

Hypolimnetic oxidation rates in Lake Superior: Role of dissolved organic material on the lake's carbon budget

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Abstract

On average, the water column of Lake Superior is undersaturated with respect to dissolved oxygen and supersaturated with respect to carbon dioxide during the summer-stratified period. On the basis of temporal changes in water column dissolved oxygen, we calculate rates of oxygen consumption that range from 0.19 to 0.75 mmol m⁻³ d⁻¹. These rates are a factor of 5–10 times larger than can be supported by the particulate carbon settling rates and benthic oxygen consumption rates. In addition, on the basis of the limited information available, dissolved allochthonous carbon inputs are insufficient to account for the calculated rates of carbon oxidation. Rates of nitrate and total CO₂ (ΣCO₂) production are 0.019 ± 0.012 and 0.13 ± 0.06 mmol m⁻³ d⁻¹, respectively, and are consistent with the oxidation of a dissolved organic component that is similar in composition (C:N ratio) to the settling particulate material. Previously published estimates of total primary production were smaller but similar in magnitude to our integrated water column respiration rates. We interpret the observed imbalance between particulate carbon delivered to the deep lake and the calculated rate of carbon oxidation to be the result of the decomposition of dissolved organic carbon that appears to have both an autochthonous and an allochthonous component.

A simplistic view of aquatic ecosystem carbon cycling is that photosynthetic production, limited by the availability of one or more major nutrients, generates a large pool of fixed (autochthonous) carbon in the euphotic zone. Most of that organic material is “recycled” within the euphotic zone with some, typically small, fraction being “exported” out of the euphotic zone. A portion of this export production is then remineralized within the deep water column or within the sediments, and the balance is permanently buried (e.g., Dymond et al. 1996 and references therein). The record of this buried “residual” production serves as the basis for paleoclimate studies. For these studies, variations in the accumulation rate of biogenic material in lacustrine systems are

interpreted as variations in the biogeochemical response (i.e., productivity) to climatic change. This model of carbon cycling, although necessary from a paleoclimate point of view, does not necessarily capture information regarding what may be one of the most important process governing carbon flow in some lacustrine systems—the cycling of dissolved organic carbon (DOC).

For many lacustrine systems, bacterial consumption of DOC may represent an important vector for carbon flow (e.g., Pomeroy 1974; Wissmar et al. 1977; Biddanda and Cotner 2002 and references therein). The aquatic DOC pool is composed of both autochthonous and allochthonous DOC, with each of these components being actively recycled within the water column (e.g., Cole et al. 1982; Baines and Pace 1991; Cole and Caraco 2001). The turnover of a large allochthonous DOC pool often results in respiration rates exceeding gross primary production—that is, the systems are net heterotrophic. Therefore, many freshwater systems are net sources of carbon dioxide to the atmosphere (e.g., Kling et al. 1991; Cole et al. 1994; Dillon and Molot 1997; Kratz et al. 1997; del Giorgio et al. 1999; Cole et al. 2000; Cole and Caraco 2001). In addition, the relative proportion of net heterotrophy appears to be related to a lake's trophic status, with oligotrophic carbon flow exhibiting a proportionally heavier reliance on heterotrophic metabolism than eutrophic systems (e.g., Wissmar et al. 1977; del Giorgio and Peters 1994; Cotner and Biddanda 2001). Although the idea of DOC turnover being a major component (if not *the* major component) of net ecosystem carbon flow may be surprising at some level, DOC decomposition has been shown to be a significant component of carbon flow in rivers (e.g., Richey et al. 2002), lakes (references as above), estuaries (Howarth et al. 1986), and the ocean (e.g., Pomeroy 1974).

Methods

The preponderance of detailed oxygen consumption or CO₂ production data for lakes comes from shallow systems.

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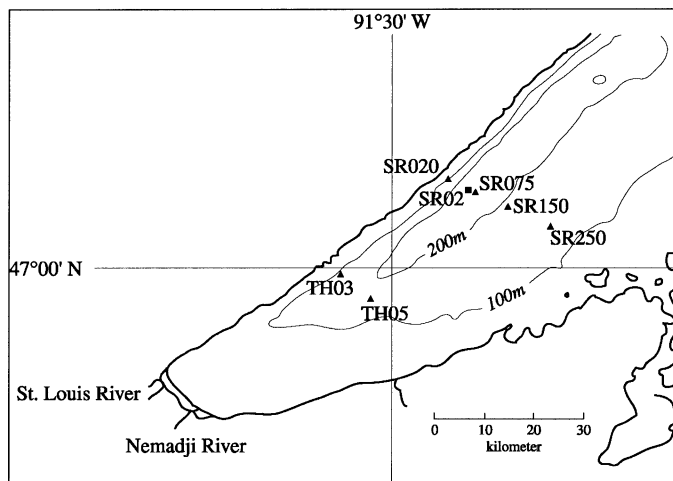


Fig. 1. Map of the study area in western Lake Superior. Countours are 100-m intervals.

For the present study, our efforts were focused on net carbon oxidation rates for the water column in western Lake Superior, one of the world's largest and deepest lakes. We used vertical profiles of dissolved oxygen (O_2), nitrate (NO_3), and total CO_2 (ΣCO_2) on two dates during the summer stratified period to estimate deep lake respiration rates. We compared these data with rates of benthic remineralization, particulate organic carbon flux, and previously published estimates of primary production and allochthonous carbon inputs to infer whether respiration of autochthonous DOC is likely to be an important component to carbon cycling in this deep oligotrophic system.

Study site—With a surface area of 82,100 km² (Herdendorf 1982), Lake Superior is areally the world's largest freshwater system containing, ~10% of the world's liquid surface freshwater. Lake Superior is an oligotrophic system with primary production estimated to be between 0.25 and 0.33×10^{12} mol C yr⁻¹ (International Joint Commission 1977). Its upper water column soluble reactive phosphorus concentrations are typically <10 nmol L⁻¹. Thus, the availability of this nutrient is likely to limit the rates of photosynthetic production, and experimental results support this contention (Rose and Axler 1998). In contrast to phosphorus, water column dissolved nitrate concentrations increased steadily throughout the past century at a rate of ~ 0.2 – 0.3 $\mu\text{mol L}^{-1}$ yr⁻¹ (Weiler 1978; Bennet 1986). This change in nitrate concentration is most likely caused by anthropogenic perturbations to the global hydrosphere (Bennet 1986).

Our study sites were located in the western arm of Lake Superior (Fig. 1). The St. Louis and Nemadji rivers enter the southwestern terminus of the western arm, delivering sediment and nutrients to the lake. Data presented here were collected as part of a 3-yr study focused on the fundamental physics and biogeochemistry of the lake's western arm. Samples used for the present study were collected during a series of cruises in the summer of 2000 aboard the RV *Blue Heron* (Fig. 1) and in the summer of 2001 aboard the RV *Noodin* (July) or the RV *Blue Heron*. Stations were located along

two transects running from the Minnesota to the Wisconsin shoreline (Fig. 1) and were preestablished as part of the existing multidisciplinary study.

Sample collection and analysis—During the summer of 2000 and the fall of 2001, water was sampled at each station using a 12-bottle General Oceanics rosette. Samples were typically collected at 12 depths, distributed throughout the water column. Temperature, conductivity, and pressure were measured concurrently with water collection using a SeaBird 911 CTD. We also present ΣCO_2 data from western Lake Superior that were collected during the summer of 2001. For the July sampling period, these data were collected using water bottles that were lowered from the surface on a wire and the bottles were tripped using messengers.

Samples for O_2 were immediately preserved and analyzed using an automated version of the Winkler titration (Carpenter 1965). Triplicate samples were analyzed at each station to determine the precision of the method; standard deviations averaged 0.5 $\mu\text{mol L}^{-1}$. Samples for nutrient analyses were filtered (0.45 μm filter) as soon as possible after collection in a laminar flow clean hood. Samples were stored frozen until analysis. Nitrate was determined using a Lachat Quickchem 8000 autoanalyzer, method 31-107-04-1-C, and the long-term precision and relative accuracy of that technique were determined to be ± 0.27 $\mu\text{mol L}^{-1}$. Samples for total alkalinity (TA) and pH were collected and analyzed within 24 h. TA was determined by a potentiometric titration technique with the Gran method for end-point determination with a precision of ± 3.2 $\mu\text{equiv. L}^{-1}$ (Edmond 1970). pH was determined using a spectrophotometric method for precise measurements of freshwater pH with a precision of ± 0.004 pH unit (e.g., French et al. 2002). ΣCO_2 and pCO_2 were calculated from the TA and pH data using CO2SYS, a computer program for carbonate system calculations in freshwater and seawater (Lewis and Wallace 1998). Calculated near-surface pCO_2 agreed to within 10% of the values measured by a commercial CO_2 instrument (SAMI- CO_2 ; Baehr and DeGrandpre 2002 and references therein), which was deployed on a companion mooring to that at Sta. SR02 (see below).

Results

Changes in deep lake O_2 , ΣCO_2 , and NO_3 inventories ($\Delta\text{Inv.}$, Table 1) were calculated using water column data from at least two sampling dates after the onset of stratification (Figs. 2 and 3). We estimated the depth below which no significant exchange occurs between the upper and deep lake to be 50 m, using temperature profiles at each station. For these calculations, we thus assume that changes in O_2 , NO_3 , and ΣCO_2 below 50 m occurs because of oxidation of organic matter (either particulate or dissolved). Water column oxygen consumption, nitrate production, and ΣCO_2 production rates are calculated as the difference between these concentration profiles below 50 m ($\Delta\text{Inv.}$, Table 1) divided by the depth over which the samples were taken and the time period between sampling intervals. Furthermore, we assume that water column property changes measured in the

Table 1. Calculated consumption and production rates.

Site	O ₂			NO ₃ ⁻		
	ΔInv. (μmol m L ⁻¹)	Rate (mmol m ⁻³ d ⁻¹)	C _{org} (mmol m ⁻³ d ⁻¹)	ΔInv. (μmol m L ⁻¹)	Rate (mmol m ⁻³ d ⁻¹)	C _{org} :NO ₃ ⁻ (mol: mol)
TH03	2,300	0.42	0.32	27	0.005	65
TH05	890	0.75	0.57	nm	nm	—
SR020	1,700	0.20	0.15	104	0.013	12
SR075	2,600	0.19	0.15	432	0.032	5
SR150	1,400	0.19	0.15	214	0.030	5
SR250	890	0.19	0.15	73	0.015	10
Average		0.32	0.25	0.019	13	
±		0.23	0.18	0.012	18	
SR075*			0.13			

* Collected at our mooring site near SR075 during summer 2001. The rate given is for 50–225 m from 23 Jul 01 to 11 Sep 01 and is calculated from ΣCO₂ profiles (Fig. 3).

deep lake are representative of the entire lake. We specifically address the veracity of this assumption later in the text.

We also present results from a sediment trap mooring and from a series of benthic incubations collected during the summer of 2000. Sediment traps were deployed from September of 1999 until September 2001; however, we focus our discussion on those data collected from May 2000 to September 2000—the sampling intervals germane to the present work. We present the deep lake annual value for comparison (Table 2). The sediment traps were located at ~100 and 250 m water depth (this latter trap is ~35 m above bottom), adjacent to our water sampling site, SR075 (Fig. 1). The traps were conical, were of fiberglass and plastic construction, and had a 0.5 m² sampling area (Dymond et al. 1996). The traps had six sample cups that were rotated during the course of deployment, allowing for a series of time-integrated samples. Cup material was preserved with a saturated sodium borate-buffered formaldehyde solution (e.g., Dymond et al. 1996). Sediment trap carbon and nitrogen were analyzed on dried sample splits using a carbon, hydrogen, nitrogen, sulfur (CHNS) analyzer (Costec). There was no inorganic carbon detected (using a Coulometrics coulometer) in these samples, consistent with the lake being undersaturated with respect to calcium carbonate (Weiler 1978). Samples of the water within the sediment trap cups were collected prior to sample processing. These samples were analyzed for dissolved phosphorus, and the soluble reactive phosphorus concentrations were assumed to result from the dissolution or decomposition of organic material within the trap cups. This additional phosphorus was used to correct the organic carbon concentrations in each cup, under the assumption that the carbon undergoing decomposition has a stoichiometry of C_{org}:P = 106:1 (Redfield et al. 1963). This correction averaged 8% for our entire data set. No such correction was made for nitrogen. Although these corrections and the introduced uncertainties are inherent in collecting sediment trap particles, we believe that the conclusions reached here are insensitive to these uncertainties. Furthermore, the benthic carbon budget shows that the annual carbon flux (~2.3 mmol m⁻² d⁻¹) is approximately equal to the sum of the calculated benthic carbon decomposition rate (~1.3 mmol m⁻² d⁻¹) and the organic carbon

burial rate (~0.5 mmol m⁻² d⁻¹) for this site (Heinen 2002). The observation of an approximate balance between the material being delivered to the sediment floor and the sum of the burial and decomposition rates suggests that the deep sediment traps provide a reasonable estimate of the material flux to the deep lake.

Benthic oxygen consumption and nitrate efflux rates were determined from a series of incubated sediment cores (E.A.H. and J.M. unpubl. data). Cores were collected using an Ocean Instruments multicorer. This device simultaneously collects four cores. Cores were retrieved with the sediment-water interface intact and showed no signs of disturbance. Once on deck, cores were removed from the multicorer and capped (within 15 min). A piston was forced through the bottom of the core, with excess water venting through a sampling port in the top cap. Cores were stored at in situ temperatures and stirred continuously at 5 or 30 rpm with a magnetic stir bar. Overlying water samples were collected every 6 h–1 d for the 2–10-d duration of the experiment. Samples were collected through the top sampling port by forcing the bottom piston upward. Dissolved oxygen samples were collected in 10-ml glass bulbs and analyzed immediately using the technique described in Broenkow and Cline (1969). Nitrate samples were filtered immediately (0.45 μm filter), stored frozen, and analyzed as described above.

Vertical distribution of dissolved constituents—Lake Superior's deep water column (>50 m) was undersaturated with respect to dissolved oxygen for the dates sampled (Fig. 2). We should note that our sampling targeted hypolimnetic processes; therefore, we do not have detailed data on the distribution of this property through the upper water column. That said, it appears that, for much of the summer productive period, dissolved oxygen is supersaturated in the euphotic zone (Fig. 2). Dissolved nitrate distributions are characterized by near-surface depletions during stratified periods, with increases at depth to near-uniform concentrations throughout the deeper water column. These near-surface depletions likely result from biological uptake. Similarly, pCO₂ profiles reflect the combined effects of biological utilization of CO₂, heating of the surface waters, and respiration. In the case of

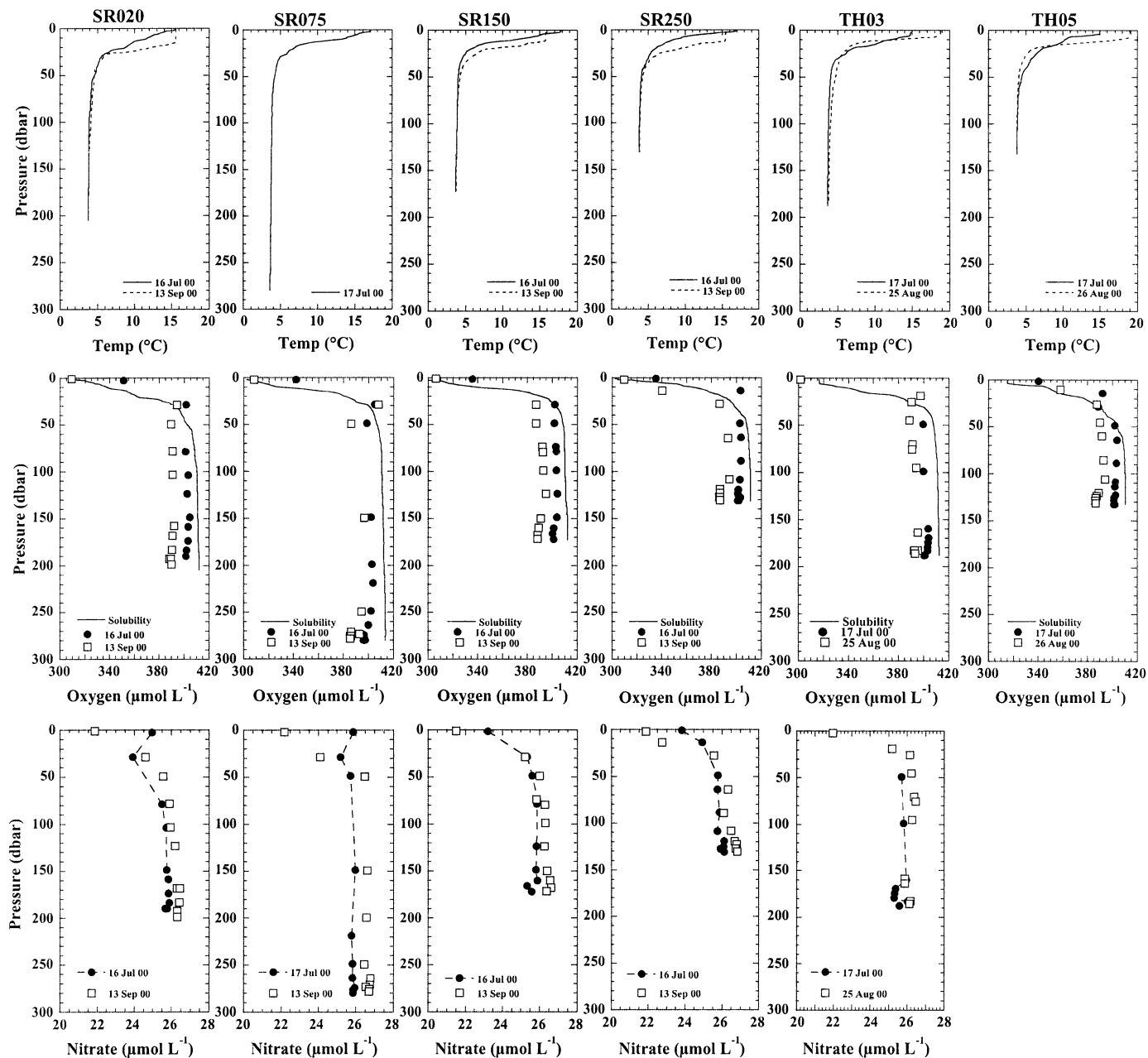


Fig. 2. Temperature, dissolved oxygen, and nitrate as a function of pressure at Sta. SR020, SR075, SR150, SR250, TH03, and TH05. Note that we use pressure rather than depth because we do not have an accurate equation of state for Lake Superior water (1 dbar is ~ 1 m, within 1%–2%). Oxygen solubility in each figure is presented for the July temperature profile. Oxygen solubility is calculated from in situ temperature data and the equations in Benson and Krause (1984).

$p\text{CO}_2$, Lake Superior was supersaturated everywhere during the stratified period (under the assumption of an average atmospheric concentration of $365 \mu\text{atm}$, Fig. 3), with the highest $p\text{CO}_2$ value at the surface ($\sim 500 \mu\text{atm}$). Thus, during the warm stratified period, Lake Superior is a net source of CO_2 to the atmosphere. This contention is tempered by the fact that $p\text{CO}_2$ calculations are highly sensitive to measured pH values, and, admittedly, the accuracy of lake water pH measurements is difficult to assess. As discussed above, however, the $p\text{CO}_2$ values presented here are within 10% of those measured directly with an in situ $p\text{CO}_2$ sensor, and our

near-surface calculated $p\text{CO}_2$ values were $\gg 10\%$ supersaturated with respect to atmospheric $p\text{CO}_2$ (surface $p\text{CO}_2$ in September, $> 500 \mu\text{atm}$ vs. an average atmospheric value of $\sim 365 \mu\text{atm}$). For the purposes of the present study, however, the oversaturation of the lake with respect to CO_2 is secondary—it is the *relative* change in ΣCO_2 that is central to our discussion (Fig. 3).

The vertical distributions of dissolved oxygen and nitrate, in 2000, and ΣCO_2 , in 2001, in the hypolimnion demonstrate systematic temporal changes in their water column inventories. Through the stratified season, dissolved oxygen de-

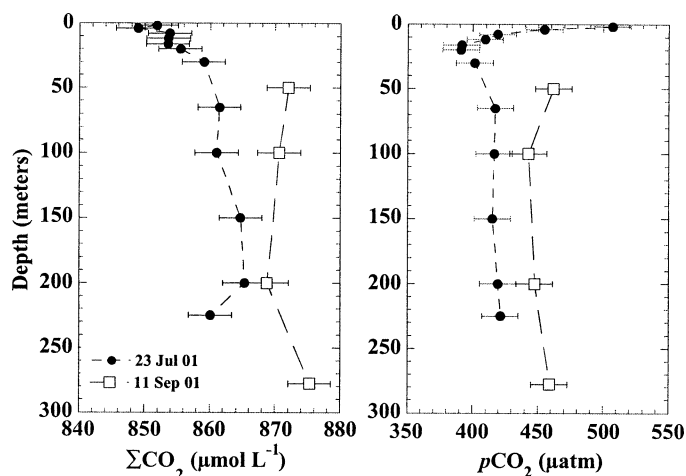


Fig. 3. ΣCO_2 and $p\text{CO}_2$ as a function of depth near Sta. SR075. Data were collected during the summer of 2001.

creased, nitrate increased, and ΣCO_2 increased (Figs. 2 and 3). What is particularly striking is the near homogeneity of the vertical change in hypolimnetic water column inventories. This pattern is consistent with the homogeneous oxidation of organic matter throughout the lakes' hypolimnion rather than the benthic oxidation of organic carbon alone. If it were caused by this latter process, we would have expected a diffusive gradient from the sediments to the upper water column. The change in dissolved oxygen and nitrate inventories yielded a C:N ratio for the decomposing organic material of 13 ± 18 (Table 1).

Because our interpretation of the water column data relies on the assumption that the changes we calculate are larger than potential calibration offsets, we consider the sensitivity of our results to potential inaccuracies in calibration. For dissolved oxygen, we observed water column changes in concentration of $8.8\text{--}17.3 \mu\text{mol L}^{-1}$. The smaller value is for the shorter time interval between sampling (i.e., Sta.

TH03). The average for the four stations that had July and September coverage is $14.9 \mu\text{mol L}^{-1}$. The automated oxygen titration was based on calibration with a gravimetric standard, with a reported accuracy of $\sim 0.1\%$ (Carpenter 1965), which at $400 \mu\text{mol L}^{-1}$ is $0.4 \mu\text{mol L}^{-1}$. If we assume, for the sake of robustness, that our uncertainty is $1\text{--}2 \mu\text{mol L}^{-1}$, the uncertainty in our change in the O_2 inventory would be $\sim 15\%$. This uncertainty is smaller than that calculated for our average carbon oxidation rate ($\sim 70\%$, Table 1). For nitrate, the average change in water column concentration ranged between 0.53 and $1.24 \mu\text{mol L}^{-1}$, with an average for the four stations that had coverage in July and September of $1.06 \mu\text{mol L}^{-1}$. We used a laboratory standard (at lake water nitrate concentration) to intercalibrate between runs. On the basis of these intercalibrations, our reproducibility between sampling events was $\pm 0.27 \mu\text{mol L}^{-1}$. As is the case for oxygen, this uncertainty is smaller than that calculated for the average nitrate production rate (Table 1). We estimate that the uncertainty in the ΣCO_2 data is $\pm 3.3 \mu\text{mol L}^{-1}$ and that for $p\text{CO}_2$ is $\pm 14 \mu\text{atm}$. These uncertainties are propagated from uncertainties in pH and total alkalinity data (and temperature in the case of $p\text{CO}_2$). We have no way of estimating a priori the absolute accuracy of these data. However, as mentioned above, in situ $p\text{CO}_2$ data suggest that the absolute accuracy of these results are within 10% . Furthermore, we used the same standard acid solution for all titrations. This acid was stored sealed, to prevent contamination and/or evaporation. Thus, we maintain that the alkalinity titrations and the resultant ΣCO_2 data sets should be internally consistent. Recognizing the uncertainties for each constituent, it is the combination of all three measurements that offers compelling evidence for the rate of deep lake respiration.

Water column consumption and production rates—If we assume that the changes in water column dissolved oxygen calculated for western Lake Superior are representative of a

Table 2. Sediment trap and benthic incubation results.

Trap results				
Trap depth (m)	Start	Finish	Carbon ($\text{mmol m}^{-2} \text{d}^{-1}$)	Nitrogen ($\text{mmol m}^{-2} \text{d}^{-1}$)
100	05 May 00	11 Sep 00	1.97	0.14
<i>Excluding</i>	<i>30 Jun 00</i>	<i>19 Aug 00</i>	<i>2.39*</i>	<i>0.17*</i>
250	05 May 00 [†]	11 Sep 00	2.47	0.16
250	23 Sep 99	11 Sep 00	2.28	0.17
Incubation results				
Date	<i>n</i>	Oxygen ($\text{mmol m}^{-2} \text{d}^{-1}$)	Nitrate ($\text{mmol m}^{-2} \text{d}^{-1}$)	$\text{C}_{\text{org}}:\text{NO}_3^-$ (mol:mol)
16 Jul 00	2	1.58 ± 0.15	0.11 ± 0.01	11
11 Sep 00	3	1.79 ± 0.21	0.09 ± 0.02	15
Average		1.70 ± 0.20	0.10 ± 0.02	13

* Because two of our deep (250 d) trap cups failed from 30 Jun to 19 Aug, we report the values in italics to compare results from the 100 m trap with the 250 m trap over the time period where both traps successfully collected data.

[†] As noted above, no samples were collected from 30 Jun to 19 Aug during this deployment because of trap failure.

lakewide process, then $0.25 \pm 0.18 \text{ mmol C m}^{-3} \text{ d}^{-1}$ was consumed within the lake (Table 1). Furthermore, if we assume that this oxygen consumption was uniform throughout the entire water column (total volume of $12,230 \text{ km}^3$) and was roughly constant throughout the year, then $1.1 \pm 0.77 \times 10^{12} \text{ mol C yr}^{-1}$ would be consumed. This extrapolation from western Lake Superior to the entire lake may seem questionable. However, previous work has demonstrated a change in the deep lake dissolved oxygen inventory through the summer stratified season of $0.14\text{--}0.22 \text{ mmol m}^{-3} \text{ d}^{-1}$ (Weiler 1978), which is consistent with the rates calculated here. Furthermore, our assumption of a uniform respiration rate throughout the water column (i.e., including the upper 50 m) is likely to underestimate total respiration, because estimates of bacterial respiration in the surface waters are reported to be higher than our integrated oxidation values ($0.48\text{--}0.73 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$, Biddanda et al. 2001).

As was discussed above, changes in both the nitrate and the ΣCO_2 inventory are consistent with the rates of oxygen consumption (Table 1). Although the calculated ΣCO_2 change is for 2001, rather than 2000, we would expect a comparable change in the inventory, under the assumption that the rate of organic carbon oxidation is approximately constant from year to year (within our uncertainties). We realize that this contention lacks sufficient data for verification; however, as mentioned above, the work of Weiler (1978) offers support for first-order interannual consistency.

In the case of nitrate, an additional comparison can be made with the historical rate of nitrate accumulation in Lake Superior. The rate of dissolved nitrate accumulation in the lake has been reported to be $\sim 0.2\text{--}0.3 \mu\text{mol L}^{-1} \text{ yr}^{-1}$ since the early to mid-1900s (Weiler 1978; Bennet 1986), and although this "nitrifying" of Lake Superior has a poorly quantified source, it is thought to be related to changes in the global hydrologic nitrogen budget (Bennet 1986). This rate of nitrate increase corresponds to $0.0005\text{--}0.0008 \text{ mmol NO}_3 \text{ m}^{-3} \text{ d}^{-1}$ (Bennet 1986), which is nearly two orders of magnitude smaller than our calculated rate of water column nitrate production (Table 1).

Particulate organic material settling rates—For the period between May and September 2000, carbon settling rates measured at 100 and 250 m were between 2.0 and $2.5 \text{ mmol m}^{-2} \text{ d}^{-1}$ and were essentially indistinguishable for the two depths (Table 2). We do not have data for the sediment trap at 100 m prior to that period; however, our deeper trap, which had similar fluxes for the same time period (Table 2), measured an annual carbon flux (September 1999–September 2000) that was approximately the same as that measured from May to September 2000. Furthermore, and as was discussed above, the near balance among the sediment decomposition rate, burial rate, and particle flux suggests that the sediment traps were capturing a representative flux of material to the deep lake. In addition, Klump et al. (1989) calculated particle settling rates from the eastern lake that were indistinguishable from those measured here, which suggests that estimates presented here are reasonable and that particle settling rates may be approximately constant across the lake. Thus, assuming an organic carbon settling rate of $2 \text{ mmol m}^{-2} \text{ d}^{-1}$ at 100 m and a mean depth for the lake of 150 m,

$0.04 \text{ mmol C m}^{-3} \text{ d}^{-1}$ are being delivered to the volume of the lake below 100 m. C:N ratios of the particulate material vary between ~ 9 and 15, with an average C:N ratio for all our sediment trap data (not shown) collected in western Lake Superior of ~ 12 ; this ratio is similar to the ratio implied by the change in the oxygen and nitrate inventories (Table 1).

Benthic oxygen demand and nitrate efflux—Benthic oxygen consumption rates and nitrate efflux rates at our mooring site averaged 1.7 and $0.1 \text{ mmol m}^{-2} \text{ d}^{-1}$, respectively, which amounts to $\sim 0.03 \text{ mmol C m}^{-3} \text{ d}^{-1}$ for the area of the lake below 100 m (Table 2; E.A.H. and J.M. unpubl. data). There was no statistical difference between the data collected in July and those collected in September; thus, we pooled the data and present an average value for the region. The stoichiometry of the efflux (C:N ~ 13) is consistent with the sediment trap data, which implies that the material undergoing decomposition is similar to that raining to the lake floor (Table 2). The benthic efflux data combined with the sediment trap data indicate that $\sim 65\%$ of the organic material arriving at the lake floor during the summer is recycled. There are a host of caveats with making this comparison on such a limited data set; however, this value is consistent with the full sediment trap data set, the lakewide organic carbon burial rate (Johnson et al. 1982), and other data on benthic carbon cycling (Klump et al. 1989; E.A.H. and J.M. unpubl. data). Furthermore, for four different sites within the western basin, sediment oxygen uptake rates averaged $2.2 \pm 0.8 \text{ mmol m}^{-2} \text{ d}^{-1}$ ($n = 16$), and nitrate efflux rates averaged 0.15 ± 0.07 ($n = 25$) (E.A.H. and J.M. unpubl. data). These averages are based on core incubations taken during field work in 2000 and 2001 (E.A.H. and J.M. unpubl. data) and lend support to our implicit assumption that organic carbon decomposition rates are relatively constant along the lake floor, both temporally and spatially. Furthermore, these rates are similar to those presented for the eastern lake by Klump et al. (1989).

Respiration versus carbon production—The lake's annual rate of primary productivity has been estimated at $0.25\text{--}0.33 \times 10^{12} \text{ mol C yr}^{-1}$ (International Joint Commission 1977 as referenced in Johnson et al. 1982); thus, oxygen consumption rates (carbon oxidation rates) are equivalent in magnitude but greater than published rates of photosynthetic production. We recognize here that these published values for primary production are nearly 30 yr old; however, to our knowledge, there are no published contemporary estimates of whole-lake primary production. In addition, it should be pointed out that previously reported values of primary production were estimated using techniques that are now viewed as potentially underestimating total primary production (e.g., Bender et al. 1999). With these caveats in mind, even if the reported values are underestimated by 50%, our calculated whole-lake oxygen consumption would still be greater than photosynthetic production. The possibility that respiration outpaces production is consistent with an upper water column that is supersaturated with respect to CO_2 (Fig. 3)—that is, whole water column respiration exceeds total primary production rates. For respiration to exceed production, an external source of organic carbon is required.

Discussion

In some systems, deep lake oxygen consumption can be entirely driven by the decomposition of *particulate* carbon exported from the upper lake (i.e., “new” or “export” production). Crater Lake, Oregon, for example, is a deep oligotrophic lake that exhibits behavior consistent with this model (Dymond et al. 1996). In contrast to this system, Lake Superior has an organic carbon settling flux that could support an oxygen consumption rate of $0.04 \text{ mmol C m}^{-3} \text{ d}^{-1}$, whereas the measured respiration rate is $0.25 \text{ mmol m}^{-2} \text{ d}^{-1}$ —a discrepancy by a factor of six. Furthermore, a significant fraction of the settling particle flux is buried within the sediments and therefore is not respired in the lower water column, creating a larger difference between deep-lake particulate carbon delivery and total water column respiration. Essentially, neither benthic oxygen consumption ($\sim 0.03 \text{ mmol C m}^{-3} \text{ d}^{-1}$) nor the total oxygen demand derived from the measured particulate carbon flux can account for the observed temporal trends in dissolved oxygen, nitrate, and dissolved inorganic carbon. This difference requires either that (1) water with lower dissolved oxygen and higher nitrate and ΣCO_2 concentrations has been advected into the western arm of Lake Superior (i.e., spatial/temporal variability can explain our observations) or (2) there is an additional sink for deep lake oxygen—DOC.

The first explanation requires that water column carbon oxidation is higher elsewhere within the lake and that water from that region of the lake is advected into the western arm, thus producing the apparent temporal differences in O_2 , NO_3 , and ΣCO_2 between sampling dates. Several observations about the lake do not necessarily preclude this possibility but make it unlikely. As discussed above, Weiler (1978) reported changes in the deep-lake water column oxygen inventory through the summer that are indistinguishable from what we estimate here. This previous work is noteworthy, because that study covered the entire lake (not just a single region, as we have done). Also, Klump et al. (1989) reported organic carbon settling fluxes from the eastern lake that are indistinguishable from those reported here. These two studies argue against large-scale differences in the deep lake’s hydrographic properties. Furthermore, it is noteworthy that the changes we observe are uniform throughout the water column. We interpret this pattern to infer that the material being oxidized is homogeneously distributed throughout the water column. Finally, if water was being advected into the western arm, we would not have expected all the SR stations (Table 1) to produce the same amount of carbon oxidation, because circulation would not bring water into the region through these stations in a uniform manner.

We thus hypothesize that the calculated changes in oxygen, nitrate, and ΣCO_2 inventories are caused by the decomposition of DOC and that this carbon has a stoichiometry similar to the particulate organic material collected by sediment traps. Previously reported DOC concentrations in Lake Superior ranged $110\text{--}210 \mu\text{mol L}^{-1}$ (Baker and Eisenreich 1989; Biddanda et al. 2001). Water column dissolved oxygen decreases $\sim 15 \mu\text{mol L}^{-1}$ from July to September. If we assume that this change is driven by DOC consumption, we

would expect to see a change in DOC concentration of $\sim 11 \mu\text{mol L}^{-1}$. This amount of DOC is a small fraction of the total pool, and a change of this magnitude would not be surprising, given the reactivity of DOC (e.g., Cole et al. 1982). Furthermore, the change in DOC concentration reported for Lake Superior surface waters between July and September 1998 was $9 \mu\text{mol L}^{-1}$ (Biddanda et al. 2001), which is entirely consistent with the expectations put forth here. No uncertainty was reported for this DOC change; however, on the basis of the experience of the first author with the technique used by Biddanda et al. (2001), this change in DOC is outside the normal analytical uncertainty for this technique. Thus, we hypothesize that the temporal changes in O_2 , NO_3^- , and ΣCO_2 inventories are dominated by the respiration of DOC.

DOC could be coming from either in situ production (autochthonous), or it could be terrestrial in origin (allochthonous) (e.g., Cole et al. 1982; Biddanda and Cotner 2002). Little information exists on the concentration of DOC in rivers and streams entering Lake Superior. However, for an annual riverine input of $4.8 \times 10^{10} \text{ m}^3 \text{ yr}^{-1}$ (Environment Canada 1999) and a mean riverine DOC concentration of 0.8 mmol L^{-1} (Meybeck 1982), we estimate terrestrial DOC input to be $0.04 \times 10^{12} \text{ mol C yr}^{-1}$. If we assume that our calculated respiration rate is constant throughout the year (an assumption that currently cannot be verified), then riverine input is more than an order of magnitude smaller than the $\sim 0.9 \times 10^{12} \text{ mol C yr}^{-1}$ being respired throughout the water column. The DOC concentration used here is a global average: it is unknown how accurate this estimate is for the tributaries of Lake Superior. However, even tripling that value would produce an insufficient quantity of carbon for our calculated oxidation rates. Although we suggest, on the basis of these calculations, that terrestrial DOC is unlikely to be the most important DOC component undergoing oxidation, the fact that the entire water column is supersaturated with respect to CO_2 during the stratified period implies that a (poorly quantified) pool of terrestrial carbon is being oxidized in Lake Superior (i.e., carbon respiration exceeds production).

If the DOC pool were allochthonous in origin, we might have expected the C:N ratio to be significantly different from the lake’s particulate ratio. Previous reports on dissolved C:N ratios suggested that dissolved organic matter is carbon-rich relative to the particulate pool (e.g., Benner et al. 1997 and references therein; McCarthy et al. 1997). We therefore anticipated that there would be a significant difference between the C:N stoichiometry of the particulate versus the dissolved phases in Lake Superior. The large uncertainty for the value of the dissolved $\Delta\text{C}:\Delta\text{N}$ ratio (Table 1) prohibits any definitive comparisons. However, if we ignore the one exceptionally high C:N value (Table 1), the dissolved C:N stoichiometry is within the range for the sediment trap particles (~ 12), the benthic efflux ratios (~ 13), as well as within the range of previously reported suspended particulate organic carbon:particulate organic nitrogen ratios (7–10; Halfon 1984). These combined data imply that the material being decomposed is similar in composition to the autochthonous particulate material.

Lake Superior’s carbon cycle is poorly quantified (e.g.,

Table 3. Carbon source and sink terms.

Overall lake sources	Rate (mmol m ⁻³ d ⁻¹)	Annual rate* (× 10 ¹² mol C y ⁻¹ r ¹)	Reference
Primary production	~4–5	0.16–0.89	1
Rivers		0.04	2
Outputs			
Water Column oxidation	0.25	0.9	3
	0.14–0.22		4
	0.48–0.73		5
Burial		0.04	6
Outflow		0.01	7

* Annual rates are reported to compare data of differing time and space scales. Primary production rates and water column oxidation rates both primarily reflect summer measurements. The river value is an annual approximation as are both the annual burial and outflow values, see reference as noted.

Note. 1. The estimate of the daily rate is from Vollenweider et al. (1974), which is the average of data from Jul to Sep 1973. The annual number includes values from the International Joint Commission (1977) as cited in Johnson and Eisenreich (1979). 2. Calculated from river inflow (Environment Canada 1999) and average river concentration (Meybeck 1982). 3. The present study. 4. Calculated from data presented in Weiler 1978. 5. Biddanda et al. 2001. 6. Johnson et al. 1982. 7. Heinen 2002.

Table 3). Because of the lack of a robust annual data set, constructing a carbon “budget” per se is not possible. Given the uncertainties in the published rates of primary production and data presented here, comparisons between our data and those published elsewhere are equivocal. Germane to this point, the relative timescales for the various measurements shown in Table 3 range from daily averages (i.e., primary production) to annual averages (i.e., riverine input). It is clear, however, that DOC oxidation is potentially an important carbon sink during the summer stratified period (Table 3). Simply comparing the rate of oxygen depletion (0.25 mmol C m⁻³ d⁻¹) with the amount of carbon delivered below 100 m (0.04 mmol C m⁻³ d⁻¹) or oxidized on the lake floor (0.03 mmol C m⁻³ d⁻¹) demonstrates a discrepancy between deep-lake carbon sources and sinks. During the warm stratified period, $\sim 2.5 \times 10^{12}$ mmol C d⁻¹ are being respired in the water column (0.9×10^{12} mol C yr⁻¹), which is more than an order of magnitude larger than our estimate of the total allochthonous carbon input ($\sim 0.04 \times 10^{12}$ mol C yr⁻¹). The magnitude of consumption is slightly larger than published rates of primary production, leading us to tentatively conclude that (1) previous estimates for primary production may be low, and (2) the DOC source is likely to be a mixture of both allochthonous and autochthonous sources. Despite our relatively low estimate for terrestrial DOC inputs, such a component is required if the water column is supersaturated with respect to CO₂, and confirmation of this assertion, as well as others put forth here, necessitates better constraints on the lake’s carbon dynamics.

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