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The dual influences of dissolved organic carbon on hypolimnetic metabolism: organic substrate and photosynthetic reduction

JEFFREY N. HOUSER[1,3,*], DARREN L. BADE[1], JONATHAN J. COLE[2] and MICHAEL L. PACE[2]

*[1]Center for Limnology, University of Wisconsin-Madison, 680 N. Park Street, Madison, WI 53706, USA; [2]Institute of Ecosystem Studies, Box AB Route 44A, Millbrook, New York 12545, USA; [3]Current address: Environmental Sciences Division, Oak Ridge National Laboratory, Building 1505, P.O. Box 2008, Oak Ridge, TN 37831-6036, USA; *Author for correspondence (e-mail: houserjn@ornl.gov; phone: 865-574-7846; fax: 865-576-3989)*

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Abstract. We investigated the effect of dissolved organic carbon (DOC) on hypolimnetic metabolism (accumulation of dissolved inorganic carbon (DIC) and methane (CH_4)) in 21 lakes across a gradient of DOC concentrations (308 to 1540 μmol C L^{-1}). The highly colored nature of the DOC in these lakes suggests it is mostly of terrestrial origin. Hypolimnetic methane accumulation was positively correlated with epilimnetic DOC concentration (Spearman rank correlation = 0.67; $p < 0.01$), an indicator of allochthonous DOC inputs, but not with photic zone chlorophyll *a* concentration (Spearman rank correlation = 0.30; $p = 0.22$). Hypolimnetic DOC concentrations declined in 19 of 21 lakes during the stratified period at rates that ranged from 0.06 to 53.9 mmol m^{-2} d^{-1}. The hypolimnetic accumulation of DIC + CH_4 was positively correlated with, and, in most cases of comparable magnitude to, this DOC decline suggesting that DOC was an important substrate for hypolimnetic metabolism. The percentage of surface irradiance reaching the thermocline was lower in high DOC lakes ($\sim$0.3%) than in low DOC lakes ($\sim$6%), reducing hypolimnetic photosynthesis (as measured by the depth and magnitude of the deep dissolved oxygen maxima) in the high DOC lakes. In June, the hypolimnia of lakes with < 400 μmol L^{-1} DOC had high concentrations of dissolved oxygen and no CH_4, while the hypolimnia of lakes with DOC > 800 μmol L^{-1} were completely anoxic and often had high CH_4 concentrations. Thus, DOC affects hypolimnetic metabolism via multiple pathways: DOC was significant in supporting hypolimnetic metabolism; and at high concentrations depressed photosynthesis (and therefore oxygen production and DIC consumption) in the hypolimnion.

Introduction

The cycling of energy, carbon and nutrients in ecosystems is dependent on the decomposition of organic matter. In lake hypolimnia, decomposition is a particularly dominant process, and strongly influences the chemical constituents therein (Hesslein 1980; Schindler 1985). The microbial respiration of organic matter consumes electron acceptors (e.g., O_2, NO_3^-, SO_4^{2-}), produces CO_2 and CH_4, and re-

generates dissolved nutrients (e.g., soluble reactive phosphorus (SRP) and NH_4^+) at rates that are determined, in part, by the rate of organic matter input to the hypolimnion (Cornett and Rigler 1979; Kelly and Chenowyth 1981; Charlton 1980). When lakes are vertically stratified, the transport of metabolic end products to the epilimnion from the hypolimnion, and the downward diffusion of oxygen and other electron acceptors into the hypolimnion is small (Bedard and Knowles 1991; Cole and Pace 1998). Thus, hypolimnetic concentrations of oxygen and other electron acceptors typically decrease over the course of the stratified season while CO_2, CH_4, and dissolved nutrients accumulate (Bedard and Knowles 1991; Mattson and Likens 1993). These dissolved nutrients are entrained into the epilimnion as the thermocline deepens and mixed to the entire lake during mixis (Soranno 1995; Lathrop et al. 1999). Similarly, the accumulated CO_2 and CH_4 are released to the atmosphere when lakes mix (Rudd and Hamilton 1978; Striegl and Michmerhuizen 1998). Thus, decomposition of organic material in the hypolimnion affects the availability of metabolic end-products (CO_2, CH_4 and dissolved nutrients) to the lake ecosystem and the atmosphere (Schindler 1985).

Nutrient inputs to lakes vary widely (largely due to anthropogenic influences) driving enormous variability in the rates of algal production, and the effects of this variability in algal production on hypolimnetic metabolism have been well studied (e.g., Cornett and Rigler (1979) and Charlton (1980)). Lakes also show a wide range of DOC concentrations (0.5 to 30 mg L^{-1}; 40 to 2500 μmol L^{-1}) (Hessen and Tranvik 1998), yet the role of DOC in hypolimnetic metabolism is poorly known. Two mechanisms through which DOC can affect hypolimnetic metabolism are 1) providing an organic substrate for microbial respiration, and 2) reducing or eliminating the irradiance reaching the hypolimnion. Colored DOC strongly reduces light penetration (Jones 1992; Williamson et al. 1999) and should reduce the irradiance reaching the hypolimnion. The extent of photosynthesis in the upper hypolimnion can affect the accumulation of DIC produced by microbial respiration of organic carbon (Rich 1980) and hypolimnetic oxygen depletion.

DIC is produced from DOC by photo-oxidation (Granéli et al. 1996) and microbial respiration (Hessen 1992). Within the photic zone, planktonic respiration often exceeds planktonic production suggesting a need for the input of allochthonous organic carbon to support planktonic respiration (Salonen et al. 1983; Rask et al. 1986; del Giorgio et al. 1999). Photic zone respiration, in the absence of eutrophication, has been shown to be correlated with DOC concentrations (Pace and Cole 2000). In lakes with high inputs of allochthonous DOC, the ratio of planktonic production to respiration, and the ratio of bacterial production to primary production can be higher than in lakes with low inputs of allochthonous DOC (Tranvik 1989; del Giorgio and Peters 1993). Though it is clear that DOC is metabolized by bacteria in lakes, the significance of DOC for hypolimnetic metabolism is not known.

Metrics related to oxygen consumption such as areal hypolimnetic oxygen demand (AHOD) are often used to discuss hypolimnetic metabolism (e.g., Cornett and Rigler (1979) and Charlton (1980)). However, in lakes where the hypolimnion is anoxic for much of the stratified period, the majority of hypolimnetic metabolism occurs via anaerobic pathways (Kelly et al. 1988; Bedard and Knowles 1991).

In these lakes, oxygen consumption represents only a small fraction of hypolimnetic metabolism and accumulation of the end-products of hypolimnetic metabolism, such as DIC, CH_4, and dissolved nutrients, is an effective measure of metabolism (e.g., Mattson and Likens (1993)).

We measured the hypolimnetic accumulation of metabolic end-products (DIC + CH_4) in 21 lakes covering a wide range of DOC concentrations to evaluate the importance of DOC in hypolimnetic metabolism and to investigate the potential mechanisms through which DOC can affect lake metabolism. Specifically, we asked: 1) Does hypolimnetic metabolism vary systematically along a gradient of DOC concentrations? 2) Is DOC an important substrate for hypolimnetic metabolism? 3) Does light absorbance by DOC affect hypolimnetic metabolism?

Methods

Survey lakes

Seventeen of the lakes were located on, or adjacent to, the University of Notre Dame Environmental Research Center (UNDERC) near Land o' Lakes, Wisconsin, U.S.A. A detailed description of this region and its lakes can be found in Carpenter and Kitchell (1993). Four lakes (Crystal, Big Muskellunge, Sparkling, and Trout) are part of the North Temperate Lakes Long Term Ecological Research Site (NTL-LTER) and are described in detail by Magnuson et al. (1990). These 21 lakes represent a wide range of morphometric, chemical and biological characteristics and were selected to span a gradient of DOC concentrations and water color (Table 1). Three of the UNDERC lakes (Peter, East Long, and West Long lakes) were experimentally fertilized with phosphorus (P) and nitrogen (N) from 1993 to 1997 as part of a set of whole-lake experiments designed to determine the effect of food web structure, nutrient inputs and DOC concentrations on primary production (Carpenter et al. 2001). P fertilization rates ranged from approximately 1 to 6 mg m^{-2} d^{-1} (N:P in the fertilizer exceeded 30 (by atoms) to prevent N limitation).

Limnological sampling

We sampled each lake early (mid-May to mid-June) and late (August) in the 1998 stratified season with approximately two months (54–69 days) between sampling dates. The lakes were sampled at multiple depths over their deepest point. Chlorophyll *a*, dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), sulfate, and color (g_{440} (m^{-1})) were measured in the mixed layer. In addition, DIC, CH_4, and DOC were measured at 4 to 6 evenly spaced depths within the hypolimnion depending on its thickness. For the early summer sampling dates water color was measured at these same depths. In a subset of lakes that were included in the 1998 survey, we obtained epilimnetic DOC concentrations and detailed profiles of light, temperature and dissolved oxygen during the 1999 stratified season.

Table 1. Morphometric and limnological characteristics of the surveyed lakes

Lake	Area (ha)	Max. depth (m)	Mean depth (m)	Early Summer Epilimnion Concentration					
				Chlorophyll *a* (ug L^{-1})	Color (m^{-1})	DOC (umol L^{-1})	SO_4^{-2}	O_2	NO_3^-
Bay-A	59.3	13.5	4.4	12.1	1.31	551.0	56.7	275	0.15
Bay-B	8.0	12.3	4.3	15.2	1.57	471.2	46.6	281	0.17
Bergner	17.8	12.0	3.6	14.6	2.69	707.0	38.2	303	0.19
Big Musky	396.3	21.0	7.6	12.1	0.28	719.0	48.7	263	0.07
Crampton	25.8	15.3	3.9	9.9	0.92	790.7	53.8	300	0.29
Cranberry	1.4	7.3	4.3	4.5	5.57	863.6	20.4	278	0.40
Crystal	36.7	20.0	10.5	6.0	0.16	336.3	44.9	256	0.06
East	2.3	16.0	5.4	10.3	8.80	1061.0	39.2	234	0.93
Ed's Bog	0.1	6.8	5.8	10.7	6.82	1102.5	13.0	138	0.39
Hummingbird	0.8	7.5	3.7	18.5	14.97	1540.6	41.2	266	0.55
Morris	5.9	6.8	2.6	7.9	3.59	1050.2	26.1	309	0.22
Paul	1.7	12.0	3.7	11.9	1.66	613.7	21.7	263	0.32
Peter	2.7	19.0	5.7	4.7	1.13	538.4	25.7	297	0.19
Raspberry	4.6	6.0	3.1	20.1	2.10	614.9	23.4	297	0.19
Roach	45.0	10.0	4.2	13.5	0.41	555.0	57.8	303	0.06
Sparkling	64.0	20.0	11.0	4.6	0.30	346.5	44.6	256	0.07
Tenderfoot	165.2	9.3	5.3	23.0	2.12	614.2	46.1	284	0.17
Trout*	1090.9	35.0	15.1	7.4	0.30	308.0	50.4	275	0.18
Tuesday	0.8	18.0	6.9	8.3	3.06	1249.3	21.5	303	0.17
Ward	2.7	8.3	2.7	8.3	1.80	719.7	26.1	309	0.13
West	5.5	17.0	3.6	20.2	4.95	855.5	42.5	263	0.43

* South basin

DIC and methane concentrations were measured by gas chromatography using a Shimadzu GC-8AIT (TCD detector). DIC concentrations were determined using the gas chromatography method of Stainton (1973). Methane concentrations were determined using a method similar to that of Cole et al. (1994) for measuring partial pressure of CO_2 in water samples. For each sample, a 2.5-liter, glass bottle was filled with water pumped from depth using a peristaltic pump. The bottle was allowed to overflow until the entire volume had been replaced and then was closed by inserting a stopper containing two valves. 60 mL of the lake water was displaced by helium gas which was then equilibrated with the lake water. Two replicate 20 mL samples of the equilibrated headspace gas were drawn into individual syringes while returning an equal volume of water to the glass bottle. The methane concentration of this equilibrated headspace gas was determined by gas chromatography. This procedure concentrated the methane, and allowed us to detect the methane using a TCD detector instead of the more sensitive FID detector which was unavailable to us in the field. The partial pressure of methane was then calculated using the water temperature at extraction, the Bunsen coefficient of methane, and the volumes of the head space and water phases. In studies that have measured both methane accumulation in the water column and methane ebullition, the mass of methane lost via ebullition is generally approximately equal to the methane that accumulates in the water column (Strayer and Tiedje 1978; Mattson and Likens 1993). We assumed that the measured methane accumulation in the water samples represented half of the methane produced and adjusted our measurements of methane accumulation accordingly. The implications of this assumptions are shown in the figures using error bars to represent an upper and lower possible value if ebullition rates were 75% and 25% respectively.

Samples for DOC analysis were filtered through 47 mm GF/F filters under low vacuum (< 200 mm Hg), preserved by reducing sample pH to < 2 with 2 N H_2SO_4 (1% final sample volume) and analyzed using a Shimadzu model 5050 high temperature TOC analyzer. Color was determined spectrophotometrically (absorbance at 440 nm) on unpreserved, filtered (GF/F) samples using a 10 cm cuvette. The absorption values were reported as absorption coefficients, (g_{440} (m^{-1}) = 2.303 × (Absorbance@440 nm)/(pathlength (m)); Kirk (1994)). Chlorophyll *a* was collected on GF/F filters, extracted using methanol, determined fluorometrically, and corrected for pheopigments (Marker et al. 1980). Sulfate samples were preserved with HCl and purged with He to remove sulfides. Samples were analyzed by ion chromatography (Dionex DX-500). Temperature and dissolved oxygen profiles were measured using a YSI temperature/dissolved oxygen meter.

Calculations of potential algal C contribution to hypolimnetic metabolism

For two of the lakes in this study that have not been experimentally enriched with N and P (Tuesday and Paul lakes), detailed data on phytoplankton production were available. We used these data to determine whether inputs of algal C were sufficient to support hypolimnetic metabolism. The potential algal C contribution to hypolimnetic metabolism (C_{hypo}) depends on three factors: the amount of C fixed by

primary production (C_{fixed}), the fraction of that C that is exported to the hypolimnion (export ratio, E_r), and the amount of the exported C that is permanently buried in the sediments (C_{buried}):

$$C_{hypo} = (C_{fixed} \times E_r) - C_{buried}$$

C_{fixed} was measured as primary production (PPR) and chlorophyll *a* concentration. Samples for chlorophyll *a* analysis (described above) were collected at the depths of 100, 50, 25, 10, 5, and 1% surface irradiance and integrated to determine the areal chlorophyll *a* concentrations (mg m^{-2}). PPR (mg C m^{-2} d^{-1}) was measured by in-situ $NaH^{14}CO_3$ incubations at each sampling depth (same depths as for chlorophyll *a*) as described in Carpenter and Kitchell (1993). Summer averages of PPR and chlorophyll *a* were used in the above calculation. For Paul lake, PPR and chlorophyll *a* data from the summer 1998 were used. Because 1998 data were unavailable for Tuesday Lake, 1993 data, the most recent year of detailed measurements, were used.

The export ratio (E_r) for these lakes has not been measured directly, but for most lakes described in the literature export ratios fall between approximately 10 and 50% (Baines and Pace 1994). We used the range 20 to 50% to bracket the potential contribution of primary production to hypolimnetic metabolism because lakes with export between 10 and 20% are generally highly eutrophic. Rates of permanent C burial in the sediments (C_{buried}) were estimated based on ^{210}Pb dated sediment cores from three of the lakes in this study (Peter, Paul, and West Long lakes) (Houser 1998).

Areal hypolimnion accumulation of DIC and methane

The hypolimnion of each lake was defined using its August temperature profile. The depth below the thermocline at which the rate of change of temperature decreased less then 1 degree per 0.5 m was defined as the top of the hypolimnion. Using a single depth defined by the August temperature profiles in this way had the following advantages: 1) The depth was clearly within the zone of CO_2 accumulation in both the spring and the fall, 2) The temperature gradient was steep enough that the diffusion rates through the thermocline should be small relative to the accumulation rates and well described by existing, experimentally determined coefficients of eddy diffusion (Hesslein and Quay 1973; Quay et al. 1980), and 3) Using a fixed depth removed the need to correct for thermocline migration which may introduce unnecessary errors due to uncertainties in the morphological data.

The mass of DIC, CH_4, DOC and dissolved oxygen in the hypolimnion of each lake was calculated as follows. The concentrations of each substance were linearly interpolated between the sampled depths at 0.25 m intervals. The concentration of each substance in each 0.25 m thick stratum was determined as the average of the concentration at the top and bottom of that stratum. The area at depth was interpolated from bathymetric maps to the same 0.25 m intervals as the limnological data. The volume of each 0.25 m thick stratum was determined assuming that each stra-

tum could be represented as a truncated irregular cone (Wetzel and Likens 1991). The mass of each substance in that stratum was determined as the product of the volume of water in the stratum and the average concentration of each substance.

The change in hypolimnetic mass ($\Delta Mass$) was calculated as follows:

$$\Delta Mass = Mass_2 - Mass_1 + D$$

Where $Mass_1$ is the mass contained in the hypolimnion (mmol m^{-2}) at the early sampling date and $Mass_2$ is the mass contained in the hypolimnion at the late sampling date. D is the diffusive flux across from the hypolimnion to the epilimnion. It was calculated using Fick's Law:

$$D = K\frac{\partial C}{\partial z}$$

where K = the coefficient of vertical eddy diffusion and $\frac{\partial C}{\partial z}$ is the vertical gradient of the concentration of the substance of interest (mmol m^{-4}). We used K = 3.6 × 10^{-3} m^2 d^{-1}. This value is the mean of the two experimentally determined values for the thermocline of similar small lakes at the Experimental Lakes Area in Ontario, Canada (actual values: 5 × 10^{-5} cm^2 s^{-1} (or 4.32 × 10^{-4} m^2 d^{-1}) and 8 × 10^{-4} cm^2 s^{-1} (or 6.9 × 10^{-3} m^2 d^{-1})) (Quay et al. 1980), and is very close to the value of 4.0 × 10^{-3} m^2 d^{-1} determined by Hesslein and Quay (1973).

Results

The importance of anaerobic metabolism, including methanogenesis, as a metabolic pathway in the hypolymnia of many of these lakes is illustrated by the amount of ″excess″ DIC accounted for by anaerobic processes. Excess DIC is the concentration of DIC (μmol L^{-1}) at depth in excess of the surface concentration, and is approximately the amount of DIC that had accumulated in a lake's hypolimnion since it last mixed (Caraco et al. 1990). Assuming that the epilimnetic concentrations in early summer (Table 1) approximately represent the water column concentrations during mixis, aerobic metabolism can account for approximately 280 μmol L^{-1} of hypolimnetic DIC accumulation and sulfate reduction can account for approximately 73 μmol L^{-1} (Table 2, Equation 1 and Equation 3). The NO_3^- concentrations of these lakes were low (Table 1) so the contribution of denitrification (Table 2, Equation 2) to DIC production was small. If O_2 and SO_4^{2-} were the dominant electron acceptors, methane would accumulate once excess DIC concentrations reach approximately 350 μmol L^{-1}.

In the surveyed lakes, methane accumulation occurred when the excess DIC concentrations reached between approximately 360 and 430 μmol L^{-1} (Figure 1). The lowest concentrations of excess DIC where methane was detected was 356

Table 2. Microbial redox reactions (adapted from Mattson and Likens (1993) and Hedin et al. (1998), Stumm and Morgan (1996)).

Process	DIC Produced
1) Aerobic	
$CH_2O + O_2 \rightarrow CO_2 + H_2O$	1 mol DIC/mol O_2 consumed
2) Denitrification	
$1.25\ CH_2O + HNO_3 \rightarrow 1.25\ CO_2 + 0.5\ N_2 + 1.75\ H_2O$	1.25 mol DIC/mol NO_3^- consumed
3) Sulfate Reduction	
$2\ CH_2O + SO_4^{2-} + H^+ \rightarrow HS^- + 2H_2O + 2CO_2$	2 mol DIC/mol SO_4^{2-} consumed
4) Methanogenesis	
$CH_3OOH \rightarrow CH_4 + CO_2$	1 mol DIC/mol CH_4 produced

μmol L^{-1} (Paul Lake), 364 μmol L^{-1} (Sparkling Lake) and 380 μmol L^{-1} (Crampton Lake). Methane did not accumulate in other lakes until slightly higher concentrations of excess DIC occurred. There is clearly substantial metabolism in the hypolimnia of these lakes beyond that which can be accounted for by aerobic metabolism. Aerobic metabolism can account for up to $\sim$280 μmol L^{-1} of excess DIC, while concentrations of excess DIC reached $\sim$2800 μmol L^{-1} (Figure 1). Across lakes and depths, once methane accumulation began, methane and DIC accumulated in approximately a 1:1 ratio as would be expected if acetate fermentation is the dominant pathway of methane formation (Whiticar et al. (1986); Table 2, Equation 4).

The variability in the initial concentrations of oxygen and sulfate present in the hypolimnion and the presence of other electron acceptors (e.g., MnO_2, FeOOH), are the likely explanations for variability in the concentration of excess DIC at which methane accumulation began. Fe concentrations were not measured, but accumulations of reduced Fe to concentrations ranging from 40–320 μmol L^{-1} would be sufficient to account for the observed variation in accumulation of DIC prior to methane accumulation. Accumulations of that magnitude are reasonable for these lakes, given that concentrations of total Fe of $\sim$230 μmol L^{-1} have been observed by mid-summer in Paul Lake (Cole, J.J and N. Caraco unpublished data).

Primary production and hypolimnetic metabolism

The prevalence of hypolimnetic anoxia in these lakes suggests that there was a large input of organic C to their hypolimnia. Most of the survey lakes were oligotrophic to mesotrophic (Table 1), and primary production was unlikely to provide sufficient C to account for the observed hypolimnetic metabolism in some of these lakes. We illustrate this with data from Paul and Tuesday lakes. These two lakes are steep sided and therefore have few macrophytes, and benthic algae production on the epilimnetic sediments should not affect hypolimnetic carbon cycling during stratification. In Paul and Tuesday lakes, average summer phytoplankton production was approximately 35 and 29 mmol C m^{-2} d^{-1} respectively. Algal C contributed be-

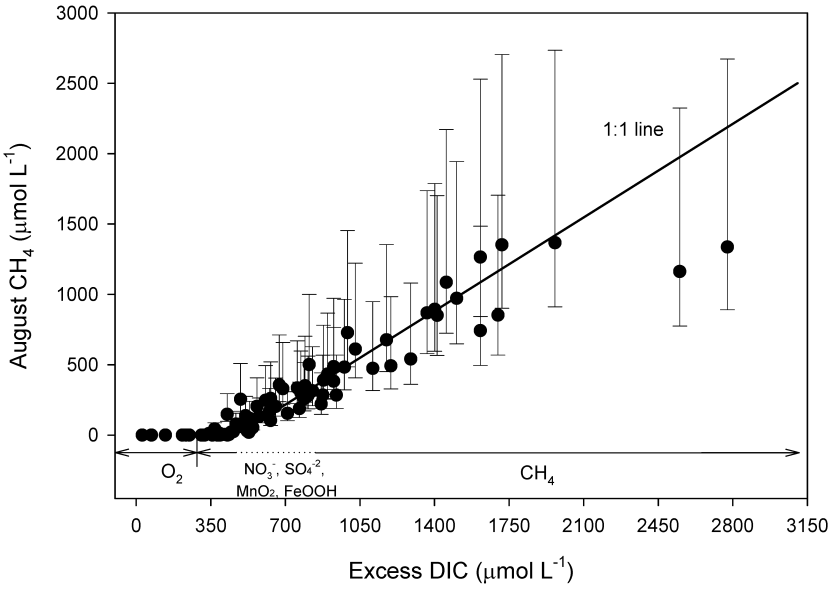

Figure 1. Plot of CH_4 concentration versus excess DIC (see text). There are 77 samples from 21 lakes because each hypolimnion was sampled at multiple depths. The 1:1 line is shown for reference (x-intercept is fit by eye to the best representation of the onset of methane accumulation). The data points represent CH_4 produced assuming 50% of CH_4 was lost via ebullition, upper error bars represent a 75% ebullition loss, lower bars represent 25%.

tween 7 and 17.5 mmol C m^{-2} d^{-1} to the hypolimnion in Paul Lake and between 6 and 17 mmol C m^{-2} d^{-1} for Tuesday lake (Figure 2). Permanent burial in the sediments (based on sediment core data (Houser 1998)) was approximately 4.4 mmol C m^{-2} d^{-1} in these lakes. Thus, the potential contribution of algal production to hypolimnetic metabolism was between 2.6 and 13.1 mmol C m^{-2} d^{-1}, and 1.5 and 10.2 mmol C m^{-2} d^{-1} for Paul and Tuesday lakes respectively (Figure 2). Thus the input of algal produced C may have been sufficient in Paul Lake but was insufficient in Tuesday Lake to account for the accumulation of metabolic end products in the hypolimnion (Figure 2).

DOC as a substrate for hypolimnetic metabolism

The results from Tuesday Lake suggest that sources of organic C other than algal C were important for hypolimnetic metabolism. Allochthonous DOC may have been one of those sources. While DOC in lakes can be from autochthonous or allochthonous sources, most of the DOC in the study lakes is presumed to arise from uplands and wetlands (Christensen et al. 1996; Gergel et al. 1999). The correlation between DOC and water color (g_{440} (m^{-1})) in these lakes ($r = 0.80$; $p < 0.001$; $N = 110$) provides some support for this inference, as light absorbing humic/fulvic DOC pools in lakes generally arise from terrestrial inputs (Wetzel 1983).

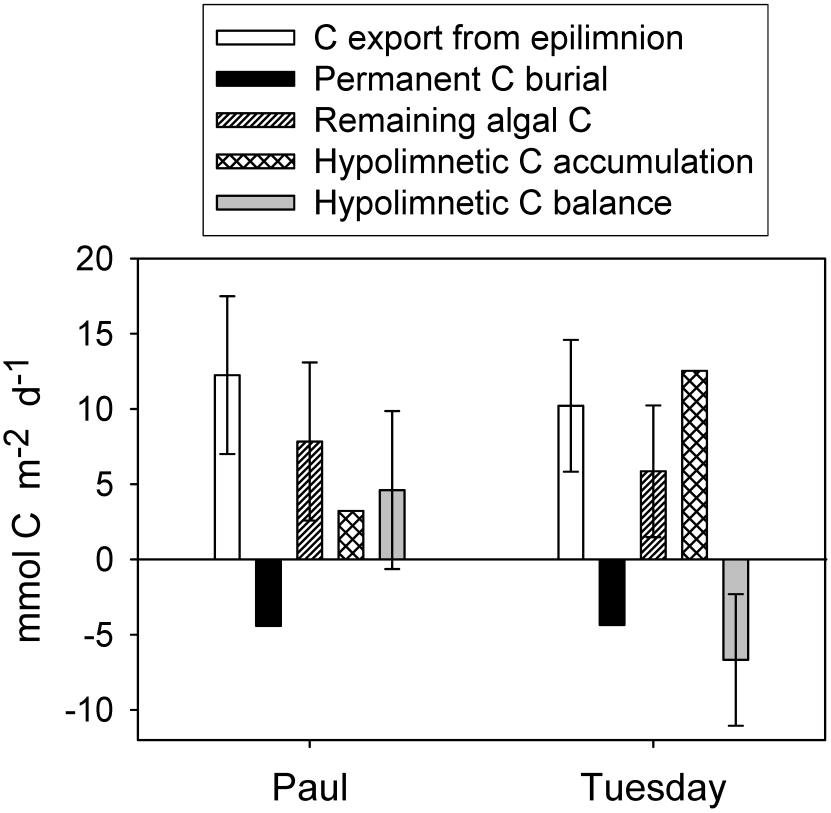

Figure 2. Hypolimnetic carbon budgets for Paul and Tuesday lakes: Open bars are the mean algal C export from the epilimnion (estimated maximum and minimum exports are represented by the upper and lower error bars (see text)). Solid black bars are the C lost to burial in the sediments. Diagonal hatched bars represent the potential contribution of algal C to hypolimnetic metabolism (algal C export less C burial in the sediments; maximum and minimum potential total algal C input are shown as the upper and lower error bars). Cross-hatched bars show hypolimnetic DIC + CH_4 accumulation; and the gray bars are the difference between the algal C inputs and accumulation of DIC + CH_4. A positive difference means there are sufficient algal C inputs to account for hypolimnetic accumulation of DIC + CH_4, a negative difference means there are insufficient algal C inputs to account for hypolimnetic accumulation of DIC + CH_4.

Multiple lines of evidence suggest that allochthonous DOC was an important C source for hypolimnetic metabolism. Methane production was positively correlated with June surface DOC (Figure 3; Spearman rank correlation = 0.67; $p < 0.01$; N = 20; Peter Lake omitted), but uncorrelated with June chlorophyll *a* (Spearman rank correlation = 0.302; $p = 0.22$; N = 20; Peter Lake omitted) suggesting that, in these lakes, DOC had more influence than algal production on lake metabolism.

DOC did decline over the summer in most (19 of 21) lakes, as would be expected if DOC was used as an organic C source for hypolimnetic metabolism (Figure 4). The absolute rates of DOC decline ranged from an accumulation of 4.2

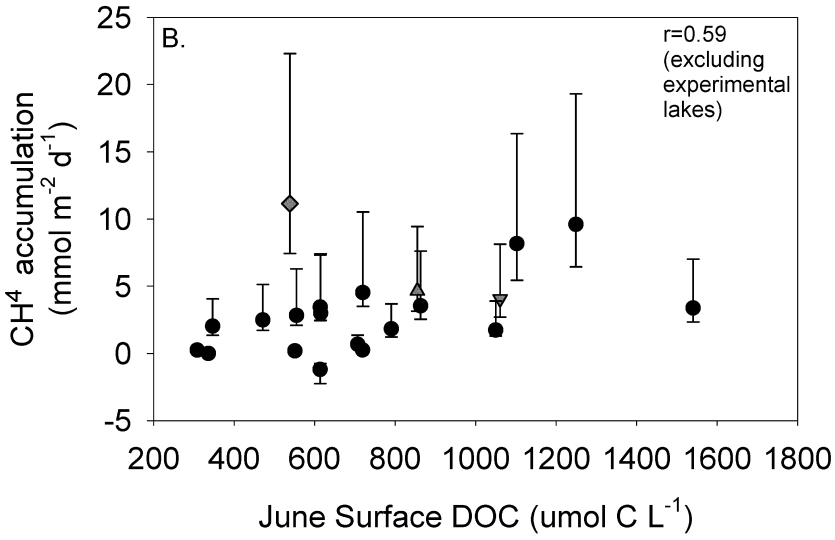

Figure 3. Areal hypolimnetic CH_4 accumulation rate (May–August) versus June surface DOC. The lakes that were experimentally enriched with N and P from 1993–1997 are identified as follows: gray diamond = Peter Lake; gray, upward triangle = West Long Lake; and gray, downward triangle = East Long Lake. Error bars as in Figure 1.

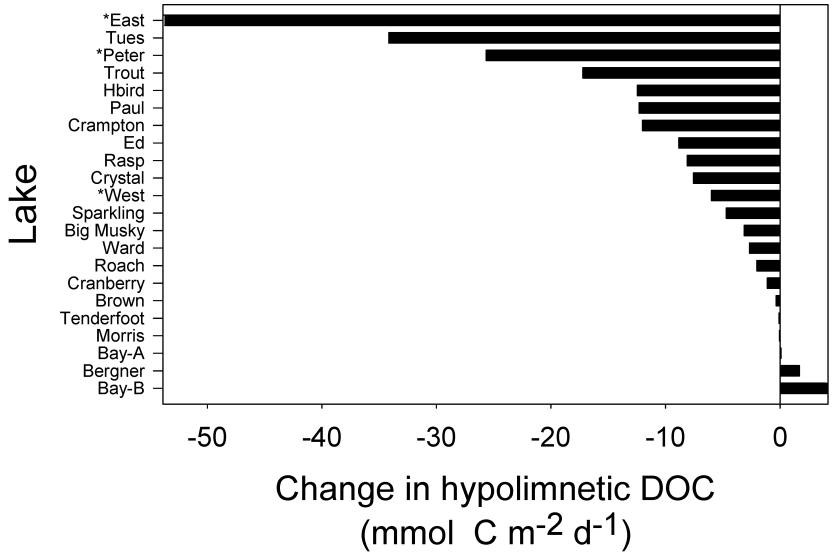

Figure 4. Rate of change in areal hypolimnetic DOC concentrations between June and August. Asterisks denote lakes that were experimentally enriched with N and P from 1993 to 1997.

mmol m^{-2} d^{-1} in Bergner Lake to a depletion of 53.9 mmol m^{-2} d^{-1} in East Long Lake and was approximately proportional to the standing stock of DOC (Spearman rank correlation = − 0.73, N = 21, $p < 0.001$). In the lakes where DOC declined,

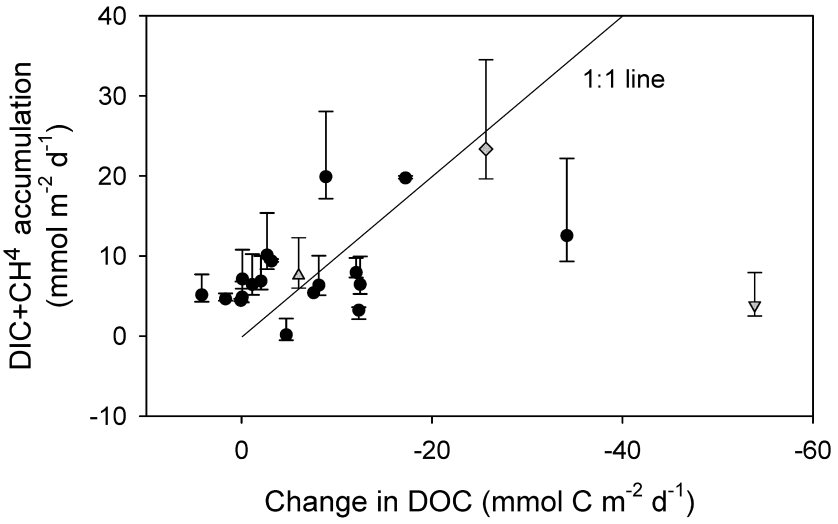

Figure 5. Relationship between areal hypolimnetic metabolism (measured as accumulation of DIC and CH_4) and hypolimnetic DOC decline (Spearman rank correlation = 0.57, N = 20, $p < 0.01$, East Long Lake omitted as an outlier). Each point represents the change in areal hypolimnetic concentration for a lake (21 lakes are shown). Symbols and error bars as in Figure 3.

the proportion of DOC lost per day ranged from 0.01% in Morris Lake to 1% in Raspberry Lake. The average hypolimnetic decline among lakes was 0.49% (+/– 0.30 (SD)) per day. The rate constant for the loss of DOC was not correlated with the concentration of DOC in the lakes (Spearman rank correlation = – 0.17, N = 21, p = 0.45), nor was it correlated with lake area, volume, or with indices of hypolimnetic morphometry. There was a positive correlation between the accumulation of DIC and CH_4 and the decline of DOC (Figure 5; Spearman rank correlation = 0.57; N = 20; $p < 0.01$; East Long Lake was omitted from the analysis as an outlier), and the data roughly clusters around the 1:1 line.

The importance of light

DOC may also influence the hypolimnetic metabolism of lakes by regulating the amount of light penetrating below the thermocline and therefore the amount of primary production occurring in the hypolimnion. Hypolimnetic algal production affects the apparent hypolimnetic metabolism (net change in DIC + CH_4 concentration) by producing oxygen and consuming DIC in the hypolimnion. Light profiles measured in summer 1999 showed that less light reaches the thermocline in lakes with higher DOC concentrations. In lakes with low DOC concentrations, the depth to which 1% of the surface irradiance penetrated was almost twice the thermocline depth. In the lakes with high DOC concentrations, the depth of 1% surface irradiance was substantially shallower than the thermocline (Figure 6). The effects of the differing light climates of these lakes can be seen in the dissolved oxygen (DO)

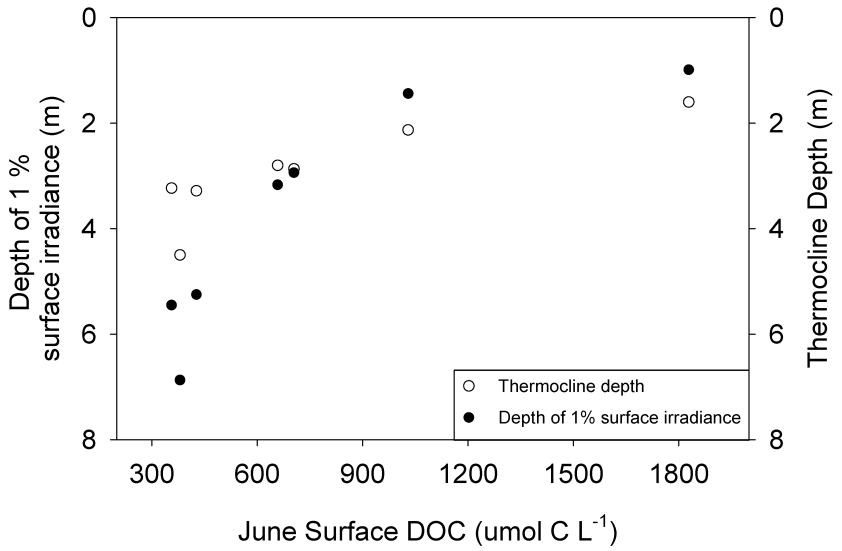

Figure 6. The depth to which 1% of the surface irradiance penetrates and thermocline depth versus June surface DOC concentrations. Open circles represent thermocline depth, closed circles represent depth of 1% light.

profiles of the lakes. In low DOC lakes, the maximum DO concentration often occurred below the thermocline. In high DOC lakes, the maximum DO concentration occurred at the surface. Thus, along the gradient from low DOC lakes to high DOC lakes, the depth and magnitude of the DO peak decreased such that high DOC lake had no deep DO peak (Figure 7).

Cumulative effect of DOC on lake metabolism

There was a clear transition from aerobic metabolism to anaerobic metabolism in the hypolimnia of these lakes along the gradient of DOC concentrations (Figure 8A). Even early in the stratified season, only the lakes with low concentrations of DOC (< 400 μmol L^{-1}) had substantial concentrations of oxygen. Lakes with intermediate concentrations of DOC (600–800 μmol L^{-1}) often had oxygen present in the upper hypolimnion, but showed CH_4 accumulation deeper in the hypolimnion, thus both oxygen and CH_4 were present in their hypolimnia. Lakes with high concentrations of DOC (> 800 μmol L^{-1}) had hypolimnia that were completely anoxic and showed variable, but sometimes quite high, concentrations of CH_4. Peter Lake was enriched with nutrients and quite eutrophic from 1993–1997 (Carpenter et al. 2001); it showed high methane concentrations despite its low DOC concentration. By August, oxygen remained only in the hypolimnia of the lakes with the lowest DOC concentration, and some CH_4 accumulation was seen in most of the lakes (Figure 8B).

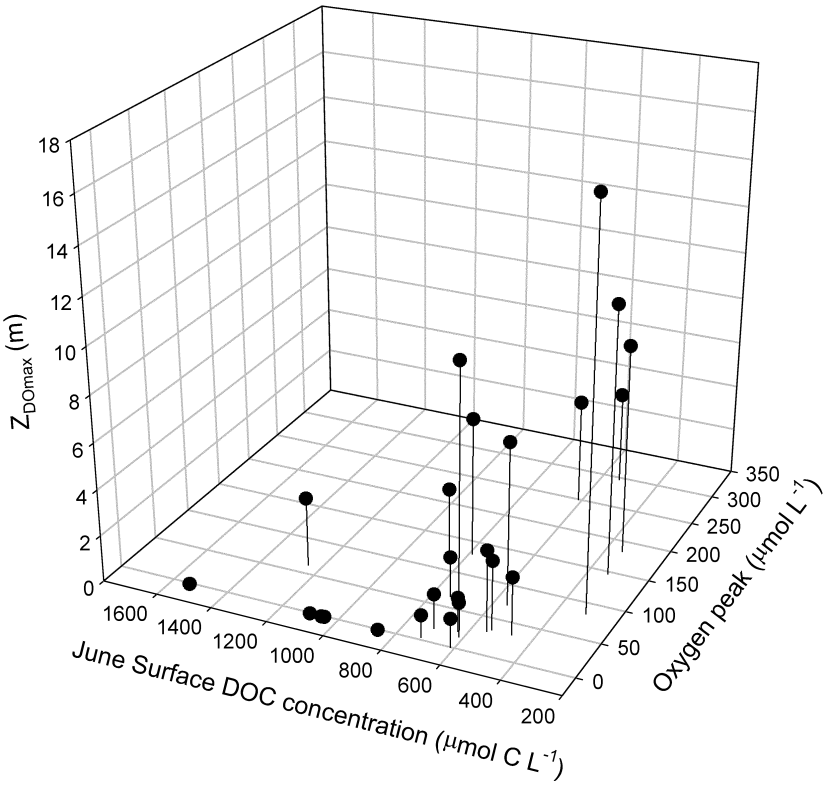

Figure 7. June surface DOC concentration vs. depth of maximum DO concentration (Z_{DOmax}) and the magnitude of the DO peak (calculated as the difference between the maximum water-column DO concentration and the surface DO concentration).

Discussion

Our results show that there was a pattern in hypolimnetic metabolism along a gradient of DOC concentrations. We present evidence supporting two mechanisms for this pattern. First, in the high DOC lakes allochthonous DOC is an important substrate for bacterial metabolism, and second, absorbance by colored DOC results in little solar irradiance reaching the hypolimnion, eliminating the possibility of substantial hypolimnetic algal production.

DOC as a substrate for hypolimnetic metabolism

The decline in DOC in the hypolimnia of these lakes is most reasonably attributed to in-lake processes. Hydrologic tracer additions to three of the lakes (Peter, East Long, and West Long lakes) showed that there are negligible inputs and outputs of groundwater to the hypolimnion during stratification, and that there is negligible

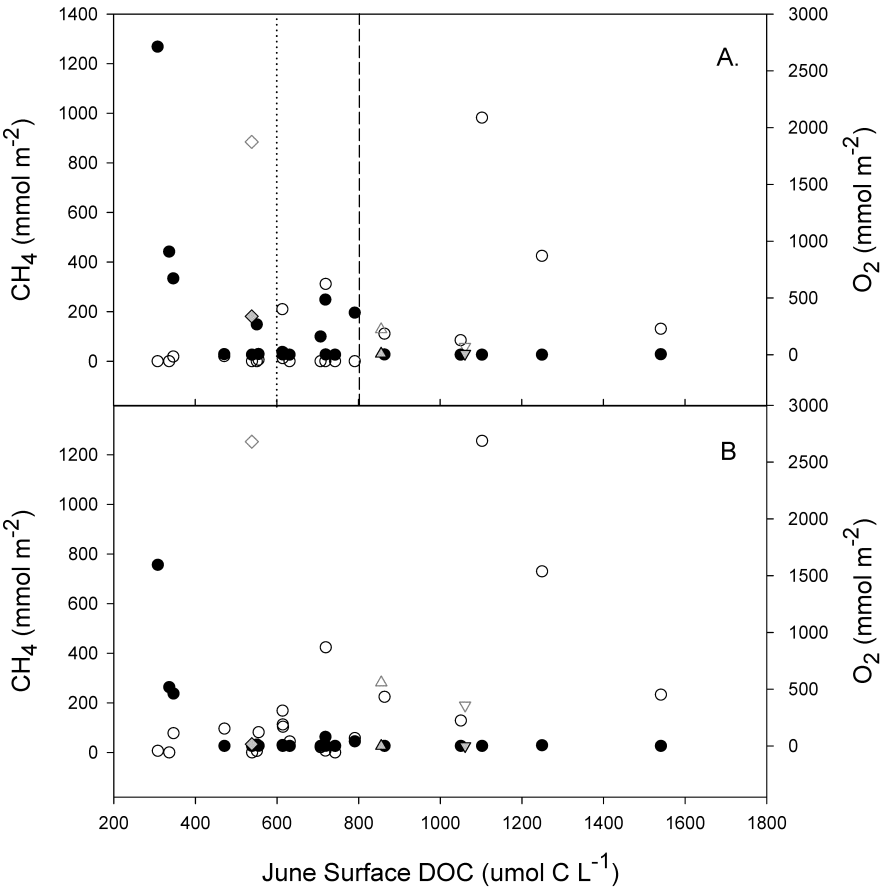

Figure 8. Hypolimnetic CH_4 and O_2 as a function of June surface DOC. A. June data (Dotted line marks the DOC concentration below which methane was not detected in unenriched lakes; dashed line marks the DOC concentration above which oxygen was not detected); and B. August data. (Open circles represent CH_4 concentrations; solid circles represent dissolved oxygen concentrations. Symbol shapes as in Figure 3).

mixing between the hypolimnion and epilimnion of these lakes other than entrainment of hypolimnetic waters due to thermocline deepening in late summer (Cole and Pace 1998). Diffusion of substances from the epilimnion is unlikely to be an important input to the hypolimnion given the slow rate of diffusion through the thermocline (Quay et al. 1980) and the large volume of the hypolimnion over which it would be diluted. Thus, the allochthonous DOC inputs to the lake are to the epilimnion, DOC is transported to the hypolimnion when the lake mixes, and the standing stock of DOC in the hypolimnion upon stratification represents the total available DOC for summer hypolimnetic metabolism.

Photodegradation has been shown to be an important mechanism of DOC loss in the surface waters of lakes (Molot and Dillon 1997; Granéli et al. 1996; Gen-

nings et al. 2001). Photodegradation can transform relatively recalcitrant DOC into more labile compounds (Moran and Zepp 1997) or can produce DIC directly via photo-oxidative pathways (Granéli et al. 1996). However, these photoreactions are generally restricted to shallow depths (< 2 m) in lakes with moderate to high DOC concentrations (Granéli et al. 1996). Previous exposure to sunlight may have important effects on the availability of hypolimnetic DOC for microbial respiration, but direct photodegradation of DOC is unlikely to be an important mechanism of DOC loss at hypolimnetic depths and light intensities. The most likely mechanisms of hypolimnetic DOC loss are flocculation and subsequent sedimentation (Effler et al. 1985; Weilenmann et al. 1989), and microbial degradation (Hessen 1992; Tranvik 1992). The decline in hypolimnetic DOC concentration was positively correlated with, and similar in magnitude to, the accumulation of DIC + CH_4 suggesting that microbial DOC consumption was an important removal process.

Our results add to a growing body of information suggesting that substantial amounts of allochthonous DOC are metabolized within the water column of most lakes (e.g., del Giorgio et al. (1999), but see Carignan et al. (2000)). Most of this information comes from measurements using epilimnetic water in bottles (Salonen et al. 1983; Rask et al. 1986), from budgetary information for whole lakes (Dillon and Molot 1997) or from gas-based metabolic estimates from epilimnetic water (Kling et al. 1992; Hope et al. 1996; del Giorgio et al. 1999). Gas based studies have shown a strong relationship between the partial pressure of CO_2 in lakes and their DOC concentrations (Hope et al. 1996; Riera et al. 1999). Two mechanisms may explain the relationship: 1) concentrations of DOC and CO_2 in the groundwater inputs covary, and 2) in-lake respiration of allochthonous organic carbon (Yavitt and Fahey 1994; Hope et al. 1996). Because we know that in at least several of our lakes there is negligible input of groundwater to the hypolimnion during stratification, in-lake respiration of allochthonous DOC is likely the dominant mechanism in these lakes. However, in a few of the lakes in this study, and for a few cases reported in the literature, DOC concentrations increased slightly during stratification (e.g., Mattson and Likens (1993)).

The rates of hypolimnetic DOC decline we measured (first-order k = 0.00012 to 0.0176 d^{-1}) are comparable to estimates of microbial consumption of DOC in aerobic waters (Tranvik 1988) and both lab (Fukushima et al. 1996) and ecosystem-based estimates of DOC losses (Curtis and Schindler 1997). Though these are low absolute rates, the large size of the DOC pool means that even small rates of loss are important in lake C cycles (Wetzel 1992). For example, in Tuesday Lake, 1% of the standing stock of hypolimnetic DOC is 54 mmol C m^{-2}, which is roughly one third of the algal C standing stock. Our estimated rates of DOC consumption are underestimates because they do not account for the inputs of DOC through the decomposition of settling particles.

Importance of light and net effect of DOC on hypolimnetic metabolism

Light absorbance by DOC may also affect apparent hypolimnetic metabolism. The light and DO profiles suggest that in low DOC lakes, hypolimnetic algal produc-

tion may recycle hypolimnetic DIC and produce oxygen, reducing the net change in hypolimnetic DIC + CH_4 concentration. However, in high DOC lakes, significant hypolimnetic algal production does not occur. Thus, even if two lakes had the same rate of organic C respiration, the hypolimnion of a low DOC lake, would show lower net accumulation of DIC + CH_4 and would be more likely to remain aerobic in upper depths. Other studies have found that hypolimnetic volumetric oxygen depletion was negatively correlated with light extinction coefficients (Fulthorpe and Paloheimo 1985) and light reaching the hypolimnion suppressed apparent oxygen demand (Rich 1980).

Primary production and hypolimnetic metabolism

Few studies have directly examined whether autochthonous production is sufficient to support hypolimnetic metabolism. A number of early studies assumed that autochthonous C was responsible for all but a negligible part of lake metabolism (e.g., Welch et al. (1976) and Herczeg (1987)). However, in Lake Washington the rate of DIC accumulation in the hypolimnion is twice the rate of epilimnetic organic carbon production (Quay et al. 1986), and in Mohonk Lake, hypolimnetic metabolism (measured as DIC accumulation) required 75 ± 20% of the epilimnetic organic C production (Herczeg 1987). These results require unusually high algal production export ratios (Baines and Pace 1994) suggesting that an alternative source of organic C is used for hypolimnetic metabolism.

The export ratio of algal C needed to support hypolimnetic metabolism and C burial in the sediments if only phytoplankton production is used was 22% in Paul lake and 58% in Tuesday Lake (Table 3). Among lakes in the literature with similar productivity to Paul and Tuesday, the mean export ratio was approximately 30%, and the range among all lakes was 10–50% (Baines and Pace 1994). Similarly, the sinking velocity of the algal C (mass of sedimenting C/C standing stock) needed to support hypolimnetic metabolism and C burial if only autochthonous production is used was 0.2 m d^{-1} in Paul Lake and 0.48 m d^{-1} in Tuesday Lake (Table 3). Sinking velocities for non-diatom algal assemblages such as occur in these lakes (Cottingham et al. 1998), range from 0.08–0.18 m d^{-1} (Hesslein 1980; Reynolds 1984). Thus, the export ratios and sinking velocities required for autochthonous production to support hypolimnetic metabolism indicate that there may have been sufficient algal C to support hypolimnetic metabolism in a low DOC lake (Paul), but not in a high DOC lake (Tuesday Lake).

We lack satisfactory error estimates for rates of C burial and C accumulation in the hypolimnion, however we can consider the potential effects of error in these aspects of the hypolimnetic C budget. Because the hypolimnetic C budget for Paul Lake is already balanced within the uncertainty of algal C export, this discussion focuses on Tuesday Lake. For C accumulation, a potential source of uncertainty is in the estimate of loss of CH_4 to ebullition. The observed relationship between CH_4 and DIC accumulation (Figure 1), and results from other studies (Strayer and Tiedje 1978; Mattson and Likens 1993) suggest that our assumed rate of CH_4 losses to ebullition is reasonable. However, if we overestimated ebullition or underestimated

Table 3. Calculation of the export ratio of primary production, and the sinking velocity of algal C standing stock needed to support hypolimnetic production. The hypolimnetic organic C requirement is the sum of DIC + CH_4 accumulation and C burial in the sediments (determined by ^{210}Pb dating of sediment cores (Houser 1998). The average summer standing stock of C in phytoplankton was estimated from chlorophyll data assuming that the C:Chlorophyll ratio is 40:1. Required sinking velocity (m d^{-1}) = proportion algal C required (d^{-1})) × (photic zone depth (m)).

Lake	Hypolimnetic organic C requirement (mmol m^{-2} d^{-1})	Avg. PPR (mmol C m^{-2} d^{-1})	Required export ratio	Avg areal algal C (mmol m^{-2})	Proportion Algal C required (d^{-1})	Photic zone depth (m)	Required sinking velocity (m d^{-1})
Paul	7.64	35.01	0.22	196.47	0.04	5.1	0.20
Tuesday	16.89	29.18	0.58	147.41	0.11	4.2	0.48

C burial, our calculated hypolimnetic C accumulation would be erroneously high. Smaller hypolimnetic C accumulation would be more easily balanced by the observed rate of C export from the hypolimnion. The magnitude of error in the our calculated hypolimnetic C accumulation required to change our conclusion concerning the hypolimnetic C budget for Tuesday Lake given the maximum, best estimate, and minimum values for C export from the epilimnion are 18%, 53% and 88% respectively.

Among the lakes in our survey, the highest hypolimnetic metabolism occurred in Peter Lake which was experimentally enriched with N and P from 1993–1997 (Carpenter et al. 2001). Of the three lakes with the next highest rates of hypolimnetic metabolism, two of them, Ed's Bog and Tuesday Lake are among the lakes with the highest DOC concentrations. This suggests that both high algal production and high DOC inputs, can lead to high rates of hypolimnetic metabolism.

Anaerobic metabolism

The hypolimnia of lakes in this study ranged from those that remained aerobic all summer to those that were essentially anoxic by early June. The only lake in which methane accumulation was not seen was Crystal Lake which has very low algal production and DOC inputs, whereas in some lakes (e.g., Tuesday and East Long lakes) CH_4 accumulation accounted for the majority of DIC + CH_4 accumulation. In 14 of the 21 lakes, methane accounted for at least 25% of the DIC + CH_4 accumulation. In these and many other lakes, hypolimnetic oxygen demand is limited in its ability to measure hypolimnetic metabolism because aerobic metabolism represents only a small part of total metabolism. For example, Mesotrophic Lake St. George (Ontario, Canada) can be completely anoxic within less than 2 months of spring turnover (Bedard and Knowles 1991); in Lake Mendota, 54% of the sedimented C is returned to the water column via methanogenesis (Fallon et al. 1980); in three Experimental Lakes Area lakes, anoxic organic C decomposition accounted for 78–97% of total decomposition in the hypolimnion (Kelly et al. 1988); and in oligotrophic Mirror Lake, aerobic metabolism accounted for only 43% of the hypolimnetic metabolism (Mattson and Likens 1993).

Conclusions

The lakes in our survey were chosen to cover a broad range of DOC concentrations and showed relatively small variability in chlorophyll *a*. In such a survey, DOC concentration clearly had important effects on hypolimnetic metabolism. We conclude that DOC, by serving as a substrate for metabolism and by reducing light penetration, can have substantial effects on hypolimnetic metabolism in lakes. Our results complement other recent studies that have demonstrated the importance of photodegradation and biological utilization of relatively refractory DOC in surface waters to overall lake metabolism (e.g., Hessen (1992) and Tranvik (1992), Moran and Zepp (1997)), the importance of DOC in the attenuation of ultraviolet and visible radiation (e.g., Morris et al. (1995)), and the interactions of DOC with metals

and nutrients influencing biological availability (e.g., Effler et al. (1985) and Jackson and Hecky (1980)). These physical, chemical, and biological processes associated with DOC extend beyond surface waters influencing hypolimnetic and likely benthic dynamics. DOC is emerging as a critical variable akin to nutrient loading and food web structure in significance as a determinant of the general properties and dynamics of aquatic ecosystems.

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