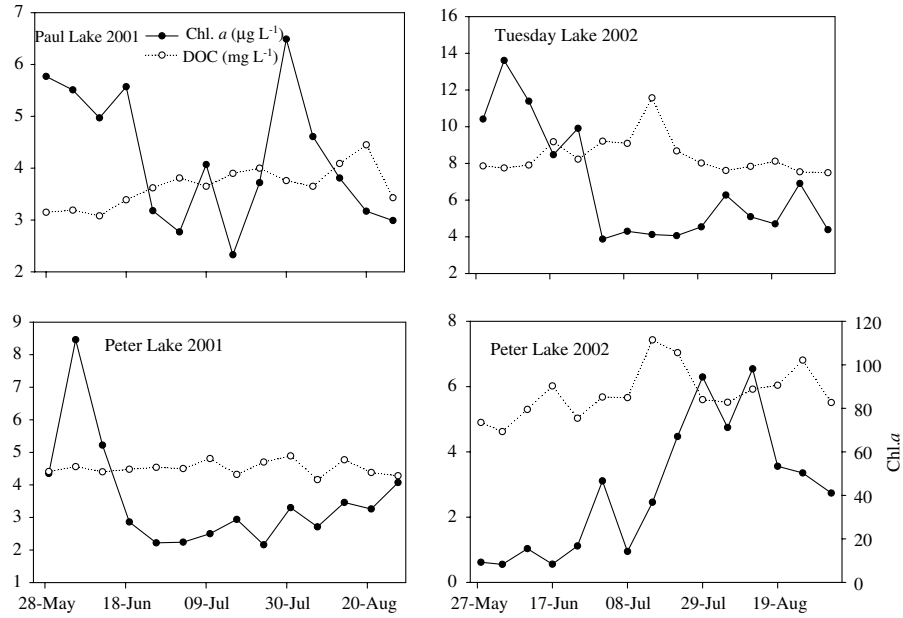

Fig. 1 DOC (mg C l^{-1}) and Chl. *a* (µg l^{-1}) concentrations for the experimental lakes

The spectroscopic and elemental analyses of dissolved organic matter in the four lakes corroborated the results of the modeling. Lower specific absorbance (SUVA-254) and C:N ratio, and higher fluorescence index generally indicates an increasingly microbial (non-terrestrial) component of DOC (Hood et al. 2003; McKnight et al. 2003). Comparing SUVA-254 for whole-water samples, Tuesday Lake had greater values than Peter Lake, as was the case for the fulvic acid fraction (Table 3). The C:N ratio of the fulvic acid fraction of the DOC was also greater in Tuesday Lake than in Peter Lake. Finally, the fluorescence index was higher in Peter Lake.

Comparative study

The δ^{13}C-DOC in lakes of the Northern Highland Lake District ranged from –22.9‰ to –29.3‰. For lakes with high color (>5 a_{440} m^{-1}), the values of δ^{13}C-DOC were very near the terrestrial carbon isotope signature with very little variation about the mean (-27.0‰±0.4‰ mean±1SD), suggesting a possible dominance of terrestrially derived material. Lakes with color <5 a_{440} m^{-1} also had a similar mean (–26.7‰±1.3‰), but the variation was higher, suggestive of multiple sources of DOC. There was no discernable pattern between δ^{13}C-DOC and Chl. *a* (Bade 2004; data not shown). Although δ^{13}C-POC may not always accurately reflect the signature of the algal end-member, this material can provide an indication of algal signature relative to the terrestrial end member. In the comparative study, δ^{13}C-POC ranged from –35.1‰ to–22.1‰. Using the color and Chl. *a* data, we estimated the percentage of algal DOC based on Equation (8). Isotope signatures were then plotted as a function of the percentage of algal DOC. Below about 25% algal DOC, the signatures of DOC were near the value expected for terrestrial material (–27‰), while the signatures of POC were more negative (Figure 4). As would be expected, the δ^{13}C-DOC was not influenced by the more depleted algal carbon in those lakes that presumably have a high loading of terrestrial DOC. Above 30% algal DOC, there was a stronger correlation between δ^{13}C-POC and δ^{13}C-DOC indicating the increased presence of algal carbon in the DOC pool. This study of natural isotope abundances therefore qualitatively corroborated the relationship observed

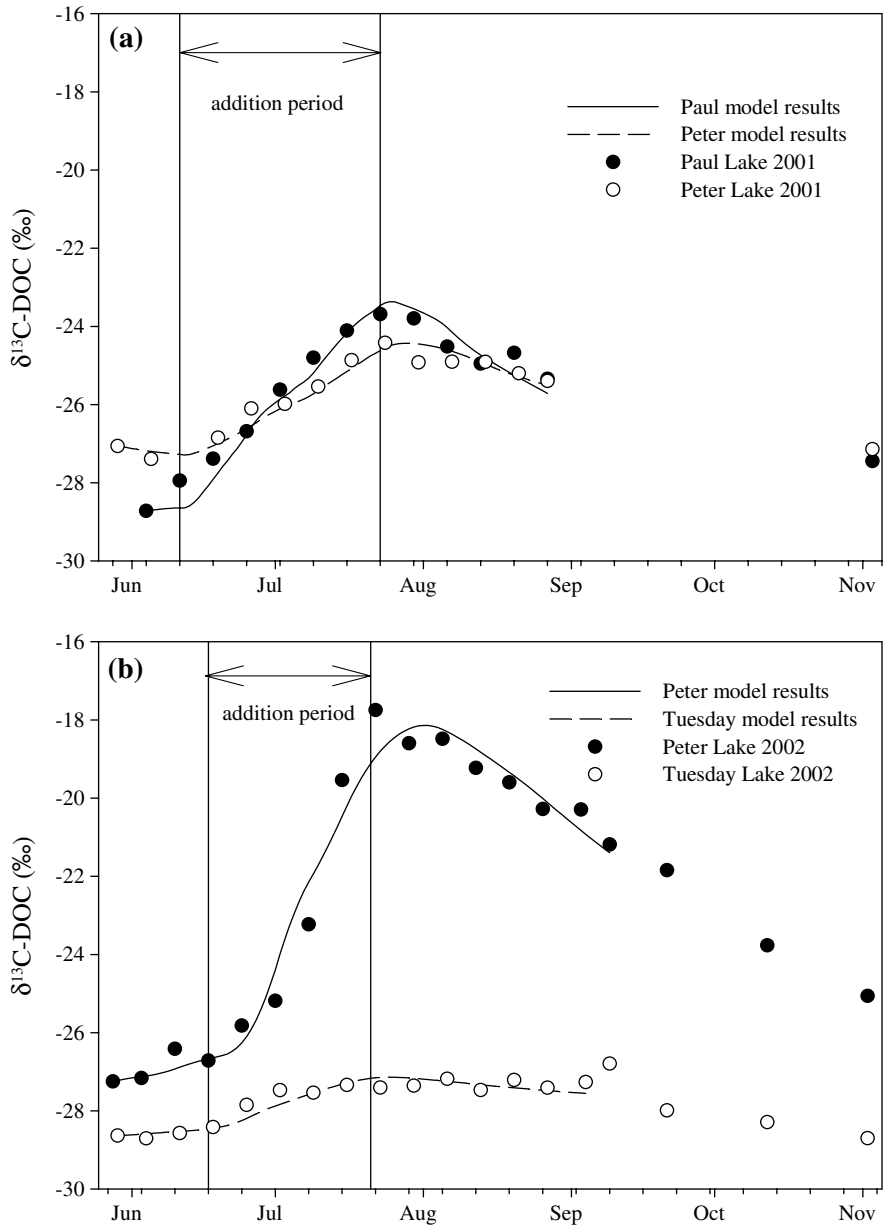

Fig. 2 δ^{13}C-DOC trends observed during the isotope addition experiments and model predictions in (a) 2001 and (b) 2002. Correlation coefficients of the model and observations are: Paul ($r = 0.98$, $p < 0.01$, $n = 13$), Peter 2001 ($r = 0.97$, $p < 0.01$, $n = 13$), Tuesday ($r = 0.94$, $p < 0.01$, $n = 15$), Peter 2002 ($r = 0.99$, $p < 0.01$, $n = 16$). The model predictions do not span the entire time period of δ^{13}C-DOC measurements presented because model inputs of algal δ^{13}C were unavailable later in the season (i.e. October and November data were not modeled)

between color:chl. *a* and the percentage of algal DOC.

Discussion

The addition of inorganic ^{13}C, as a tracer, provided a means to quantitatively determine the contribution of algal and terrestrial sources to the DOC pool in four lakes. This study is one of the few attempts to quantify both terrestrial and algal contributions to DOC, and subsequent losses, in lakes where one source is not obviously dominant. The addition caused large changes in δ^{13}C-DIC and caused phytoplankton to become distinctly labeled. Pace et al. (2004) and Bade et al. (2006) describe the fractionation of tracer from inorganic-C into algal-C for these experiments. Some of this labeled primary production was released as DOC. Although some DOC was

Table 2 Fluxes estimated by the models (mmol C m^{-3} d^{-1})

Lake	Year	PP	T_{in}	R	L_{fp}	% algal DOC	% GPP
Paul	2001	2.2 (0.2)	7.6 (1.0)	6.0 (1.1)	3.8	22.1 (1.4)	10.5
Peter	2001	1.6 (0.2)	7.9 (1.2)	4.8 (1.4)	4.7	16.9 (1.0)	13.1
Peter	2002	5.3 (0.4)	7.8 (1.0)	7.1 (1.3)	6.0	40.6 (1.8)	12.1
Tuesday	2002	1.1 (0.2)	18.1 (4.7)	10.4 (4.8)	8.8	5.8 (1.4)	4.6

PP is the DOC from primary production, T_{in} is the DOC of terrestrial origin calculated by mass balance ($T_{in} = R+L_{fp}–PP$), R is respiration, and L_{fp} is the loss of DOC from flushing and photo-oxidation. The percentage of algal DOC is based on inputs (% algal DOC=PP/(PP+T_{in})), and % GPP is the percentage of measured GPP that becomes DOC (% GPP=PP/GPP). Standard deviations, in parentheses, were estimated by bootstrapping

utilized by bacteria (Kritzberg et al. 2004), not all of it was immediately consumed, and the DOC pool became labeled with ^{13}C. Because of the dynamic created in the experiments, steady-state mixing models were inappropriate to calculate the contribution of algal and terrestrial DOC. Therefore, a ^{13}C-dynamic model was constructed to estimate the relative contribution of DOC from primary production and terrestrial loading. From the estimates of the model parameters we determined the percentage of DOC that was autochthonous. Carpenter et al. (2005) present three models that calculate the amount of allochthonous and autochthonous carbon in many other pools (e.g., POC, zooplankton, fish, etc.) within the lakes, and they briefly discuss DOC. This paper provides a more detailed description of the DOC isotope results using a model that is less complicated but otherwise similar to the 12-box, dual isotope flow model of Carpenter et al. (2005). Conclusions from all the models are similar.

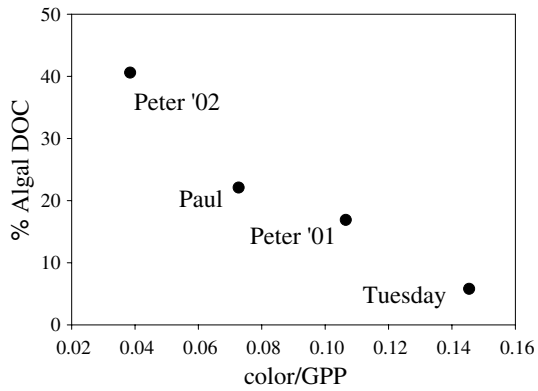

Fig. 3 Percentage of autochthonous DOC as a function of the ratio of color (a_{440}; m^{-1}) to GPP (mmols O_2 m^{-3} d^{-1}). A linear equation fit to the data is: % algal DOC = –308.12 × [color:GPP]+49.32; $R^2 = 0.94$. An exponential equation fit to the data is: % algal DOC = 83.04 × exp(–17.33 × [color:GPP]); $R^2 = 0.95$.

Theoretically, for a given loading of terrestrial DOC and a fixed percentage of GPP being released as DOC, increased productivity should lead to an increased proportion of autochthonous DOC. This trend was observed in an earlier whole-lake ^{14}C addition where increased productivity also increased the ^{14}C activity of the DOC pool (Hesslein et al. 1980; Bower et al. 1987; Schindler et al. 1992). Analogously, for a fixed rate of GPP, increased terrestrial loading should lead to a decreased proportion of autochthonous DOC. Since color is generally considered an indication of the terrestrial loading of DOC (Rasmussen et al. 1989), we plotted our results against the ratio of color:GPP (Figure 3). DOC of algal origin has little color, compared to the colored humic substances of terrestrial DOC (Meili 1992). Although sample size is small, the percentage of DOC from primary production decreased as color:GPP increased.

The spectroscopic and elemental characteristics of dissolved organic matter that may be indicative of terrestrial vs. aquatic microbial sources can be examined against the quantitative results of the isotope addition. For Peter and Tuesday lakes, the characteristics of specific absorbance, fluorescence index and C:N ratios suggest a higher contribution of algal material in Peter Lake than Tuesday Lake, substantiating conclusions based on the isotope addition. There are few other examples where the contribution of terrestrial and algal DOC has been estimated and compared against spectroscopic and elemental measurements, as was done in our experiments.

Table 3 Optical and chemical properties of the fulvic acid and whole-water fraction of dissolved organic matter in Peter and Tuesday Lake from 23 and 24 July 2002

Lake	Fraction	SUVA 254 (l mol^{-1} cm^{-1})	Fluorescence index	C:N (molar)
Peter	Fulvic acid	428	1.33	47
	Whole water	118	1.40	
Tuesday	Fulvic acid	486	1.21	66
	Whole water	181	1.31	

SUVA is the specific ultraviolet absorbance measured at 254 nm

Because the model parameter estimates represent ecosystem rates, we compared them with observed measurements in the experimental lakes and with estimates from other studies to evaluate reliability of the model estimates. The *R* term in the model matches closely with respiration rates measured by dark bottle incubations except in Tuesday Lake and Peter Lake (2002) (Tables 1, 2). The model values are generally lower than dark bottle respiration rates. In the model, *R* represents bacterial respiration only, whereas the dark bottle measurements also include respiration of all plankton. The large discrepancy in Peter Lake (2002) is due to the increased algal biomass and associated higher autotrophic respiration under nutrient enrichment (Pace and Cole 2000). We cannot explain the discrepancy in Tuesday Lake. Estimates of *R* from continuous oxygen measurements by *in situ* sondes should more closely represent whole-ecosystem *R*, and are much greater than the modeled *R*. The sonde estimates, however, include benthic respiration while respiration of water column DOC is mainly a pelagic process. Thus, model *R* is lower than bottle and sonde measurements of respiration consistent with the expectation that bacterial respiration is lower than the respiration rates measured by these two methods.

Direct measurements of photo-oxidation were not made in these lakes. For several Swedish lakes with varying levels of color, Granéli et al. (1996) concluded that surface rates of planktonic *R* and photo-oxidation were similar. Ignoring the small loss to flushing, the model estimates of *R* and our *a priori* estimate of photo-oxidation are in good agreement with Granéli et al. (1996). However in the study by Granéli et al. (1996), if rates were integrated over depth, *R* dominated over photo-oxidation. Therefore, we may have overestimated photo-oxidation, by assuming it

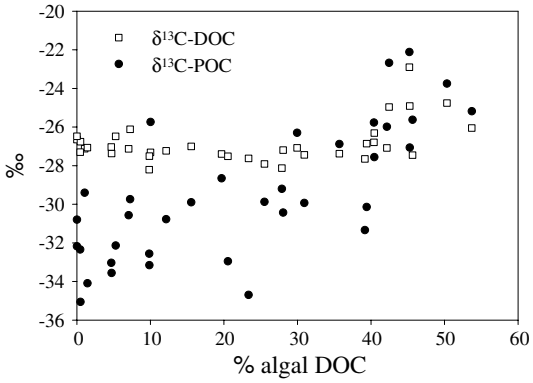

Fig. 4 Using the exponential equation in Figure 3, values of δ^{13}C-DOC and δ^{13}C-POC were plotted against the predicted algal DOC percentage for each lake in the comparative study. Four lakes from the study of 32 lakes were sample twice; therefore, 36 data points are present in this figure

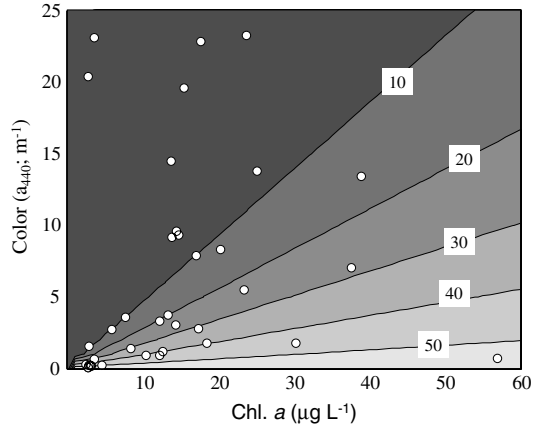

Fig. 5 Contour plot of the percentage of algal DOC as a function of Chl. *a* and color. The percentage of algal DOC is based on Equation (8). The 32 lakes from the comparative study are plotted for illustration of representative lakes

occurs at the same rate throughout the mixed layer instead of declining with depth. In the model, the estimate of R varies inversely with the photo-oxidation parameter, a condition imposed by the steady-state nature of the total DOC pool in the model. Therefore, if photo-oxidation were actually lower, bacterial respiration estimates would be correspondingly higher. Since we assumed that this process does not fractionate, there would be no change in the model prediction of δ^{13}C-DOC due to inaccuracies in the assumed photo-oxidation rate. The same case could be made for inaccuracies in the flushing estimate.

The percentage of GPP that is released as DOC varied in the model from about 5–13% (Table 2). This yield is similar to results from the meta-analysis conducted by Baines and Pace (1991), who found an average algal release near 13% of total net primary productivity.

The estimates of terrestrial inputs also appear qualitatively plausible. Estimates for Peter and Paul lakes are similar, which might be expected because they are situated close together and surrounded by similar topography and vegetation. These lakes were once a single lake before being separated by an earthen dike (Johnson and Hasler 1954). The estimate of terrestrial inputs in Peter Lake also remained fairly constant between the 2 years, despite the drastic alteration of algal contributions. Color, an indicator of terrestrial loading, in Peter and Paul lakes are also similar. In contrast, the terrestrial loading estimate in Tuesday Lake was higher consistent with higher color of this lake (Tables 1, 2).

One weakness of our model is the assumption that there is no difference in the respiration of algal and terrestrial DOC. Increasing the model complexity to incorporate these differences would have at least doubled the number of fitted parameters, and increased the uncertainty given the limited number of data points. The good fits of the model for each lake and the consistency of model parameters with measured values suggest that the model captures the key features of the problem and additional complexity may not add insight. The model implies that some proportion of algal and terrestrial DOC must be similarly bioavailable. This hypothesis is amenable to experimental tests.

Based on bacterial carbon isotope results, our present estimates of algal DOC release to the total DOC pool are likely conservative. Kritzberg et al. (2004) found that during the ^{13}C-labeling experiments in 2001 bacteria were more labeled with ^{13}C than the DOC pool, suggesting a preferential uptake of algal carbon. If algal carbon is respired by bacteria in a similar proportion as its incorporation into biomass, then a some amount of algal DOC may have been released, consumed by bacteria, and not accounted for in our model. This unaccounted for DOC could represent a small pool of highly labile algal DOC that turns over very quickly. Conceptually our model may not account for this fast pool but instead tracks a larger, more slowly degrading pool of algal DOC.

Qualitatively, the increase of δ^{13}C-DOC caused by the addition suggests that the accumulation of autochthonous DOC was significant. In other words, the idea that the algal DOC pool is primarily characterized by a small pool size and fast turnover may be incorrect. Similarly, the loss rate of autochthonous DOC could not exceed inputs or no increase in δ^{13}C-DOC would be detected. Although there was some variability in the δ^{13}C of algae during the experiment, the fact that δ^{13}C-DOC did not appear to reach an equilibrium value during the experiments leads to the conclusion that the addition of tracer from algae to the DOC pool exceeded losses of tracer from the DOC pool. This could be explained by the addition of algal carbon that is, or becomes more recalcitrant, accumulating over time (Fry et al. 1996; Benner and Biddanda 1998). Cole et al. (1984) also concluded that algal DOC is not all immediately respired and some proportion accumulates over time. The slow decrease in δ^{13}C-DOC after the addition ended (especially noticeable in Peter Lake 2002, Figure 2b) also suggests that some DOC from primary production is slow to degrade as found by Schindler et al. (1992).

The presence of algal and terrestrial carbon in the DOC pool was compared in 32 lakes. Although two-source mixing models could not be applied due to uncertainty in the algal end-member, the natural abundance isotopes still provided valuable qualitative information. The

differences in isotope signature between δ^{13}C-POC and δ^{13}C-DOC validated the prediction of low algal DOC influence in lakes with a high color:Chl *a* ratio. In contrast, those lakes that were predicted to have a larger proportion of algal DOC because of a low color:Chl *a* ratio had δ^{13}C-POC and δ^{13}C-DOC that were much more similar.

Few studies have examined δ^{13}C-DOC comparatively. The δ^{13}C-DOC and δ^{13}C-POC values from 28 lakes located in Sweden and Finland (Jones et al. 1999; Kritzberg 2000, Karlsson et al. 2003) were similar to those we observed (Bade 2004). Most δ^{13}C-DOC values were near the terrestrial signature, with some values that were more enriched in ^{13}C. Jones et al. (1999) also demonstrate that lakes with low color had more variability in δ^{13}C-DOC than lakes with higher color, and those lakes with high color had δ^{13}C-DOC near the terrestrial signature.

Taking the results from the experimental isotope addition (Figure 3), which appear to be substantiated by the comparative study (Figure 4), we can develop a general model for DOC sources. To do so, we plotted the lakes from the comparative study in bivariate space of Chl. *a* and color against the backdrop of the percentage of algal DOC predicted based on the color:Chl. *a* ratio (Figure 5). This plot indicates lakes with Chl. *a* concentrations less than 5 μg l^{-1} have DOC that is mostly terrestrial in origin (<5–10% algal DOC). In contrast, those lakes with color values <1 m^{-1} have a significant contribution from algal DOC. A large portion of the overall space is occupied by lakes that have an algal contribution of less than 10%, potentially corroborating the paradigm that many lakes are dominated by terrestrial DOC (Wetzel 2001). Additionally, the oligotrophic lakes (low Chl. *a* and color) occupy a space where small changes in the predictor variables drastically alters the conclusion regarding the percentage of algal DOC. Our results only cover the range of algal contribution from 5 to 40%, and further exploration of the relation of color:Chl. *a* to algal contribution would be beneficial.

In conclusion, several studies indicate the dominance of either terrestrial (e.g., Gorham et al. 1983; Rasmussen et al. 1989; Dillon and Molot 1997) or algal (e.g., Likens 1985; McKnight et al. 1994; McKnight et al. 1997) DOC in lakes. Our four whole-lake DI^{13}C addition experiments clearly show the dual sources of DOC to lake ecosystems. Chemical and spectroscopic characterization of the dissolved organic matter corroborated the ^{13}C labeling results. Our comparative study of DOC natural abundance isotopes also showed the possibility of varying importance of algal and terrestrial material. Clearly, both sources of DOC can be significant. Further studies using tracers, detailed budgets, or spectroscopic/elemental analysis will prove useful for understanding how the percentage of autochthonous DOC varies with levels of GPP and terrestrial loading of organic carbon. Future studies should also examine the possibility that some algal and terrestrial DOC may be similarly bioavailable, and consider how this could influence the movement of carbon through the microbial pathways in lakes that vary in productivity and terrestrial carbon loading (e.g. Kritzberg et al. 2005).

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