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Carbon cycling in Lake Superior

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[1] Carbon (C) cycling in Lake Superior was studied within the Keweenaw Interdisciplinary Transport Experiment in Superior (KITES) project to assess (1) whether the lake is net heterotrophic, (2) sources, sinks and residence time for dissolved organic carbon (DOC), (3) importance of terrigenous organic C subsidies, and (4) factors limiting C flow through bacteria. During 3 years of fieldwork, measurements were made of spatial and temporal distributions of C pools and rates of photosynthesis, community respiration, and bacterial production. Measurements were made of the composition of dissolved organic matter (DOM), rates of DOM photolysis, lability of DOM toward microbial consumption, and river inputs of DOM. All measurements suggest the lake is net heterotrophic. The C:N ratios of DOM suggest that it is primarily of terrigenous origin, but other characteristics (size distribution, UV absorption) point to the presence of autochthonous DOM and to alteration of terrigenous material. The lake mass balance indicates that the residence time (~8 years) of the DOC pool (17 Tg) is short relative to the hydrologic residence time (170 years). The known flux of terrigenous DOC (~1 Tg/yr) is too low to support annual bacterial carbon demand (6–38 Tg/yr), but microbial respiration is the major sink for terrigenous DOC. A rapidly cycling, autochthonous DOC pool must exist. Microbial activity was correlated with temperature, phosphorus availability, and DOC concentration but not with photosynthesis rates. Measurements of respiration (~40 Tg/yr), photosynthesis (2–7 Tg/yr), and bacterial production (0.5–2 Tg/yr) are not all mutually compatible and result in a discrepancy in the organic carbon budget.

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1. Introduction

[2] Recent studies have shown that many lakes are net sources of CO_2 to the atmosphere [*Anderson et al.*, 1999; *Cole and Caraco*, 1998; *Cole et al.*, 1994; *del Giorgio et al.*, 1999; *Dillon and Molot*, 1997; *Kling et al.*, 1991; *Striegl et al.*, 2001; *Wachniew and Rozanski*, 1997]. Emission rates from individual lakes (<0–150 g C/m^2 yr) are inversely proportional to lake area [*Striegl et al.*, 2001]. *Del Giorgio et al.* [1999] found that only in the most productive lakes was there a net uptake of atmospheric CO_2. Net emission of CO_2 from lakes and net carbon (C) storage in sediments would not be possible if autochthonous, organic carbon (OC) production were the only source of C to lakes. However, lakes have several other significant sources of C including ground and surface water inputs of inorganic carbon (DIC), mineral dissolution, and inputs of allochthonous OC [*Anderson et al.*, 1999; *Striegl et al.*, 2001; *Wachniew and Rozanski*, 1997]. It has become clear that inputs of allochthonous OC to many lakes are a significant component of the C budget. If DIC inputs are ignored, for lakes to be net sources of CO_2 the amounts of allochthonous OC inputs that are respired or photolyzed in lakes must exceed the amount of autochthonous OC that is buried in sediments.

[3] This finding that respiration of allochthonous dissolved OC (DOC) inputs is larger than burial of autochthonous OC in many lakes has three major implications. First, allochthonous inputs of DOC represent organic matter produced in terrestrial ecosystems (terrigenous OC), and flow of this OC into streams and lakes can be a significant component of regional carbon budgets [*Dillon and Molot*, 1997; *Kling et al.*, 1991]. In the boreal region, DOC yields (3–7 g/m^2 yr [*Dillon and Molot*, 1997]) represent ~1–3% of net primary production (NPP)

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[*Gower et al.*, 2001]. On a global basis, efflux of CO_2 from lakes (~140 Tg C/yr [*Cole et al.*, 1994]) is estimated to be three times larger than burial of OC in lake sediments. In the flow of DOC from land to lakes to rivers to oceans, approximately 20% is converted to CO_2 in lakes, another 30% in rivers [*Cole and Caraco*, 2001], and only 50% reaches the oceans [*Hedges et al.*, 1997; *Wollast*, 1998].

[4] A second implication is that respiration (or photolysis) of terrigenous OC in lakes represents one step in conversion of young OC [*Schiff et al.*, 1990, 1997] into old, recalcitrant DOC residing in the deep oceans [e.g., *Guo and Santschi*, 2000]. This conversion involves breakdown of relatively large organic molecules that are typical of soil and wetland waters into low-molecular-weight (LMW) compounds. In oceans and in saline lakes with long residence times, terrigenous OC has already been converted into LMW compounds [*Amon and Benner*, 1994; *Benner et al.*, 1992; *Waiser and Robarts*, 2000]. In estuaries, rivers, and, presumably, lakes, a greater fraction of terrigenous OC still comprises larger molecules that are amenable to breakdown via photolysis and bacterial respiration [e.g., *Guo and Santschi*, 1996; *Hedges et al.*, 2000]. In lakes with short residence times, conversion of terrigenous OC into recalcitrant LMW compounds cannot be observed [*Schiff et al.*, 1990], but lakes with longer residence times such as Lake Superior provide a good location to study this transformation.

[5] The third implication is that many lakes are heterotrophic with negative net community production (NCP) or with ratios of photosynthesis to respiration (P:R) less than one. The magnitude of terrigenous DOC inputs relative to lake NPP depends largely on the ratio of catchment to lake surface area; for catchment:lake area ratios of 10–100 and NPP of 100–300 g C/m^2 yr, typical yields of terrigenous OC represent 10–700% of lake NPP. Clearly, in some lakes, respiration of even a small fraction of this terrigenous DOC loading would result in a condition of net heterotrophy. Net heterotrophy in many lakes has been demonstrated by direct comparison of rates of photosynthesis and bacterial respiration [*del Giorgio and Peters*, 1994; *del Giorgio et al.*, 1997; *del Giorgio and Peters*, 1993]. These studies demonstrate oligotrophic aquatic systems to be heterotrophic as a rule, and P:R ratios above one to be characteristic only of highly productive waters. Associated with net heterotrophy is a dominance of heterotrophic bacterial biomass over autotroph biomass [*Biddanda et al.*, 2001; *del Giorgio and Gasol*, 1995], increased importance of bacterioplankton in carbon and nutrient flows [*Suzuki et al.*, 1996], and an increased importance of the microbial food web (MWF).

[6] This study focuses on the flow of OC from terrestrial systems into a lake with a long residence time (~170 years in Lake Superior [*Quinn*, 1992]), the subsequent transformation of that terrigenous OC, and the significance of this terrigenous OC input relative to bacterial carbon demand and photosynthesis. The objectives of the study were to determine residence times of OC within the major pools, the sinks for terrigenous OC, whether the lake is net heterotrophic, and what factors limit bacterial production in the lake. These objectives were met by measuring the major fluxes of OC within the lake, constructing a mass balance for OC for the lake, and statistically assessing the factors regulating carbon flow through bacteria.

2. Methods

2.1. Site Description

[7] Lake Superior is a large (surface area 8.2×10^{10} m^2), deep (mean depth 150 m, maximum depth 406 m) lake that generally is dimictic [*Assel*, 1986]. A thermal bar develops in spring (April) and gradually moves offshore until the lake stratifies vertically in middle to late July [*Bennett*, 1978; *Ullman et al.*, 1998]. The thermocline is typically located at 25–35 m depth through early September, and then gradually descends until the lake becomes isothermal in mid December [*Assel*, 1986]. Ice cover in winter varies from negligible to complete coverage roughly once per decade. The lake is oligotrophic with a total phosphorus concentration of 1.5–3.5 mg P/m^3 [*Siew*, 2003], and chlorophyll-a concentrations of 0.2–1.5 mg/m^3 [*Bub*, 2001]. The lake is undersaturated with respect to calcite, and surface sediments do not contain carbonates except in narrow outcrops of postglacial clays [*Thomas and Dell*, 1978].

[8] This study was conducted along approximately 170 kilometers of coastline on the northwest side of the Keweenaw Peninsula in Lake Superior (Figure 1). Within the study area, sampling was conducted in three main regions primarily along transects extending from 0 to 21 km offshore. The regions are called southwest (individual transects include OS, ON), central (transects include HS, HC, HN), and northeast (transects include EH, CH). The lake bathymetry changes from a gentle slope (0.007) in the southwest region to a narrow shelf followed by a steep slope (0.035) in the central and northeast regions. In the northeast region, water depths increase rapidly from 50 m at 0.5 km offshore to 200 m at 1.5 km offshore.

[9] Previous investigations have reported the presence of a strong northeastward coastal current off the Keweenaw Peninsula, commonly referred to as the Keweenaw current [*Ragotzkie*, 1966; *Viekman and Wimbush*, 1993]. Numerical modeling by *Chen et al.* [2001] and *Zhu et al.* [2001] has indicated that the current is, in part, a thermally driven current, caused by rapid warming of nearshore (versus offshore) water. In response to the bathymetry, current velocities are low in the southwest region of this study and increase to maximum speeds of 70–90 cm/s in the northeast region.

[10] The coastline in the study region has about nine tributaries with continuous flow, but only two of these, the Sturgeon and Ontonagon Rivers, are of significant size. The study region also may be influenced by inputs from the Bad River located approximately 110 km southwest of the Ontonagon River. Combined, the three rivers account for 58% and 33% of the inputs of suspended sediments and phosphorus from U.S. rivers and streams into Lake Superior [*Robertson*, 1997]. Outflow from the Sturgeon River enters the study region only intermittently [*Churchill et al.*, 2004], and some fraction of DOC and nutrient loads are retained within the Keweenaw Waterway.

2.2. Field Sampling

[11] Sampling was performed primarily from ships (R/V *Laurentian*, R/V *Blue Heron*). Ship cruises were conducted

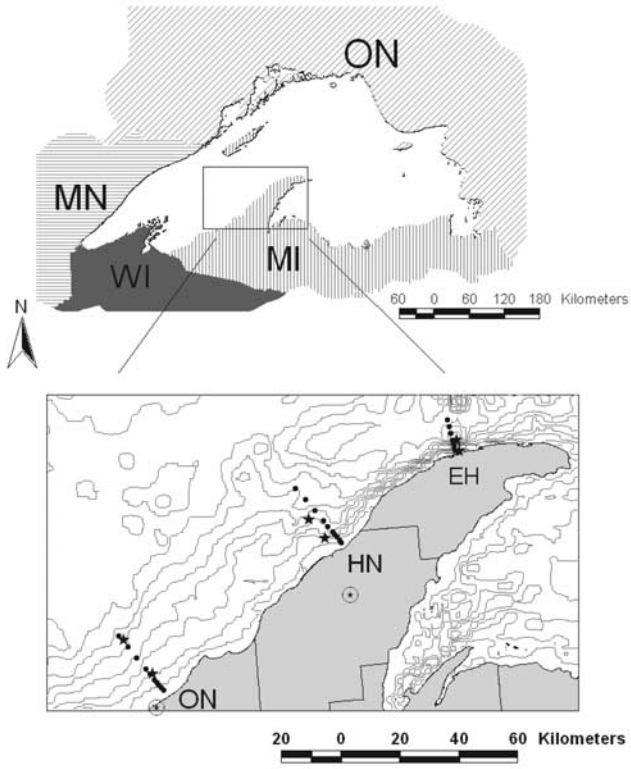

Figure 1. Study area and locations of three major study transects (solid circles) with associated sediment traps (stars).

approximately monthly from May to July in 1998 and from May to October in both 1999 and 2000. One sampling cruise in March 1999 was conducted aboard the ice breaker *Samuel Risley*. On each cruise, sampling was conducted in each of the three regions of the study area along one or more transects oriented perpendicularly to shore (305°–350°). Nine stations were visited along each transect.

[12] At each station, water samples were collected in Niskin bottles after a profile of the water column was obtained with a Seabird (SBE-19 or SBE-25) conductivity-temperature-depth probe (CTD). Also measured with the CTD profile (1 m depth resolution) were dissolved oxygen (Seabird), pH (Seabird), chlorophyll fluorescence (WET Labs WET Star fluorometer), and transmissivity (WET Labs C-star transmissometer). Calibration of probes on the CTD was checked monthly for pH and transmissivity and annually for dissolved oxygen. Discrete water samples were collected throughout the water column (surface to 3 m above bottom) at depth increments of 5–50 m for characterization of chemical (nutrients, major ions, trace metals) and biological (carbon fixation, respiration, bacterial abundance and growth, algal abundance zooplankton abundance) parameters.

2.3. Sample Processing and Analysis

2.3.1. Carbon Analyses and DOM Characterization

[13] Samples for analysis of DOC were filtered immediately onboard ship through 0.2 μm nylon filters (Gelman Sciences) and stored in precombusted amber glass vials at 4°C until analysis. Analysis (persulfate-assisted UV digestion) was performed on an OI Analytical 1010 Wet Oxidation TOC Analyzer. The analytical detection limit was 0.2 mg/L and precision was generally better than 5%. Field blanks were subtracted from all samples. In 2000, filtration of samples was discontinued because it was found that DOC and TOC were indistinguishable. However, the precision of measurements in 2000 samples was much poorer, and these results are not reported.

[14] Particulate organic carbon (POC) was measured by filtering (onboard ship) 2–20 L of lake water through precombusted glass fiber filters (Gelman GF/F). After drying (60°C, 24 hours) and weighing, the filters were analyzed for carbon (C) and nitrogen (N) on a Carlo Erba NA-1500 Elemental Analyzer. Precision for these analyses was 5% and results were always within 5% of certified standards (NIST Buffalo River Sediments) as found by *Anderson* [1998] who used a similar technique.

[15] In 2002 and 2003, a total of 13 DOC samples were concentrated by tangential flow ultrafiltration (TFF) and the DOC fraction >1 kDa in size was subsequently analyzed for element and isotopic composition [*Lu*, 2004]. Samples (20 L) were prefiltered through 0.45 μm (Gelman Aquaprep 600 capsule with Supor filter) and 0.1 μm filters (Pall SpiralCap Filter capsules with Supor membranes) prior to concentrating with a Millipore TFF unit (0.23 m^2 cellulose ester membrane with 1 kDalton pore size). With an inlet pressure of 10 psi, a permeate flow of 0.25 L/hr was obtained. The 20 L samples were concentrated to a final volume of 0.5 L; this material was freeze dried and homogenized with mortar and pestle. The dried material was exposed to acid fumes to remove inorganic carbon, and then analyzed for carbon and nitrogen content (Carlo Erba Element Analyzer), and C and N isotope ratios at the Environmental Isotope Laboratory (University of Waterloo). Isotope ratios are expressed in the conventional delta notation relative to PeeDee Belemnite and atmospheric nitrogen. Precision on isotope ratios was 0.1‰ for $\delta^{13}C$ and 0.2‰ for $\delta^{15}N$; ratios for NIST SRM #2704 (Buffalo River Sediments) were within 1% of the round robin value for $\delta^{13}C$ and within 10% for $\delta^{15}N$.

2.3.2. Respiration

[16] Community respiration was measured with bottle incubations (3–5 day duration) in the dark under in situ temperatures. Details of the protocols are provided by *Apul* [2000] and *Urban et al.* [2004a]. Incubations were started in 300 mL glass BOD bottles onboard ship immediately after sample collection. Oxygen consumption in the bottles was assayed with an automated Winkler titration technique [*Carignan et al.*, 1998] with sodium azide added to minimize interference from nitrate [*Graneli and Graneli*, 1991]. A respiratory quotient of one was used to convert oxygen consumption to carbon. Precision of the technique was ±10–15% of the respiration rate.

2.3.3. Photosynthesis

[17] Net primary production (NPP) was measured as ^{14}C uptake in 8 hour incubations. An 8 hour incubation yields C fixation rates closer to net than to gross production [*Peterson*, 1980], and hence these measurements include autotrophic respiration as well as photosynthetic C fixation. Details of the measurements are provided elsewhere [*Auer and Bub*, 2004; *Bub*, 2001]. Water samples were stored at lake temperatures in the dark, and ^{14}C uptake was measured within 24 hrs following the procedure of *Wetzel and Likens*

[1991]. Samples were transferred to 60 mL glass BOD bottles, inoculated with 5 μCi $NaH^{14}CO_3$, and incubated at saturating light intensity (600–800 μE/m^2 s) for 8 hours, and then filtered. Filters were air dried, exposed to acid fumes, and placed in 20 mL scintillation vials with cocktail prior to counting on a Beckman LS 6000 IC Liquid Scintillation Counter (LSC). No quench correction was necessary. To correct rates measured at saturating light intensities to ambient conditions, the photosynthetic response to light intensity (*P-I* curve) was measured on eight occasions in 1999–2000. When the lake was isothermal, a single *P-I* curve was measured using a surface water sample. When the lake was stratified, two *P-I* curves were measured: one from the surface, and one from the deep chlorophyll maximum (typically 30–35 m). Each *P-I* curve utilized 20–25 light intensities within the range of 0–1200 μE/m^2 s. Dark controls were measured in triplicate.

[18] On each cruise, ^{14}C uptake was measured at 10 surface stations and 3–15 depths at two stations. Areal rates of NPP were calculated for the two stations by integrating volumetric rates over specified depths of the water column. Volumetric rates were adjusted for ambient light intensity using the half saturation constant obtained from *P-I* curves. Ambient light intensity was calculated on an hourly basis, using a seasonal average hourly value for incident light, and cruise- and station-specific light extinction coefficient values (0.15–0.4/m (S. Green, Michigan Technological University, unpublished data, 2003)). Hourly rates of photosynthesis were summed for each depth to yield daily rates prior to integration over the water column (or mixed layer depth) to yield daily, areal rates.

[19] Excretion of ^{14}C was measured concomitantly with fixation. After the incubated water samples were filtered to remove the particulate ^{14}C, the water was acidified and bubbled to remove CO_2 prior to counting by LSC. The light dependence of excretion was measured identically as for fixation.

2.3.4. Bacterial Production

[20] Bacterioplankton production was assayed using tritiated thymidine [*Bell*, 1993]. Detailed procedures are available in the work of *Elenbaas* [2001]. Triplicate 20 mL water samples were amended with tritiated thymidine (1–1.8 mCi, 20 nM final concentration; New England Nuclear) and incubated for six hours in the dark at in situ temperatures. Blanks (samples receiving 2% formaldehyde immediately after thymidine addition) were subtracted from all samples. Uptake was terminated by addition of formaldehyde (2% final concentration). Samples were extracted in 5% trichloroacetic acid solution for 15 min on ice and then filtered through 0.22 μm mixed cellulose filters at gentle pressure. Filters were rinsed with cold 80% ethanol before placement in scintillation vials and dissolution in 1mL ethyl acetate. Ten milliliters of Scintiverse BD (Sigma Chemicals) was added and samples were counted with a Beckman LS 1600 IC Liquid Scintillation Counter. Counting efficiency was determined with external standards. Bacterial production was calculated using conversion factors of 2×10^{18} cells per mole thymidine and 20 fg C per cell [*Bell*, 1993].

2.3.5. Statistics

[21] Temporal and spatial variation in DOC concentrations was evaluated with ANOVA (GLR model, SAS® version 8), and significant differences were ascertained with Tukey's Studentized Range Test. To evaluate factors influencing bacterial production rates (480 measurements), product-moment correlation coefficients (pairwise) were calculated for the log-transformed variables including BP, chlorophyll-a concentration, total dissolved P concentration, DOC concentration, and temperature. Student t-tests were used for most other comparisons of means.

3. Results

3.1. Concentrations of DOC and POC

[22] The DOC concentrations measured in open lake waters (>5 km from shore) in this study (mean ± 95% CI = 1.42 ± 0.02 mg/L or 118 μM) were relatively constant (range 0.8–3.2 mg/L, Figure 2a). The maximum value observed in nearshore waters (0.1–5 km from shore) was 6.4 mg/L. These values agree well with those reported previously in the literature (1.3–2.5 mg/L [*Baker and Eisenreich*, 1989; *Baker et al.*, 1985; *Biddanda et al.*, 2001; *Maier and Swain*, 1978b]). Stable concentrations that vary little in space or time would be expected for a conservative or slowly reacting substance.

[23] However, statistically significant spatial and temporal variability was observed in DOC concentrations in this study. Concentrations of DOC at the southwestern end of the study region (ON and OS transects) were higher in each year (1998 mean ± 95% CI = 1.43 ± 0.01 mg/L, 1999 mean = 1.61 ± 0.03 mg/L) than at either of the other two major study areas (central transects 1998 mean = 1.35 ± 0.04 mg/L, 1999 mean = 1.46 ± 0.02 mg/L, northeastern transects 1998 mean = 1.35 ± 0.02 mg/L, 1999 mean = 1.49 ± 0.02 mg/L). Both the Bad River (mouth located 110 km southwest of the study region) and the Ontonagon River are large sources of DOC to the lake (8.4 and 13 Gg/yr, respectively) and might contribute to the high DOC concentrations in the southern end of the study region. The trajectory of the Keweenaw Current also might cause river inputs in this region to be diluted with open lake water more slowly than further to the north.

[24] Concentrations of DOC were significantly higher in the nearshore region (<5 km from shore) than offshore prior to summer stratification (Figure 2a). Such a distribution is consistent with a terrestrial source for a large fraction of the DOC. However, higher chlorophyll concentrations also were found in the nearshore region [*Bub*, 2001; *Warrington*, 2001], and thus production of autochthonous DOC also is likely to be higher in the nearshore region. Autochthonous production probably is responsible for the higher concentrations observed in surface waters as compared with deeper waters during the period of stratification (Figure 2a). A significant ($P < 0.01$) correlation exists between chlorophyll-a and DOC concentrations for all samples in the top 25 m of the water column (Figure 2b). This relation may indicate that upon a constant background of terrigenous DOC (1.39 ± 0.03 mg/L) are superimposed variations in the amount of autochthonous DOC; alternatively, the "background" DOC may comprise both autochthonous and allochthonous OC and may be maintained by limitations on bacterial uptake capacity or simply a balance of production and decay.

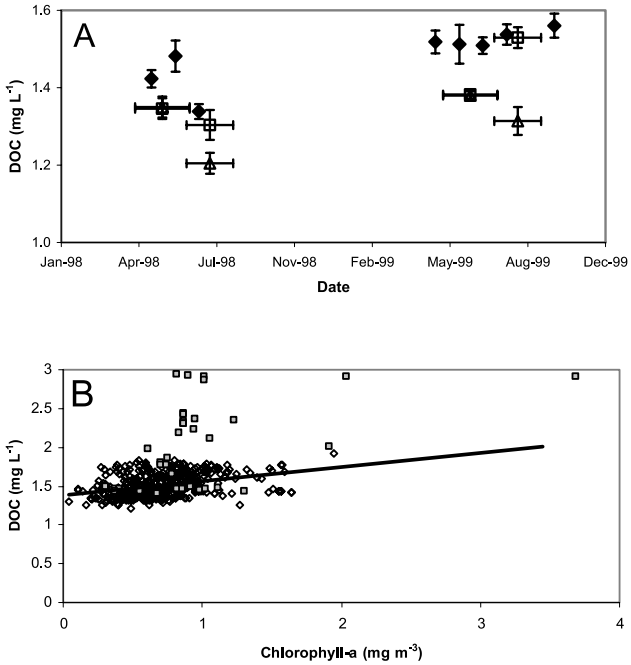

Figure 2. (a) Temporal changes in dissolved organic carbon (DOC) concentrations. Vertical error bars represent 95% confidence intervals about the values. Solid diamonds represent monthly means based on all samples (4–460) collected in any given month. Open squares are offshore (>5 km from shore) samples from surface waters (0–25 m); means are shown for stratified and unstratified periods (indicated by horizontal error bars) of each year. Open triangles are offshore samples from deep waters (>40 m) with means for stratified and unstratified periods. Surface and deep waters have identical DOC concentrations prior to stratification, but epilimnetic waters in summer have significantly higher concentrations than hypolimnetic waters. (b) Correlation between concentrations of chlorophyll-a and DOC for samples from the top 25 m of the water column. Shaded squares represent samples collected within 1 km of the shore near the mouth of the Ontonagon River. The solid line is the regression for the open symbols; the regression is significant ($P < 0.01$), the slope is significantly greater than zero, and the intercept is 1.39 ± 0.03 mg L^{-1} (±95% CI).

[25] Significant temporal variations were observed on annual and seasonal timescales (Figure 2). The mean DOC concentration for 1998 (mean ± 95% C.I. = 1.39 ± 0.02 mg/L) was significantly lower than the annual means for 1999 or 2000 (1.52 ± 0.01 and 1.47 ± 0.06 mg/L, respectively). The water level in the lake was higher in 1998 than in 1999 or 2000, and thus it would appear that lower DOC concentrations in the lake in 1998 were not a result of lower inflows but most likely due to internal processes. 1998 was an El Niño year with high surface water temperatures and an early onset of stratification. Chlorophyll concentrations were not higher in 1998 than in the other two years of the study, but community respiration rates were markedly higher [*Urban et al.*, 2004a].

[26] In 1999, DOC concentrations in offshore, surface (0–25 m) waters were significantly higher during the period of lake stratification (July–November) than during the unstratified period (Figure 2a). Water level in the lake peaks annually in August as a result of river flow exceeding evaporation. In the rivers studied in this project, highest DOC concentrations were observed at times of highest water flow (February–April). Thus the seasonal peak in DOC concentrations within the surface waters is not synchronous with the period of maximum DOC input from the watershed although confinement of river inputs to the smaller volume of the summer epilimnion could induce an increase in DOC concentrations in surface waters. Autochthonous production of DOC might be expected to peak between June and August when chlorophyll concentrations and rates of primary production are maximal. If the difference (0.07–0.15 mg/L) between DOC concentrations in the epilimnion and hypolimnion during summer stratification represented only autochthonous DOC production, this newly produced autochthonous DOC would constitute 5–10% of the total epilimnetic DOC.

[27] Particulate organic carbon (POC) suspended in the water column is not a large reservoir in Lake Superior, and much of it is derived from sediment resuspension. The average POC (±95% CI) of 293 samples was 0.08 ± 0.005 mg/L, or only 5% of the average DOC concentration. Hence given an analytical precision of 5%, there is no significant difference between DOC and TOC. The organic carbon content (mean ± 95% CI) of the seston (n = 293) was found to be 220 ± 18 mg/g. The KITES results agree with earlier studies; *Halfon* [1984] reported a range of POC of 0.05–0.31 mg/L, *Anderson et al.* [1998] reported a value of 0.07 mg/L, *Ostrom et al.* [1998] reported concentrations of 0.01–0.04 mg/L, and *Baker et al.* [1985] and *Baker and Eisenreich* [1989] reported a range of 0.09–0.48 mg/L with organic carbon contents of 220–420 mg/g. At first glance, the organic carbon content appears inversely proportional to the suspended solids concentration (Figure 3). However, at suspended solids concentrations between 0.2 and 0.8 mg/L, there is a large spread in the organic carbon content. Higher suspended solids concentrations (>1 mg/L) are generated only by resuspension of sediments with an organic carbon content of about 50 mg/g. Organic carbon contents of 25–30 mg/g have been reported for the "fluff" or unconsolidated layer of sediments [*Baker and*

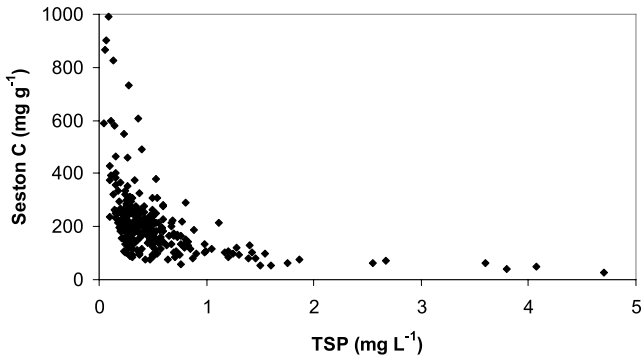

Figure 3. Organic carbon content of total suspended particles (TSP). The inverse relationship results from mixing of two end-members: resuspended sediments with low carbon content and autochthonous organic matter.

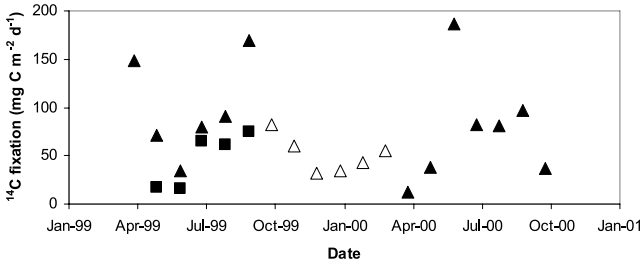

Figure 4. Seasonal pattern of integrated photosynthesis rates at offshore (solid triangles) and nearshore (solid squares) sites. The offshore site is 21 km from shore along the HN transect and has a water depth of 180 m; the nearshore site is 3 km from shore with a water depth of 22 m. Open triangles represent modeled rates of photosynthesis during winter months.

Eisenreich, 1989; *Chai*, 2005]. The spread in organic carbon content at low suspended solids concentrations reflects the fact that two sources of particles (phytoplankton, resuspended sediments) with very different carbon contents each contribute significantly to the inventory of suspended solids.

[28] Colloidal organic carbon (1 kDa < COC < 0.2 μm) collected by tangential flow filtration and freeze drying represented 35–50% of total DOC (<0.2 μm). The average C:N ratio of this material was 25.7 ± 2.6 (mean ± S.D., n = 13); isotope ratios were −27.1 ± 1.0 for δ^{13}C and 4.0 ± 1.7 for δ^{15}N.

3.2. Respiration

[29] Community respiration rates measured with bottle incubations ranged from 2 to 166 μg C/L d. The average rate for 1998 (72 ± 50 μg C/L d, mean ± S.D.) was much higher than the average in 1999 (12 ± 7 μg C/L d) presumably as part of the complex response of the lake to the strong El Niño conditions in 1998. The few values of bacterial and community respiration rates (5–16 μg C/L d) in surface waters of Lake Superior measured by *Biddanda et al.* [2001] are within the same range as the 1999 rates. These rates are at the low end of values reported for oligotrophic lakes (1–500 μg C/L d [*Ahrens and Peters*, 1991; *Carignan et al.*, 1998, 2000; *Cole et al.*, 1984; *Cornett and Rigler*, 1986, 1987; *del Giorgio and Peters*, 1994; *Linsey and Lasenby*, 1985]) and about 2–10 times higher than rates in the open ocean (0.3–10 μg C/L d [*Emerson et al.*, 1995; *Kepkay and Johnson*, 1989; *Williams and Purdie*, 1991]). The rates measured with bottle incubations agreed well with estimates based on hypolimnetic oxygen consumption (3–12 μg C/L d) and rates of gas exchange (<0–17 μg C/L d) for the KITES study region [*Urban et al.*, 2004a], and also agreed well with hypolimnetic oxygen consumption rates (equivalent to 2–9 μg C/L d) estimated for the western basin of Lake Superior [*McManus et al.*, 2003]. Accounting for the decrease in respiration rates with depth during the stratified season [*Urban et al.*, 2004a], a better estimate of the lake-wide mean for 1999 is 9.7 μg C/L d.

[30] No seasonal differences were observed in rates of respiration. Although laboratory incubations at different temperatures showed a clear response to temperature, there was no correlation between rates measured on different dates and the ambient water temperatures. Similarly, there was no significant difference between rates measured in the shallower and warmer waters of the southwest region of the study area and rates in the deeper, cooler northeast region. Respiration rates in nearshore (<5 km) waters were, however, significantly (paired t-test, $p < 0.05$) higher than rates in offshore (>5 km) waters.

[31] Community respiration rates include contributions from autotrophs, heterotrophic bacteria, and zooplankton. On the basis of the abundances of these organism groups in Lake Superior as reported by *Fahnenstiel et al.* [1998] and on specific respiration rates measured in lakes [*Ahrens and Peters*, 1991], *Apul* [2000] estimated that bacteria contributed 80%, autotrophs 15%, and zooplankton 5% of total community respiration. Paired measurements of bacterial and community respiration rates in Lake Superior indicated that bacteria accounted for closer to 98% of community respiration [*Biddanda et al.*, 2001]. Thus it would appear as if there is little (∼0.8 Tg/yr) overlap (i.e., double counting of autotrophic respiration) in the measurements of community respiration and NPP.

[32] The mean rate given above for 1999 (9.7 μg C/L d) represents the mean for only seven months, but several features of the lake facilitate extrapolation to an annual rate. First, as mentioned above, no seasonal variations were observed in the seven months of respiration measurements [*Urban et al.*, 2004a]. Second, although a moderate temperature dependence of respiration rates (Q_{10} of 1.5) was observed in the laboratory [*Urban et al.*, 2004a], the small seasonal variations in mean lake temperature in Lake Superior (monthly means range from minimum of 1.3°C in March to 5.1°C in September [*Bennett*, 1978]) result in only small temperature-induced variations in respiration rates through the majority of the lake volume. The range in extrapolated annual respiration rates obtained with and without the temperature correction is only 41.5–42.3 Tg C/yr. The only statistically significant spatial variation that was observed was a difference between near- and offshore waters; the lake-wide mean rate was calculated by weighting the mean near- and offshore rates by their respective fractions of the total lake volume resulting in a difference between the estimate of the lake-wide mean (9.7 μg C/L d) and the KITES area mean (12 μg C/L d).

3.3. Photosynthesis

[33] Volumetric rates of ^{14}C uptake ranged from <0.05 to 5 mg C/m^3 hr under saturating light intensities and ambient nutrient and temperature conditions [*Bub*, 2001]. A similar range was reported in the 1970s (0.5–3.5 mg C/m^3 hr [*El-Shaarawi and Munawar*, 1978]). Rates of 2.2–8.8 mg C/m^3 hr (also for optimal light intensities of 8000–30,000 lux) were reported by *Vollenweider et al.* [1974] based on a review of earlier literature. *Fee et al.* [1992] also reported volumetric rates of 0.5–3 mg C/m^3 hr under optimal light intensities. There appears to be general agreement as to the range of instantaneous, volumetric rates of photosynthesis in the lake.

[34] Very different monthly patterns of areal rates of C fixation were observed in offshore waters in 1999 and 2000 (Figure 4). In 1999, rates declined from early May

(150 mg C/m^2 d) through June and then climbed through summer to reach a maximum rate in September (160 mg C/m^2 d). In 2000, low rates in April and May (10–40 mg C/m^2 d) were followed by very high rates in early June (200 mg C/m^2 d), fairly uniform rates through summer (~100 mg C/m^2 d), and low rates (<50 mg C/m^2 d) in September and October. The reason for these different patterns is not known. The lake had no ice cover in the 1998–1999 winter and only a maximum of about 20% ice cover in the 1999–2000 winter; ice cover is thought to control the amount of phosphorus added to the Great Lakes by fall and winter resuspension [*Nicholls*, 1998]. Total dissolved phosphorus (TDP) concentrations were only about half as high in 2000 as in 1999 [*Siew*, 2003]. The increase in photosynthesis rates in September 1999 occurs at least a month before the fall increase in TDP concentrations [*Siew*, 2003].

[35] The total areal production measured in the seven months of each year amounted to 18 and 16 g C/m^2 at the offshore stations. Extrapolation to a lake-wide annual mean must account for potential spatial and seasonal variations. The lake-wide survey in 1973 indicated that approximately 85% of the lake area could be characterized by a single rate of primary production [*El-Shaarawi and Munawar*, 1978]; assuming that situation existed in 1999 and 2000 as well, the offshore rates measured in this study should be representative of about 85% of the lake surface area. Because no measurements were made in the region of higher productivity (as reported by *El-Shaarawi and Munawar* [1978]) we use our offshore mean for the entire lake; even if our measured rate in the offshore area were only half of the higher rate in the remaining 15% of the lake, the error incurred by using only the offshore rate to extrapolate to the entire lake is only about 13%. The effect of seasonal changes in temperature and light availability can be modeled explicitly to arrive at an annual rate if the measured *P-I* and temperature relationships [*Bub*, 2001] remain valid during late fall and winter. Results of such modeling are shown in Figure 4 which uses mean monthly chlorophyll concentrations for winter months measured at a water intake on the north shore (Ontario Ministry of the Environment, unpublished data, 2004). The average NPP for the two years is 25 g C/m^2 yr using the modeled values for months in which no measurements were made in this study. While this value is uncertain, the annual rate probably lies between 16 g C/m^2 yr (the total for the 7 months of measurements) and 36 g C/m^2 yr (the sum of the 7 months of measurements plus 5 months at the average daily rate measured in this study). These estimates of annual production are near the low end of the range of estimates (30–65 g C/m^2 yr [*Fee et al.*, 1992; *Johnson et al.*, 1982; *Maier and Swain*, 1978a; *Vollenweider et al.*, 1974]) previously reported in the literature.

[36] For the period April–June, chlorophyll concentrations are higher in nearshore (within 5 km of shore) waters [*Auer and Bub*, 2004]. Remote sensing confirms that this generality holds for most of the lake [*Budd*, 2004]. However, comparison of depth integrated rates of C fixation indicate that in spring and summer, areal rates of photosynthesis are higher in offshore waters because of the deeper mixed layer [*Bub*, 2001, Figure 4]. Because there is no net sediment accumulation in the nearshore zone, some fraction of the carbon fixed in this region is exported to offshore waters. Indeed, it is this export of labile material that is thought to be responsible for the organic rich particles in the benthic nepheloid layer [*Urban et al.*, 2004b] and for supplying the food to support a narrow ring of high densities of benthic organisms located generally between 4 and 10 km from the shoreline [*Auer and Kahn*, 2004]. If all primary production in nearshore waters (~30% of lake total) were exported to the offshore zone, the rate of input of autochthonously produced carbon to the mid-lake area would be increased by 40%.

[37] A fraction of photosynthetically fixed carbon is quickly excreted to the water column. This pool of DOC has been found to be primarily high molecular weight and labile in marine systems as well as a significant contributor to marine snow [*Amon and Benner*, 1994; *Amon et al.*, 2001]. Excretion of ^{14}C during 8 hour incubations was, on average, 35% of the rate of carbon fixation. *Laird et al.* [1986] observed no bacterial uptake of the excreted ^{14}C during 8 hour incubations of Lake Michigan water although *Baines and Pace* [1991] report that microbial uptake can be 50% of release. Integrated depth profiles of carbon excretion yielded areal rates of 1–45 mg C/m^2 d; these rates represented 2–50% of the simultaneous areal rates of carbon fixation. Excretion rates ranged from 2–21% of fixation rates in Lake Michigan [*Laird et al.*, 1986], and *Teira et al.* [2001] reported rates ranging from 4–42% across a range of oceanic waters. Rates measured in this study appear consistent with these earlier values.

3.4. Bacterial Production

[38] Rates of bacterial production ranged from 0.01 to 0.4 mg C/m^3 hr [*Auer and Powell*, 2004; *Elenbaas*, 2001]; the mean (±95% CI) of nearly 400 measurements was 0.034 ± 0.006 mg C/m^3 hr. These rates compare well with those (0.01, 0.11 mg C/m^3 hr) reported by *Hicks and Owen* [1991] for surface and near-bottom waters of an open-lake station, and with the two values (0.024, 0.048 mg C/m^3 hr) reported by *Biddanda et al.* [2001] for an open-lake station. Bacterial production in 2000 (undetectable to 0.22 mg C/m3 hr, mean ±95% CI = 0.013 ± 0.003 mg C/m^3 hr) was significantly lower than in 1999 (undetectable to 0.40 mg C/m3 hr, mean ±95% CI = 0.054 ± 0.012 mg C/m^3 hr). Seasonally, bacterial production rates in both 1999 and 2000 were markedly higher during summer stratification than in the period of May to mid-July (Figure 5a). Such seasonality is expected in response to lake temperatures [*Cotner et al.*, 2000]. In contrast, bacterial abundance exhibited different seasonal patterns in 1999 and 2000 (Figure 5b).

[39] Spatially, bacterial production was higher in nearshore than offshore waters (in 1999 0.039 ± 0.016 versus 0.014 ± 0.007 mg C/m^3 hr, in 2000 0.009 ± 0.003 versus 0.004 ± 0.001 mg C/m^3 hr) prior to stratification. This trend was statistically significant (Student's t-test) in both 1999 and 2000. During the stratified season, there was no significant difference between bacterial production in near- and offshore surface waters. In offshore waters during summer stratification, bacterial production was significantly higher in the epilimnion than in the hypolimnion in both 1999 (0.09 ± 0.03 versus 0.007 ± 0.002) and 2000 (0.016 ± 0.005 versus 0.004 ± 0.001).

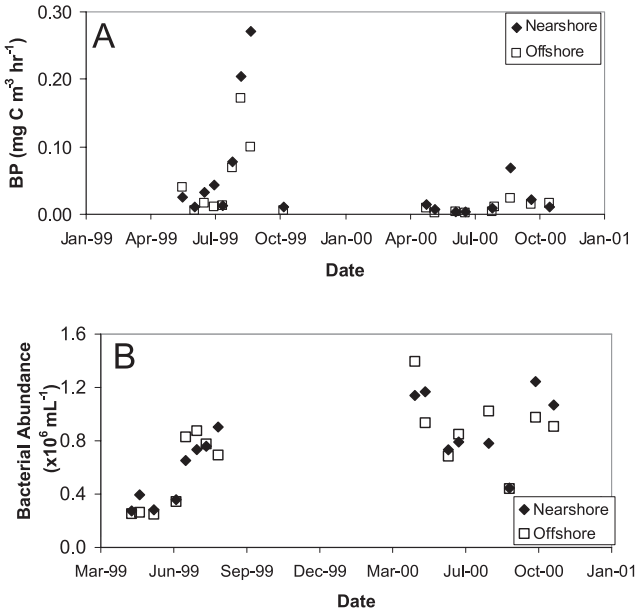

Figure 5. (a) Temporal variations in bacterial production rates. Shown here are the averages for all measurements made along the central transects; offshore rates are the averages for stations 6–21 km from shore, and the nearshore rates average those measured 1–5 km from shore. All water depths were included in the averages. (b) Temporal variations in bacterial abundance in surface waters. As in Figure 5a, nearshore averages all measurements within 5 km of the shore, and offshore averages measurements made 6–21 km from shore.

[40] The differences between 1999 and 2000 render estimation of a ''typical'' lake-wide rate of bacterial production difficult. The lake was partitioned into nearshore (5-km-wide zone representing 30% of the lake area but only 5% of the lake volume) and offshore zones and into stratified and unstratified periods. The stratified period typically extends from late July to mid-December [*Assel*, 1986; *Bennett*, 1978] and represents ~40% of the year. The estimated lake-wide rate of bacterial production in 1999 (0.018 mg C/m^3 hr or 1.8 Tg/yr) was more than threefold higher than the estimate for 2000 (0.005 mg C/m^3 hr or 0.5 Tg/yr).

[41] On several occasions, measurements of bacterial production and community respiration were measured simultaneously. Bacterial respiration was estimated to represent 80% of community respiration based on average abundance of phytoplankton and bacteria [*Apul*, 2000]. Bacterial growth efficiencies were calculated to be in the range of 3–65% [*Apul*, 2000]; if bacterial respiration represented closer to 98% of community respiration [*Biddanda et al.*, 2001], these efficiencies would be reduced to 2–52%. Growth efficiencies in offshore surface waters (3–20%) were consistently lower than growth efficiencies in nearshore surface waters (6–46%). In both near- and offshore sites, growth efficiencies increased with depth in the water due presumably to the harmful effects of UV radiation in surface waters. The growth efficiencies measured in this study span the range of those reported for freshwaters [*Biddanda et al.*, 2001; *Pace and Cole*, 1996].

[42] Correlation analysis (Table 1) indicates that bacterial production was significantly correlated with DOC and P concentrations but not with chlorophyll concentrations. A significant correlation also was observed between temperature and bacterial production.

3.5. River Loadings

[43] Approximately 100 water samples were collected from 12 tributaries between the Bad River in Wisconsin and the Eagle River in Michigan. Among the 59 samples analyzed for DOC the range of concentrations was 2.8–15 mg/L with a mean (±S.D.) of 7.9 ± 3 mg/L. *Maier and Swain* [1978a] reported a similar range of DOC of 5–36 mg/L for tributaries to Lake Superior in Minnesota and Canada. Most of the twelve rivers in this study are small and contribute negligibly to mass inputs to Lake Superior [*Robertson*, 1997]. The three largest rivers (Ontonagon, Bad, Sturgeon) in the study region rank 7th, 11th, and 13th among all tributaries to Lake Superior in terms of average flow rates. Concentrations of DOC in these three rivers were similar to the larger set (range = 3.7–15 mg/L, mean ± S.D. = 8.3 ± 3.0). As has been reported for numerous other rivers [e.g., *Mulholland and Kuenzler*, 1979; *Schiff et al.*, 1997], DOC concentrations increased with flow in the three large rivers studied here (Figure 6).

[44] Estimation of the riverine loading of DOC to Lake Superior is complicated by the nonlinear relationship of flow to DOC concentration. Use of the mean concentration (8.3 mg/L) measured in this study for all tributaries yields an input (0.44 Tg/yr) that is 25% lower than that calculated using the flow-weighted mean concentration (10.7 mg/L) measured in this study. Another alternative is to apply the relationship between flow and concentration measured in this study (Figure 6) to the mean flow rates for all of the major tributaries; this approach yields an even higher

Table 1. Correlation Coefficients Between Bacterial Production (BP) and Related Water Quality Variables (All Log-Transformed)

	Chlorophyll-a	TDP[a]	DOC[b]	Temperature	BP
Chlorophyll-a, mg m^{-3}	1				
Total dissolved P, mg m^{-3}	0.036	1			
DOC, mg L^{-1}	0.365[c]	0.112	1		
Temperature, °C	−0.018	0.538[c]	0.273[c]	1	
BP, mg C m^{-3} hr^{-1}	0.057	0.267[c]	0.426[c]	0.380[d]	1

[a]Total dissolved phosphorus.
[b]Dissolved organic carbon.
[c]Significant at $P < 0.01$.
[d]Significant at $P < 0.05$.

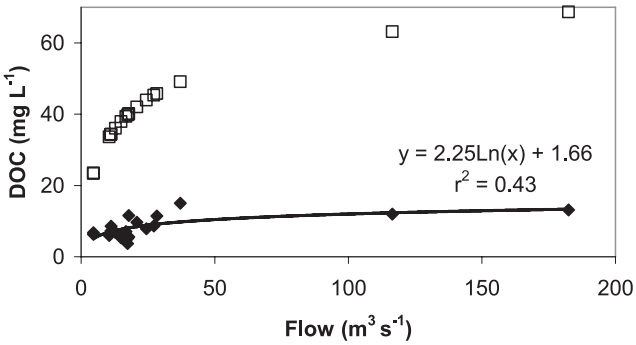

Figure 6. Relationship between river flow and DOC concentrations. Solid diamonds are data for the three large rivers in this study (Ontonagon, Bad, Sturgeon). Open squares are data for the Sturgeon River flowing into Lake Michigan (data from *Geffert* [1999]).

estimated input of 0.76 Tg/yr. The validity of applying this relationship to all tributaries is questionable as illustrated by the very different DOC-flow relationship exhibited by another river in the upper peninsula of Michigan (Figure 6). Loads estimated using the range of reported DOC yields from forested catchments at this latitude (3–7 g/m^{2}yr [*Dillon and Molot*, 1997; *Maier and Swain*, 1978a]) yield a range of 0.4–0.9 Tg C/yr.

3.6. Budgets for Organic and Inorganic C

[45] The organic carbon budget for Lake Superior (Table 2) is out of balance. Atmospheric deposition of organic C to Lake Superior was not measured directly. A range of 0.02–0.1 Tg/yr was estimated from the typical DOC concentrations observed in marine and continental rainfall [*Willey et al.*, 2000]. This range spans the average loading (0.84 g C/m^2 yr or 0.07 Tg/yr) measured for small lakes in Ontario [*Dillon and Molot*, 1997]. The input from shoreline erosion was estimated from the shoreline erosion rate [*Kemp et al.*, 1978] and the OC content of postglacial clays, the major fine-particle component of the eroded material. The basis for the range of river loadings was discussed above. Inputs from photosynthesis include both ^{14}C fixation and excretion (on average, 35% of fixation). The range of fixation rates reported for the lake is 18–60 g C/m^2 yr or 1.5–4.9 Tg C/yr [*Bub*, 2001; *Fee et al.*, 1992; *Johnson et al.*, 1982; *Maier and Swain*, 1978a; *Vollenweider et al.*, 1974] yielding a photosynthetic input (including excretion) of 2.0–6.7 Tg/yr. Lake outflow has been estimated simply as the mean concentration measured in this study (1.42 mg/L) times the mean water outflow (2218 m3/s [*Quinn*, 1992]). The estimated burial rate undoubtedly has a large uncertainty; it is an average surface OC accumulation rate for 32 dated (^{210}Pb) and focusing-corrected sediment cores [*Johnson et al.*, 1982; *Kemp et al.*, 1978; *Klump et al.*, 1989]. The range of respiration rates measured in 1999 corresponds to 13–81 Tg C/yr; as discussed above, the "best estimate" based on spatial variations is 42 Tg C/yr. The sum of inputs (2.4–7.7 Tg/yr) is much less than the sum of outputs (13.2–83.1 Tg/yr).

[46] Double counting of autotrophic respiration contributes negligibly to the imbalance in the organic carbon budget. Autotrophic respiration (AR) is included in NPP (NPP = GPP − AR where GPP is gross primary production) and in community respiration (CR = BR + AR + ZR where ZR is zooplankton respiration). Autotrophic respiration was not measured directly, but it may be estimated in two ways. First, the comparison of community and bacterial respiration [*Biddanda et al.*, 2001] suggested that autotrophic respiration must be less than 2% of community respiration or <0.8 Tg C/yr. Autotrophic respiration generally is found to be less than 15% of the maximum rate of algal photosynthesis under saturating light (Pmax [*Peterson*, 1980]). On the basis of the measured profiles of P_{max}, a maximum annual rate of autotrophic respiration is estimated to be 0.7–1.1 Tg C/yr. Clearly, autotrophic respiration is not large enough to account for the discrepancy between OC inputs and outputs in Lake Superior.

[47] A mass balance for dissolved inorganic carbon (DIC) was also estimated to interpret the estimated fluxes of CO_2 above the lake. The average DIC concentration in the lake is calculated to be 10.2 mg/L based on previous literature [*Thompson*, 1978; *Weiler*, 1978; *Zarull and Edwards*, 1990] and 10.9 mg/L based on KITES measurements. Using the average lake concentration and outflow, an output of 0.71–0.76 Tg/yr is calculated. The input from precipitation is negligible (~0.01 Tg/yr [*Dillon and Molot*, 1997; *Willey et al.*, 2000]). There is probably some DIC input from disso-

Table 2. Summary of Organic C Fluxes Into and Out of Lake Superior

Source/Sink	C Flux, Tg yr^{-1}	Notes and References
Total inputs	2.4–7.7	
Shoreline erosion	0.02	shoreline erosion rate (4.6 million ton/yr) [*Kemp et al.*, 1978], C content of postglacial clays (0.5%) [*Johnson et al.*, 1982]
Rivers	0.4–0.9	explanation given in text
Precipitation	0.02–0.1	based on precipitation to lake of 70 cm/yr, DOC concentration range of 23–160 μM [*Dillon and Molot*, 1997; *Willey et al.*, 2000]
Photosynthesis	2.0–6.7	annual NPP has been reported in range of 18–60 g C m^{-2} yr^{-1} [*Bub*, 2001; *Fee et al.*, 1992; *Johnson et al.*, 1982; *Maier and Swain*, 1978a; *Vollenweider et al.*, 1974]
Total outputs	13.2–83.1	best guess for 1999 is 42.6
Lake outflow	0.1	lake concentration 118 nM and mean outflow 2210 m^3 s^{-1}
Respiration	13–81	measured community respiration (this study)
Sediment burial	0.16	*Johnson et al.* [1982]
	0.6–2.0	*Klump et al.* [1989]
	0.06–1.8	*Kemp et al.* [1978] mean = 0.45

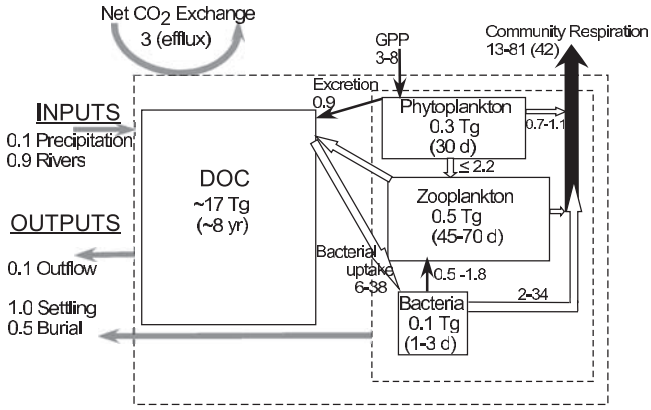

Figure 7. Carbon cycle in Lake Superior. Fluxes are in Tg C yr^{-1}, pool sizes are in Tg C, and residence times (pool/total influx) are given in parentheses. Shaded arrows denote system-scale measurements, black arrows denote process rates measured in small discrete samples, and white arrows are fluxes calculated by difference or using efficiencies discussed in the text. Net heterotrophy is indicated by (1) an excess of inputs over outputs (system scale), (2) a net degassing of CO_2, and (3) community respiration in excess of net primary production (NPP). There remains an imbalance between estimated rates of photosynthesis (GPP) and respiration (CR) that is not explained by system-scale inputs and outputs.

lution of calcite in the postglacial clays that are exposed in small areas of the lake [*Thomas and Dell*, 1978]. The major input is via rivers. *Thompson* [1978] estimated a river loading of 0.9–1.0 Tg/yr. The average DIC concentration measured in the 12 rivers of this study was 23 mg/L, slightly above the 17 mg/L reported by *Thompson* [1978] for the Ontonagon River. Thus the DIC mass balance suggests that the lake should evolve some CO_2 (~0.2–0.3 Tg/yr). Whether this evolution occurs in embayments close to river mouths or whether it occurs in the open lake is unknown. Superimposed on these net fluxes are the annual degassing and uptake of CO_2 in response to changes in temperature. The mean temperature of the lake changes only from 1.3°C in March to 5.1°C in September [*Bennett*, 1978], but this small change would be enough to cause evolution (spring, summer) and uptake (fall, winter) of ~40 gC/m^2 or 3.4 Tg C if the entire lake equilibrated with the atmosphere.

4. Discussion

4.1. Budget and Cycle for Organic Carbon

[48] A budget for organic C in Lake Superior (Table 2) makes several points immediately obvious. Photosynthesis represents the largest source of organic C to the lake, and respiration is the largest sink. Discharge of organic C from the lake is much smaller than the riverine input; apparently much of the terrigenous DOC supplied by rivers is degraded in the lake or lost to the sediments. Tabulated influxes (2.4–7.7 Tg/yr) are less than the sum of measured outputs (13–83 Tg/yr); either there are large errors in some measured fluxes or some inputs have as yet to be measured (e.g., photosynthesis in embayments, DOC in shallow subsurface flows, leaf and woody debris). Before examining this discrepancy further, it is useful to examine the pool sizes and other characteristics of C cycling in the lake.

[49] As do many oligotrophic aquatic systems [*Gasol et al.*, 1997], Lake Superior has an "inverted pyramid" of biomass with heterotrophic biomass greater than that of autotrophs (Figure 7). Phytoplankton biomass may overestimate autotrophic biomass because some fraction of the cryptophytes and chrysophytes (together accounting for ~50% of phytoplankton biomass [*Barbiero and Tuchman*, 2001; *Fahnenstiel et al.*, 1998, 1986]) are undoubtedly mixotrophic [e.g., *Sherr and Sherr*, 2000; *Turner and Roff*, 1993]. Picoplankton represent nearly 50% of the phytoplankton biomass, but bacteria represent only 10–15% of the heterotrophic biomass [*Fahnenstiel et al.*, 1998]. The total pool of particulate organic carbon (~1 Tg) is only 5–7% as large as the pool of DOC (~17 Tg), and biomass as reported by *Fahnenstiel et al.* [1998] can account for 70–90% of the POC. It has been suggested [*Zhou et al.*, 2001] that mortality and growth rates of large mesograzers in Lake Superior make possible the inverted pyramid (mesograzers represent ~60% of total heterotrophic biomass [*Fahnenstiel et al.*, 1998]), but an alternative hypothesis is that organic carbon inputs from the catchment support a significant portion of the heterotrophic biomass.

[50] Autochthonous DOC production and organic carbon inputs from the catchment support the largest pool of organic C in the lake, the DOC (Figure 7). The specific absorbance (absorbance at 285 nm divided by DOC concentration) of the lake DOC (~50 L/mole cm [*Ma and Green*, 2004]) is much lower than that of DOC in the inflowing Sturgeon River (300 L/mole cm) suggesting that lake DOC is not highly aromatic and may contain a substantial fraction of nonterrigenous origin [*Chin et al.*, 1994]. The mass balance for organic carbon (Table 2, Figure 7) also points to autochthonous sources; the excretion rate of DOC by phytoplankton (0.9 Tg/yr) is comparable in magnitude to the estimated input of DOC in rivers (0.4–0.9 Tg/yr). Ultrafiltration and characterization of the colloidal organic carbon (i.e., 1 kDa < COC < 0.2 μm) also confirm that the DOC pool has both terrigenous and autochthonous components. The colloidal fraction (35–50% of bulk OC) in Lake Superior is intermediate in size between that of terrigenous material (40–80% [*Guo et al.*, 2003; *Hedges et al.*, 2000]) and the mixture of well-aged terrigenous DOC and autochthonous DOC found in the oceans (22–35% colloidal [*Amon and Benner*, 1994; *Benner et al.*, 1997, 1992]) or in shallow lakes with long residence times (27% colloidal [*Waiser and Robarts*, 2000]). Clearly, the DOC pool is not unaltered terrigenous material. Because the $\delta^{13}C$ values of terrigenous DOC (−25.3 to −30.3‰ [*Guo et al.*, 2003; *Lara et al.*, 1998; *Lobbes et al.*, 2000; *Schiff et al.*, 1990, 1997]) and photochemically altered terrigenous DOC (−25.8 to −26.6‰ [*Opsahl and Zepp*, 2001]) overlap with that of autochthonous OM in Lake Superior (−26 to −27.8 [*Keough et al.*, 1996; *Lu*, 2004; *Ostrom et al.*, 1998]), the $\delta^{13}C$ value for the colloidal OC (−27.1 ± 1.0) is not helpful in resolving its source. The molar C:N ratio of the colloidal fraction (25.7 ± 2.6, mean ± S.D.) is much lower than ratios for riverine colloidal OC (34–48 [*Guo et al.*, 2003; *Hedges et al.*, 2000]) but higher than in

the surface oceans (C:N $\sim$ 16) where the colloidal pool is largely of algal origin [*Amon and Benner*, 1994; *Benner et al.*, 1997]; evidently, a significant fraction of the colloidal organic carbon (COC) pool in Lake Superior is of autochthonous origin. The fraction of the COC that is of terrestrial origin may be calculated to be 55–85% for a range of C:N ratios for autochthonous COC of 8–16 and for terrigenous COC of 35–48. If all low-molecular-weight (LMW) DOC were of terrigenous origin, terrigenous OC would constitute 80–95% of the total DOC (i.e., LMW + COC) pool. This estimate agrees with our earlier estimate of autochthonous DOC in the summer epilimnion of 0.07–0.15 mg/L (5–15% of total DOC) based on seasonal DOC concentration changes (Figure 2a) and with the estimated terrigenous DOC concentration of 1.39 mg/L based on Figure 2b. Thus although the terrigenous DOC appears to have been altered in the lake, it nevertheless may be the major constituent of DOC in the lake.

[51] The dynamics of the DOC pool further suggest that the majority of the pool is only moderately reactive. The entire DOC pool (Figure 2a) undergoes only minor seasonal changes in concentration ($\leq$0.2 mg/L), and those changes (Figure 2b) are consistent with enhanced production in surface waters and continued decay of the bulk DOC pool in the hypolimnion during summer stratification. Division of the terrigenous DOC pool size (80–95% of total DOC = 14.7–16.8 Tg) by the estimated DOC influx in rivers (0.4–0.9 Tg/yr) suggests a residence time of 16–42 years, much less than the lake's hydrologic residence time (170 years) but very long relative to turnover of the biota. If the terrigenous input has been underestimated, the residence time will be correspondingly lower.

[52] The relative importance of respiration, photolysis, and particle scavenging as sinks for DOC may be estimated from data collected in this study. Lower DOC concentrations in the summer hypolimnion as compared to the well-mixed lake in spring (Figure 2a) suggest that dark processes such as microbial respiration or particle scavenging must be capable of degrading terrigenous DOC. Low C:N ratios in the sediments (8–10 [*Urban et al.*, 2004b]) indicate that particle scavenging is unimportant. A pseudo first-order rate constant (k_{resp}) and turnover time ($1/k_{resp}$) for microbial respiration may be estimated from measured bacterial production (1999 BP = 0.018 mg C/m^3 hr), bacterial abundance (BA = 0.6 $\times$ 10^6/mL), bacterial C content (f = 20 fg C/cell [*Bell*, 1993; *Fukuda et al.*, 1998]), and bacterial growth efficiency (BGE = 5–30%):

$$k_{resp} = \frac{BP}{BA \cdot f} \cdot \frac{1}{BGE}. \quad (1)$$

The calculated turnover times (1.5–8.3 days) are much too short; much higher input rates would be needed to sustain the measured DOC concentration at such a high rate of consumption. If the DOC concentration in the hypolimnion decreases only 0.1–0.2 mg/L (7–13%) over a 1–3 month period (Figure 2a), the turnover time for DOC would be 0.6–3.7 years (assuming negligible production in the hypolimnion). Although this rate is much slower than that calculated based on measured bacterial production, it is still much faster than the residence time estimated for terrigenous DOC in the lake (16–42 years).

[53] Similarly, the potential role for photolysis may be estimated by extrapolation from in situ incubations. In situ incubations (4–8 hours) of DOC in quartz tubes yielded a half-life of 144 hours (6 days) of daylight at the lake surface [*Ma and Green*, 2004]. Dividing the measured half-life by the photoperiod at the time of measurement accounts for the period of darkness, but the rate is probably still an overestimate because it spanned the period of maximum solar intensity rather than the whole period of daylight. Measured extinction coefficients for UVA light (324–380 nm) ranged from 0.4–0.9/m in offshore waters (S. Green, unpublished data, 2003). Accounting for seasonal variations in solar irradiation at the lake surface as well as for seasonal changes in photoperiod and integrating over the mixed layer (25–150 m depending on season [*Assel*, 1986; *Bennett*, 1978]) the turnover time (1/first-order rate constant) of DOC by photolysis is estimated to be between 4 and 8 years. Because the more energetic wavelengths are attenuated more rapidly in water and because wavelengths of $\sim$320 nm are most effective at photolyzing DOC [*Gao and Zepp*, 1998], the turnover time is likely to be at the long end of this range. These calculations suggest that respiration is 1.1–13 times faster than photolysis. However, because these turnover times are still shorter than the estimated residence time for terrigenous DOC in the lake (16–42 years), the entire pool of terrigenous DOC must not be susceptible to either photolysis or microbial decomposition at the rates calculated above. Rather, some fraction of the DOC pool must be less reactive or recalcitrant to both processes. In the study of *Ma and Green* [2004], rate constants decreased with increasing incubation time due to preferential loss of chromophoric DOC, and other studies have also reported that photobleaching is more rapid than photolytic mineralization of DOC [e.g., *Gao and Zepp*, 1998]. An upper limit for the labile fraction (f_{labile}) of terrigenous DOC is calculated to be 15% using the rate constants for photolysis and microbial respiration given above and the estimated residence time of terrigenous DOC in the lake (16–42 years) in equation (2):

$$\text{observed rate} = (k_{resp} + k_{photolysis}) f_{labile} \cdot [DOC] + k_{refractory}(1 - f_{labile})[DOC]. \quad (2)$$

[54] The high respiration rate constant calculated above from bacterial production points to a large bacterial carbon demand that must be met by a small pool of labile DOC that is cycled rapidly. Bacterial regrowth bioassays indicated the existence of a labile fraction (15–50% of DOC) that had a turnover time of a few days under the bioassay conditions [*Apul*, 2000; *Elenbaas*, 2001]. The calculated carbon demand of the bacteria (BP/BGE = 6–38 Tg C/yr in 1999 assuming BGE of 5–30%) is much larger than the estimated rate of carbon fixation (2.5 Tg/yr). There is at least a factor of 2 uncertainty in the thymidine:bacterial cell conversion factor [*Ducklow et al.*, 2002], but this uncertainty is not enough to account for the discrepancy between bacterial carbon demand and photosynthesis rates. For a growth efficiency of 5%, the bacterial production measurements predict a microbial respiration rate of 36 Tg/yr in 1999, close to the measured rate of community respiration (42 Tg C/yr). The

discrepancy between the estimated rate of bacterial carbon uptake (6–38 Tg/yr) and the supply rate of DOC to the lake (1.8 Tg/yr) reflects in part the unmeasured DOC production via viral lysis of cells, sloppy feeding by zooplankton, DOC release from fecal pellets and microbial breakdown of particulate organic carbon [e.g., *Sondergaard et al.*, 1995; *Strom et al.*, 1997]. However, estimated rates of microbial respiration require an additional input to the lake of up to 35 Tg/yr of organic carbon. Thus the apparent imbalance of the organic carbon budget (Table 2) points to a need to understand the constraints on microbial growth efficiencies. The respiration and bacterial production rates are consistent with a bacterial growth efficiency of ~5%, a value in line with recent literature [*Biddanda et al.*, 2001; *del Giorgio and Cole*, 1998] while the measured rates of photosynthesis and bacterial production are consistent with a BGE slightly above 20%. In other words, either the measured rates of respiration or photosynthesis must be in error.

[55] The most likely sources of error in estimation of photosynthesis rates are methodological issues with ^{14}C fixation and assumptions made in extrapolation from point measurements to the entire lake. The ranges of volumetric rates of photosynthesis reported for five studies made over a 30 year period in Lake Superior agree well with one another (2.2–8.8 mg C/m^3 hr [*Vollenweider et al.*, 1974], 0.5–3.5 mg C/m^3 hr [*El-Shaarawi and Munawar*, 1978], 0.5–3 mg C/m^3 hr [*Fee et al.*, 1992], <0.05–5 mg C/m^3 hr [*Bub*, 2001]). Consequently, the extrapolated annual rates of primary production also agree within a factor of about two (30–65 g C/m^2 yr) but they are at the low end of the range reported for both lakes and oceans. This is not reassuring given that an awareness of the importance of trace metal clean techniques [e.g., *Fitzwater et al.*, 1982] was developed during this 30 year period. Until ultraclean techniques are shown to yield identical results with less rigorous techniques, the possibility for metal inhibition cannot be excluded. Trace metal contamination may cause photosynthesis rates to be underestimated by up to a factor of 2.5 [*Fitzwater et al.*, 1982], but this is still less than the discrepancy between respiration and measured photosynthesis rates. All estimated lake-wide rates have been based on rates measured under light-saturated conditions and then extrapolated to the entire water column based on *P-I* curves. It is well known that parameters in *P-I* curves change with depth and season [e.g., *Fahnenstiel et al.*, 1989, 1984]. In situ incubations would remove some uncertainty in extrapolations based on P-I models [*Ondrusek et al.*, 2001]. Additional uncertainties arise in attempting to partition the lake spatially into nearshore and offshore areas; while photosynthesis rates were found to vary between these two zones, the differences changed seasonally. The contribution of embayment areas to the lake-wide rate of photosynthesis is unknown; remote sensing shows that these areas have higher chlorophyll concentrations [*Budd*, 2004]. Rates of DOC excretion by phytoplankton (Figure 7) may have been underestimated because they were not corrected for bacterial C uptake [*Baines and Pace*, 1991] and may have been underestimated for the same reasons just discussed for photosynthesis. We suggest that it is important (1) to prove that trace metal clean techniques do not result in higher rates than the protocols followed in the KITES study, (2) to conduct in situ incubations to verify that vertical distributions of chlorophyll and photosynthetic parameters are accurately incorporated into integrated areal rates of photosynthesis, and (3) to measure more accurately photosynthetic contributions of embayments and nearshore regions to the entire lake.

[56] Another critical research need is to conduct measurements during winter. The organic carbon budget for the lake has been extrapolated based on measurements made between April and October. If the average bacterial production value during the 5 month period of November–March is substantially less than during April–October, the respiration rate may have been overestimated by about a factor of two. We did not use a temperature coefficient to reduce the estimated bacterial activity in winter because respiration rates showed no seasonal response to temperature [*Urban et al.*, 2004a] and recent work has shown that enhanced nutrient supplies compensate for reduced temperatures in winter months in Lake Michigan [*Cotner et al.*, 2000]. While it does not seem inconceivable that primary production may have been underestimated by even a factor of 5 and may be as large as 200 g C/m^2 yr, it is difficult to believe that it could be as high as 500 g C/m^2 yr, the estimated rate of respiration.

4.2. Heterotrophy

[57] Lakes play a dual role in regional carbon cycling. On the one hand, lake sediments sequester organic carbon at globally significant rates [*Dean and Gorham*, 1998]. This fact is consistent with the classic view that lakes are carbon sinks with autotrophic production balanced by respiration and burial in sediments [e.g., *Eadie and Robertson*, 1976]. However, recent studies have clearly shown that many if not most lakes are sources of CO_2 to the atmosphere [*Anderson et al.*, 1999; *Cole et al.*, 1994; *del Giorgio et al.*, 1999; *Dillon and Molot*, 1997; *Kling et al.*, 1991; *Striegl et al.*, 2001; *Wachniew and Rozanski*, 1997]. Measurements of $\delta^{13}C$ have indicated that the evolved CO_2 comes, in most cases, from respiration [*Striegl et al.*, 2001]. The view that has evolved is that lakes receive organic carbon subsidies from their catchments (or from macrophytes in littoral areas and adjacent wetlands [*Wetzel*, 1990]) in the form of DOC, and that some fraction of this DOC is respired within the lake. As a result, heterotrophic bacteria (and potentially lake food webs) are not solely dependent on pelagic photoautotrophs for their carbon supply. In oligotrophic systems, the allochthonous organic carbon that is respired is greater than the autochthonous organic carbon that is buried. As a consequence, oligotrophic lakes tend to be net heterotrophic with rates of respiration in excess of rates of photosynthesis [*del Giorgio and Peters*, 1994, 1993].

[58] On the basis of observations in other lakes, ultraoligotrophic Lake Superior would be expected to be net heterotrophic ($P/R < 1$). However, Lake Superior also has a small ratio (1.55) of catchment area to lake surface area. This small catchment size might limit the organic carbon subsidy available from the watershed.

[59] Regardless of what measures are used, Lake Superior appears to be net heterotrophic. Small-scale, point measurements of photosynthesis, respiration, and bacterial growth made in this study all indicated a condition of net heterotrophy. In 14 of 16 cases where photosynthesis and com-

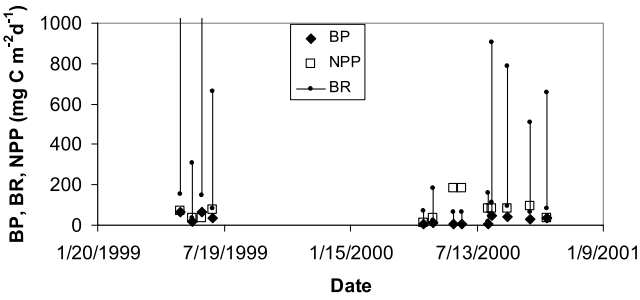

Figure 8. Comparison of areal rates of photosynthesis (NPP), bacterial production (BP), and bacterial respiration (BR). Bacterial respiration rates were calculated from bacterial production for the range of bacterial growth efficiencies of 5–30%; vertical lines between solid circles indicate the range of possible bacterial respiration rates. Values represent integrated profiles through the entire water column at station HN210 (21 km from shore, 180 m water depth).

munity respiration were measured simultaneously in surface waters, volumetric respiration rates were higher than rates of ^{14}C fixation into particulate matter [*Urban et al.*, 2004a]. This comparison does not account for excretion of photosynthate by autotrophs, and autotrophic respiration is included in measurement of both particulate OC fixation and community respiration. However, if bacterial respiration represents ~98% of community respiration in Lake Superior [*Biddanda et al.*, 2001], the latter error is small. Integration of profiles of point measurements into areal rates of respiration and photosynthesis always revealed P:R ratios less than one [*Urban et al.*, 2004a]. More frequently, photosynthesis and bacterial production (rather than respiration) were measured simultaneously; these measurements show that, for the range of bacterial growth efficiencies of 5–30%, areal rates (integrated over the entire water column) of bacterial respiration exceeded areal photosynthesis rates 40–80% of the time (Figure 8). This comparison is compromised by the uncertainty in the conversion factor between thymidine uptake and bacterial growth [e.g., *Ducklow et al.*, 2002]. When the areal rates are extrapolated to the entire lake for an annual period (Figure 7, Table 2), the P:R ratio (0.02–0.38) is much below one.

[60] Measurements made at the ecosystem scale agree well with the magnitude of rates measured at the point scale and also point to a condition of net heterotrophy in Lake Superior (Table 2, Figure 7). From the mass balance equation, the difference between respiration (R) and photosynthesis (P) should equal the difference between nonphotosynthetic inputs (I) and nonrespiratory outputs (O):

$$R - P = \sum I - \sum O = I_{\text{river}} + I_{\text{atmos}} + I_{\text{erosion}} - (O_{\text{burial}} + O_{\text{outflow}}). \quad (3)$$

From Table 2, the terms on the right hand side of equation (3) total −1.66 to 0.76 Tg C/yr; only if river inputs are at the low end of the estimated range or if rates of OC burial are at the high end of the estimated range is NEP (P-R) positive. If inflows and outflows of DIC are balanced (see above), the annual exchange of CO_2 across the lake surface should equal the difference between photosynthesis and respiration. The P_{CO_2} values (>360 μatm) calculated from measured pH and alkalinity [*Urban et al.*, 2004a] indicated that the lake was supersaturated with respect to atmospheric CO_2 for most months between April and November. Gas fluxes calculated with the wind speed–dependent transfer velocities of *Wanninkhof et al.* [1991] or *Cole and Caraco* [1998] averaged ~3 Tg C/yr out of the lake. This CO_2 efflux is of the same order of magnitude as NEP predicted by other inputs and outputs. The estimate of CO_2 efflux also is in good agreement with CO_2 production rates estimated with bottle incubations and hypolimnetic mass balances [*Urban et al.*, 2004a]. The estimated CO_2 efflux is an order of magnitude larger than the annual degassing predicted (0.2–0.3 Tg/yr) from river DIC loadings but about equal to the seasonal CO_2 uptake and degassing expected due to temperature changes in the lake. Accurate determination of NEP from gas flux measurements would require either year-round measurements or accurate corrections for temperature-induced fluxes.

[61] Other independent measurements also point to the net heterotrophic status of the lake. If respiration exceeds photosynthesis, there must be a net influx of oxygen into the lake. Indeed, P_{O2} values did indicate an oxygen flux into the lake from April–October 2000 except from late July through late August [*Russ et al.*, 2004]. Measurements of $\delta^{18}O$ in dissolved oxygen profiles led to a similar conclusion; P:R ratios calculated from the stable isotope ratios were consistently below one except during summer stratification when ratios above one were observed in the epilimnion [*Russ et al.*, 2004]. An earlier study [*Kelly et al.*, 2001] had reported undersaturation of epilimnetic waters with CO_2 and predicted a net influx of CO_2; however, that study reported measurements only for the months of August to early October, a period slightly longer than the period of oxygen evolution from the epilimnion in 2000 [*Russ et al.*, 2004]. The CO_2 influx (0.09 g C/m^{2}d) reported by *Kelly et al.* [2001] is fivefold to 20-fold smaller than the rate of hypolimnetic oxygen consumption (0.4–1.8 g C/m^{2}d) reported in this study and that of *McManus et al.* [2003] and is, therefore, still consistent with a state of net heterotrophy even during summer. Although each individual approach has considerable uncertainty in the estimation of the small net flux of CO_2, the consistency among all of the approaches in estimation of the direction of the net flux (out of the lake) leads us to conclude that Lake Superior is net heterotrophic on an annual basis and during each season of the year.

4.3. Factors Regulating Bacterial Production

[62] It is generally accepted that, over long timescales and across systems, heterotrophic activity is limited by production of labile carbon substrates by autotrophs. Thus across a wide range of ecosystems, *Pace and Cole* [1996] demonstrated that bacterial activity is proportional to autotrophic production (chlorophyll-a used as a surrogate). Similarly, in a survey of lakes, epilimnetic bacterial production was best explained by trophic status (i.e., nutrient concentrations), the regulator of autochthonous organic carbon production [*Cimbleris and Kalff*, 2003]. However, over short timescales within individual systems, heterotrophic activity may be limited by other factors including temperature [*Pomeroy*

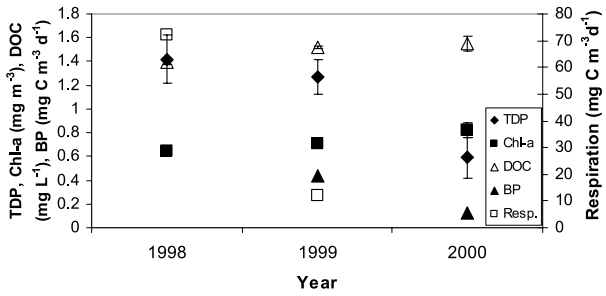

Figure 9. Annual mean values for total dissolved P (TDP), chlorophyll-a, DOC, bacterial production (BP), and respiration rates. Values of DOC, BP, and respiration rates were discussed above; values for TDP are from *Siew* [2003], and chlorophyll means represent all KITES data. Concentrations of DOC and chlorophyll-a increased during the study, while rates of respiration and bacterial production declined, as did concentrations of TDP.

and Wiebe, 1988], inorganic nutrients [e.g., *Chrzanowski and Grover*, 2001; *Skoog et al.*, 2002], or more proximal sources of DOC [*Ducklow et al.*, 2002; *Sondergaard et al.*, 1995].

[63] Rates of bacterial production within Lake Superior are not well predicted by the empirical relationships observed for other aquatic systems. The empirical relationship between total P and BP observed by *Cimbleris and Kalff* [2003] in 14 Canadian lakes overpredicts BP in Lake Superior by over a factor of 10; the deeper mixed layer depth in Lake Superior may result in lower photosynthetic production per unit of nutrient because of light limitation and concomitantly lower production of carbon substrates for bacterial use. In contrast, the empirical relationship between chlorophyll-a and BP observed by *Cole et al.* [1988] for lake and marine systems underestimates the BP measured in Lake Superior; this discrepancy could point to low bacterial mortality in Lake Superior [*Pace and Cole*, 1996] or to allochthonous sources of labile organic C.

[64] The few data available to evaluate factors regulating BP on an annual timescale suggest that temperature and P availability may be important. Within this limited data set (Figure 9), several observations stand out. The highest lake temperatures on record were measured in 1998, a strong El Niño year. This year also witnessed much higher rates of community metabolism and significantly higher TP concentrations [*Siew*, 2003] than in 1999. Chlorophyll concentrations increased each year of the study, and DOC concentrations in 1999 were higher than in 1998. Only TDP concentrations show decreases between years that exhibit decreases in community respiration rates and BP rates. Clearly, the significance of these observations will require a longer period of measurements to evaluate.

[65] On shorter timescales, KITES data point to interactions between BP, DOC concentrations, temperature, and P concentrations but little dependence on either chlorophyll concentrations or rates of ^{14}C fixation. Volumetric rates of ^{14}C fixation and BP in surface waters measured in 1999 showed no significant correlation when all data were pooled; segregating data into near- and offshore samples on each transect and analyzing each month separately (ANOVA indicated significant interactions between transect, distance from shore and month), only 2 of 20 subsets showed significant correlations with slopes of 0.3–0.4. Areal rates of BP and ^{14}C fixation (adjusted for light attenuation) showed disparate patterns in both near- and offshore waters (Figures 4, 5, and 8). Statistically, there were significant correlations between BP and temperature, DOC concentrations, and TDP concentrations (Table 1) but not between BP and chlorophyll concentrations. Although the bacteria are indirectly dependent on phytoplankton for fixation of the carbon that ultimately ends up in the labile DOC pool, either the bacteria are more limited by temperature and availability of phosphorus than by availability of labile DOC, or phytoplankton excretion is not the major mechanism for generation of labile DOC.

Notation

C	carbon.
P	phosphorus.
TDP	total dissolved phosphorus.
DOM	dissolved organic matter.
DOC	dissolved organic carbon.
COC	colloidal organic carbon (1 kDa < COC < 0.2 μm).
BP	bacterial production.
BA	bacterial abundance.
BGE	bacterial growth efficiency = carbon assimilation/carbon uptake.
f	cell carbon content (fg C per cell).
P	photosynthesis.
NPP	net primary production.
NEP	net ecosystem production.
R	respiration.
k_{resp}	pseudo first-order rate constant for microbial respiration of DOC.
$k_{photolysis}$	pseudo first-order rate constant for photolysis of DOC.
$k_{refractory}$	first-order rate constant for breakdown of refractory fraction of DOC.
f_{labile}	labile fraction of DOC.
I	input.
O	output.
I_{river}	inputs from rivers.
I_{atmos}	input from atmospheric deposition.
$I_{erosion}$	input from shoreline erosion.
O_{burial}	carbon output due to burial in sediments.
$O_{outflow}$	carbon outflow via the lake outlet.

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