Natural variability of carbon dioxide and net epilimnetic production in the surface waters of boreal lakes of different sizes

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Abstract

The variability of surface water carbon dioxide concentration, or partial pressure (pCO_2), was studied in 11 lakes of greatly varying size (2.4 ha up to 8 million ha) in Northwest Ontario, Canada. Six of these lakes were chosen to be as similar as possible in all respects except surface area (the Northwest Ontario Lake Size Series [NOLSS], which range from 88 to 35,000 ha). Spatial and temporal variability of pCO_2 within a single lake was no greater in the larger lakes than in the smaller lakes. Interannual variability was significant and synchronous, which indicates that weather patterns were important and affected the different lakes within the region in a similar manner. However, annual pCO_2 averages were not related to annual differences in planktonic photosynthetic activity, measured by $^{14}CO_2$ fixation. In the six NOLSS lakes, there was not a significant relationship of average pCO_2 with lake size. For all 11 lakes, however, there was a significant negative correlation of pCO_2 with lake size, which was likely due to several characteristics of the very small and very large lakes that covaried with size. The larger lakes were deeper and had longer water residence times and lower DOC, which suggests lower CO_2 production from allochthonous organic carbon inputs. Also, the ratio of epilimnetic sediment area/epilimnetic volume (A_e/V_e) was smaller in the larger lakes, which likely resulted in lower rates of recycling of fixed carbon to CO_2 during summer stratification.

Measurement of dissolved CO_2 in the surface waters of lakes is as useful as measurement of dissolved oxygen in determining net biological activity in lakes, especially when examining interactions between lakes and their watersheds (Kling et al. 1991; Dillon and Molot 1997). For example, the finding that average CO_2 concentrations in many lakes are above atmospheric equilibrium indicates that allochthonous contributions to lake metabolism often exceed net autochthonous fixation (Cole et al. 1994). This link with watersheds is demonstrated, in a series of Wisconsin lakes, by the positive correlation of surface water CO_2 with the ratio of drainage area to lake area, and with the extent of wetland area surrounding the lake (Hope et al. 1996). Artificial lakes (reservoirs) tend to have higher CO_2 concentrations than natural lakes due to decomposition of flooded vegetation or peat, which could also be considered "allochthonous" carbon sources (Duchemin et al. 1995; Kelly et al. 1997). Where degradation of allochthonous carbon is small, or quantifiable, measurements of CO_2 can give information about the extent of use of autochthonous carbon, i.e., the fraction of photosynthetically fixed CO_2 that is respired after fixation by the algae, grazers, and the rest of the lake's biota.

In addition to biological processes within lakes that affect CO_2, external inputs via streams or groundwater inflows contribute dissolved CO_2 (Kratz et al. 1997) and bicarbonate ions (HCO_3^-) that can be converted to CO_2 after entering lakes (Dillon and Molot 1997). It is difficult to distinguish between inorganic and organic allochthonous sources of CO_2, but the combination of dissolved oxygen measurement with CO_2 measurements is a promising approach because organic degradation consumes oxygen, whereas inorganic inputs should have no effect on oxygen (Carignan 1998).

Previous studies have examined the diel (Sellers et al. 1995) or seasonal variability of CO_2 concentrations in surface waters (Hesslein et al. 1990; Cole et al. 1994) of one or a few lakes. Geographic variability has also been studied, with the data set including a wide variety of lakes, but with few data points from each lake (Cole et al. 1994). The study reported here is the first to carry out long-term (8 yr), regular interval measurements on a fairly large set of lakes in one geographic location and to include measurements of photosynthesis and other parameters that can be used to understand patterns in CO_2. These lakes are generally remote, with minimal anthropogenic impacts. At the core of the study were six remote boreal lakes, the northwest Ontario lake size series (NOLSS, Fee and Hecky 1992). These lakes were chosen to be similar in most characteristics except for surface area, which ranged from 88 to 35,000 ha. We also studied five additional Ontario lakes, extending the size range down to 2.4 ha and up to over 8 million ha. In contrast to the NOLSS lakes, some characteristics of these additional lakes,

Table 1. Characteristics of the study lakes. A_0 = surface area, A_d = drainage area, Z_{max} = maximum depth, τ_w = water residence time, g C m^{-2} yr^{-1} and g C m^{-3} yr^{-1} = annual rates of photosynthetic carbon fixation. **NOLSS lakes are shown in bold.**

Lake	Years Sampled	Average Open Water* pCO$_2$ (μatm)	Average Mid-Summer pCO$_2$ (μatm)†	A_0 (ha)	A_d/A_0	Z_{max} (m)	Z_{mean} (m)	A_e/V_e	τ_w (yr)	DOC (μmol L^{-1})	Photosynthesis gC m^{-3} yr^{-1}	Photosynthesis gC m^{-2} yr^{-1}
979	1991–1992	1,080		2.4	34	1.2	0.7	1	0.008	816		
114	1991–1993	723		12.1	4.7	5	1.7	0.58	2.3	691		
240	1991–1996	559	452	44	16.4	14	6.1	0.11	1.9	575	3.2	24
Green	**1988–1995**	**504**	**366**	**89**	**2.6**	**19**	**7.7**	**0.079**	**13**	**535**	**5.5**	**27**
Orange	**″**	**554**	**375**	**167**	**6.6**	**29**	**14.4**	**0.042**	**11.6**	**675**	**6.1**	**30**
Linge	**″**	**600**	**410**	**706**	**4.2**	**23**	**8.4**	**0.088**	**9.8**	**636**	**7.3**	**35**
Musclow	**″**	**547**	**353**	**2,220**	**14.8**	**46**	**19.2**	**0.024**	**7.5**	**733**	**6.7**	**49**
Sydney	**″**	**469**	**335**	**5,750**	**8.1**	**73**	**20.0**	**0.035**	**9.5**	**545**	**5.8**	**42**
Trout	**″**	**426**	**298**	**34,700**	**2.1**	**49**	**13.6**	**0.043**	**22.3**	**334**	**4.0**	**37**
Nipigon	1989–1990	152	136	484,800	5	143	58.5	0.007	35	441	4.5	43
Superior	1989	183	227	8,220,000	2	403	148.7	0.003	180	149	2.5	52

* From May through October.
† From 15 June to 15 August.

such as water residence time and epilimnetic sediment area, covaried with size, and this was considered in the analyses of the data.

We used the results of these studies to test the following hypotheses, the first two of which are null hypotheses: (1) spatial variability of surface water CO$_2$ concentrations does not increase with lake size; (2) temporal variability of surface water CO$_2$ concentrations does not increase with lake size; (3) annual variation in average CO$_2$ concentrations is significant because weather affects processes involving CO$_2$; (4) long-term average CO$_2$ concentrations for individual lakes are not related to lake size because other factors are more important; (5) average CO$_2$ concentrations are negatively related to photosynthetic rates because photosynthesis removes CO$_2$; and (6) average CO$_2$ concentrations are positively related to the ratio of the epilimnetic area to the epilimnetic volume (A_e/V_e) because epilimnetic sediments are an important site of degradation of organic carbon to CO$_2$.

Methods

Study sites—The lakes studied were all drainage lakes located in, or bordering on, northwestern Ontario (Table 1). The six lakes studied in most detail were the northwest Ontario lake size series (NOLSS; Fee et al. 1989; Fee and Hecky 1992), located near Red Lake, Ontario (94°W, 51°N). Measurements were also made in Lake 240, a smaller clear lake, and in Lake 114 and Lake 979, two small, colored lakes, all located in the experimental lakes area (ELA) near Kenora, Ontario (94°W, 50°N). The largest lakes sampled were Lake Nipigon and Lake Superior. Lake Nipigon is located within northwestern Ontario (88°30′W, 50°N) and drains into Lake Superior (88°W, 48°N). Basic characteristics of each lake, and the years sampled, are shown in Table 1.

Sampling and analysis of dissolved CO$_2$—The determination of dissolved CO$_2$ (CO$_{2(aq)}$) is usually done by head space equilibration (e.g., Hesslein et al. 1990) and measure-

ment of the partial pressure of CO$_2$ (pCO$_2$), which is directly related to CO$_{2(aq)}$ by Henry's Law

$$CO_{2(aq)} = K_H \times pCO_2, \qquad (1)$$

where K_H is Henry's constant adjusted for water temperature. We report results as pCO$_2$ rather than as CO$_{2(aq)}$ because the units of partial pressure are more convenient for comparison to the atmospheric equilibrium value (ranging from 351 μatm in 1988 to 363 μatm in 1996, at sea level; Keeling and Whorf 1998). When this value is subtracted from the measured value, the sign of the difference indicates whether CO$_2$ is being drawn into the lake (negative) or being released to the atmosphere (positive).

Water samples were collected just below the surface (5 to 10 cm) using evacuated 150-ml serum bottles sealed with Vacutainer® stoppers (Hesslein et al. 1990). Each bottle contained 10 ml nitrogen, to provide a head space after filling, and 8.9 g KCl, which when mixed into the 135-ml water sample inhibits microbial activity for at least 2 weeks. Batches of KCl were tested for acidity/alkalinity and were used only if the effect on the water sample was less than ±3 μeq L^{-1}. In the laboratory, water and head space were equilibrated at a controlled temperature and the head space was sampled with a pressure-locking syringe (DynaTech). CO$_2$ concentrations in the head space were measured using a Hewlett Packard gas chromatograph with a thermal conductivity detector or a Shimadzu gas chromatograph with a methanizer and flame detector. Both instruments were equipped with a Porapak D column (180 mesh). Sample peak areas were compared to peak areas of certified air–CO$_2$ standards (Linde) in the range of 50 to 3,500 parts per million. There were some changes in analytical personnel during the study, but the same CO$_2$ standards were used throughout, and all field samples were taken by the same person.

pCO$_2$ measured under laboratory conditions was converted to in situ pCO$_2$ using the appropriate temperature and salt (KCl) relationships for CO$_2$ solubility and Henry's Law and

k_1 and k_2 values for carbonate equilibria equations (Hamilton et al. 1994). The accuracy of these calculations was tested empirically by comparison to measurements made in situ, using an underwater equilibration chamber and infrared detection (Sellers et al. 1995). The results of the two methods were indistinguishable, as tested by a standard *t*-test, and the difference in values obtained was usually less than 2%, never more than 10%.

Sampling frequency—The NOLSS lakes were sampled every 3 weeks, from the end of May through October. Lake Nipigon and Lake Superior were sampled from June to October. Lake 240 was sampled almost every day in 1991, weekly in 1992, 1993, and 1994, every 2 weeks in 1995, and every 3 weeks in 1996. Lake 979 was sampled 4 d per week, every other week, in 1992 and 1992. Lake 114 was sampled weekly in 1991, 1992, and 1993.

The time of day that samples were taken differed randomly. Time of day was not important in studies of diel variability on Lake 240 from 1991 to 1994. On the 18 dates that diel samples were taken (4–5 samples over the 24-h period), the coefficient of variation (C.V.) ranged from 2 to 22%, and there was no pattern as to when the highest or lowest values occurred.

Annual photosynthetic rates—Samples for measurement of photosynthesis were taken from the mixed layer (0–3 m integrated). Photosynthetic rates were measured using $H^{14}CO_3^-$ additions to lake water samples incubated under controlled light and in situ temperature in the laboratory. Incident photosynthetically active radiation (PAR) was measured continuously at the experimental lakes area (for Lake 240) and at Red Lake (for all other lakes) with a Li-Cor LI-190SR quantum cell (flat plate, cosine corrected collector) mounted at the top of a high tower or building. Light extinction coefficients were measured for each lake each time it was sampled for photosynthetic measurements. Daily photosynthesis (^{14}C uptake) for each lake was calculated using the programs of Fee (1990).

Annual wet precipitation—Wet precipitation (rain and snowfall) was collected with event samplers using standard Atmospheric and Environment Service (AES, Canada) procedures at the ELA meteorological site and at the Red Lake Airport.

Results

Spatial variability—Because of the large size of some of the lakes, complete spatial sampling required many hours, or, in the case of Lake Nipigon, 3 d. Thus, the variability in pCO$_2$ observed is not necessarily due to spatial heterogeneity alone. However, on most of the dates when spatial surveys were done, variability from one site to another was not very high. The range of C.V. values for samples taken in one lake at multiple sites was 5.0 to 17.7%, with one exception (Sydney Lake on 21 June 1987), when it was 39.7% (Table 2).

There was sometimes a pattern to the spatial distribution of pCO$_2$ values over the lake surface. For example, in Lake 240 on 14 July 1997, pCO$_2$ values were about 20% higher

Table 2. Spatial surveys of pCO$_2$ in surface waters.

Lake	Date	Number of sites	µatm (Average ± SD)	C.V. (%)
Lake 240	14 Jul 1997	19	424 ± 37	8.7
	26 Aug 1997	19	390 ± 19	5.0
Lake Nipigon	24 Jul 1989	23	340 ± 39	11.4
Trout Lake	25 May 1987	19	285 ± 36	12.5
	4 Aug 1987	19	200 ± 36	17.7
	14 Sep 1987	4	475 ± 50	10.4
Sydney Lake	21 Jun 1987	6	104 ± 41	39.7
Green Lake	1 Sep 1987	3	207 ± 31	15.1

at shallower areas near one end of the lake than in the middle of the lake. However, this pattern was not repeated on the second spatial survey date for this lake (26 August 1997). In Trout Lake there was a tendency for values in the eastern, shallower bays to be slightly higher. However, one of these bays was sampled repeatedly over 4 yr for comparison with values in the middle of the lake, and it averaged only 9% higher (data not shown).

We expected spatial variability to be greatest in Trout Lake because it has many bays and islands, but its range of C.V. on each set of spatial samplings (10.4 to 17.7%, Table 2) was not very different from the range for the two smallest lakes (5.0% to 15.1%, Table 2). The largest lake sampled for spatial variability, Lake Nipigon, showed no greater variability than the smallest lake (Table 2).

Day-to-day variability and seasonal patterns—In all lakes sampled, changes in pCO$_2$ from one day to the next were greatest during the spring and fall and least during summer stratification (Fig. 1a–c). The C.V. of daily values for the whole open water season, compared to the open water mean for each lake-year, was commonly between 35 and 46%, with the full range between 17 and 89%. The shape of the seasonal pattern, with higher values in spring and fall and lower values in midsummer (Fig. 1a–c), was typical of north temperate stratified lakes (Hesslein et al. 1990).

Over multiple years, open water averages were always above atmospheric equilibrium (Fig. 2a), as has been observed for many other lakes (Cole et al. 1994). However, midsummer pCO$_2$ averages were sometimes above atmospheric equilibrium and sometimes below, depending on the year (Fig. 2b).

The seasonal data were not as complete for the two largest lakes, Lake Nipigon and Lake Superior. However, the results showed less fluctuation in pCO$_2$ in the summer and not as much increase in the fall as in the smaller lakes (Fig. 1b,c). Early spring data were lacking, but the earliest dates for Lake Nipigon suggest the ''typical'' decline after ice-off (Fig. 1b). It should be noted that the term ''open water'' season does not apply in the strict sense to Lake Superior because some open water remains year round in most years (Saulesleja 1986).

Average CO$_2$ concentrations for the midsummer (15 June to 15 August) and open water periods (May to October)—
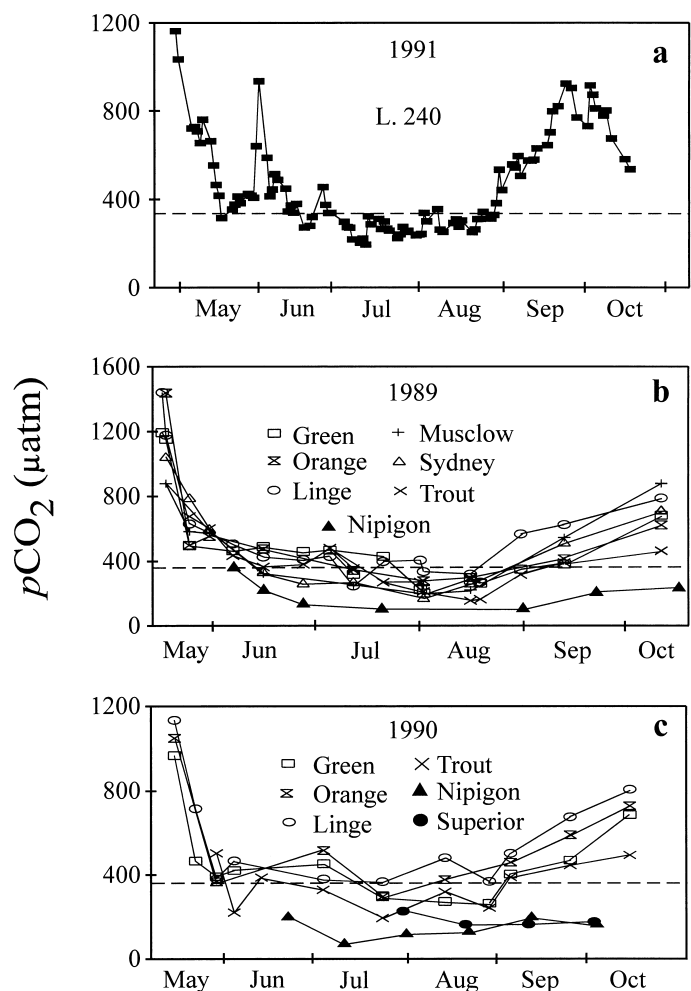
Fig. 1. Seasonal variation in surface water pCO$_2$ values for (a) Lake 240 (ELA) in 1991, (b) the six NOLSS lakes in 1989, and (c) the NOLSS lakes, Lake Nipigon, and Lake Superior in 1990.
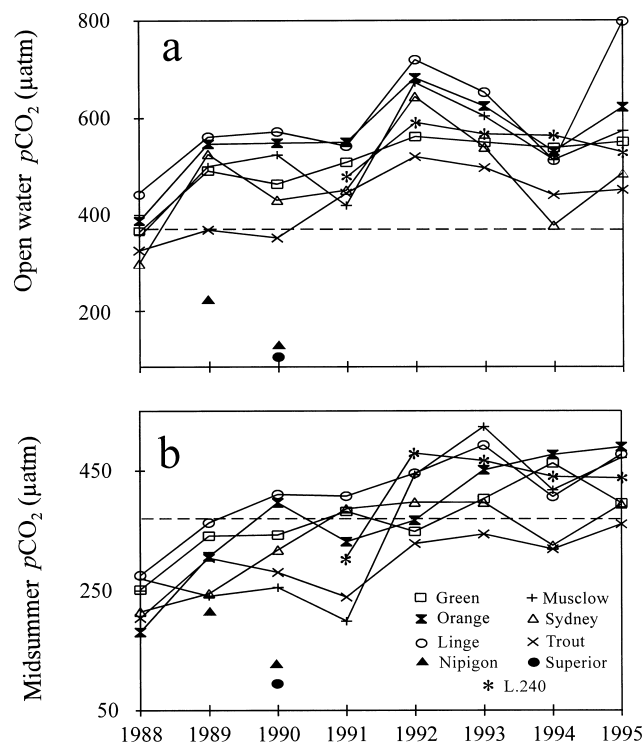

Fig. 2. (a) Interannual variation in open water pCO$_2$ averages for the six NOLSS lakes (1989–1995). Data for Lake 240 (1991–1995), Lake Nipigon in 1989 and 1990, and Lake Superior in 1990 are also shown. (b) Interannual variation in midsummer pCO$_2$ averages for the six NOLSS lakes (1989–1995). Data for Lake 240 (1991–1995), Lake Nipigon in 1989 and 1990, and Lake Superior in 1990 are also shown.

Because pCO$_2$ values were higher in spring and fall in most of the lakes, average midsummer (stratification period) values were about 30% lower than averages calculated for the entire open water period. However, the two averages were linearly related to each other ($r^2 = 0.61$; $p = 0.01$). Thus, either time period could be used for the purpose of establishing simple rankings for pCO$_2$ levels among different lakes and years, e.g., from highest to lowest. A positive cor-

relation between open water and midsummer pCO$_2$ values was also observed in the data of Cole et al. (1994).

Given the strong seasonality of pCO$_2$ values (Fig. 1), one might expect that many sampling dates are required in most lakes to obtain an accurate average value for the open water period. However, randomly chosen subsets of the Lake 240 data, made up of four to nine dates fairly evenly spaced over time, produced averages that were well within 1 standard deviation (SD) of the average calculated from the full data sets of 103 dates in 1991 and 24 dates in 1992 (Table 3). This exercise indicated that a sampling program with only four dates (evenly spaced) would give a reasonable indication of the average pCO$_2$ value for the year and would ac-

Table 3. Comparison of open water average values for pCO$_2$ (μatm) in Lake 240, obtained with different sampling schedules (indicated by letters A–E for 9 d).

			μatm					
	9 day schedule					6 day schedule	5 day schedule	4 day schedule
	A	B	C	D	E			
1991 Data								
(Avg = 466 ± 217, n = 103)	432	426	492	452	505	537	461	489
1992 data								
(Avg = 713 ± 332, n = 24)	610	728	627	627	772	648	665	665

curately show that the average pCO_2 level was higher in 1992 than in 1991 (Table 3). This is likely because boreal lakes are strongly stratified for most of the open water period and pCO_2 values tend to be fairly constant during stratification in these low productivity lakes (Fig. 1a–c). Of course, the fewer dates sampled, the lower the confidence level.

Interannual variation—The results for the six NOLSS lakes covered eight consecutive years, from 1988 to 1995. For each lake, the open water average pCO_2 value was significantly different from one year to another (nested ANOVA, $p = 0.0001$; Fig. 2a). For each year, however, there was no significant difference among lakes ($p = 0.995$). Thus, each year was different, but all six NOLSS lakes behaved synchronously, i.e., the open water average pCO_2 values of the group as a whole tended to increase or decrease during the years of the study (Fig. 2a). Duncan's Multiple Range test ($p = 0.05$) identified three groupings of years: those with high pCO_2 averages (1992, 1993, and 1995), a medium group (1989, 1990, 1991, and 1994), and a single, especially low year (1988).

The midsummer pCO_2 averages also changed synchronously from year to year (Fig. 2b, nested ANOVA, $p = 0.49$), and different years were significantly different from each other ($p = 0.0001$). From 1988 to 1991, midsummer average values were often below equilibrium (Fig. 2b), which indicates that CO_2 fixation was greater than respiration and decomposition of allochthonous carbon during these periods. From 1992 to 1995, however, average midsummer values were usually greater than equilibrium. Thus, in these years, respiration and decomposition must have been greater than fixation even at the time of year when fixation rates are at their highest.

Lake 240 is located at the ELA, about 140 km south of Red Lake, Ontario, and is only about half the size of the smallest NOLSS lake (Table 1). However, in the years where data from Lake 240 overlapped with the NOLSS data set (1991–1995), the Lake 240 open water and midsummer average pCO_2 values were not distinguishable from the NOLSS data set, showing the same year-to-year trends (Fig. 2a,b).

The year-to-year variation in average open water pCO_2 values, over many years, showed a positive trend with annual precipitation levels and a negative trend with annual photosynthesis in Lake 240, but neither trend was statistically significant (Fig. 3a,b). For the six NOLSS lakes, there was also a slight positive trend (not significant) with annual precipitation (Fig. 4a) but no trend with photosynthetic activity, either on an areal basis (Fig. 4b) or on a volumetric basis (data not shown). The same lack of trend was obtained whether the open water average pCO_2 values or the midsummer average values for each year were used.

Lake Nipigon and Lake Superior were not sampled over as many years as were Lake 240 and the NOLSS lakes, and so their interannual variability cannot be examined.

Differences among lakes, and relationship to size—In order to compare one lake to another, long-term (multiyear) average values of pCO_2 were calculated from all the annual open water and midsummer averages for each lake. For the data set including Lake 240 (44 ha) and the six NOLSS lakes
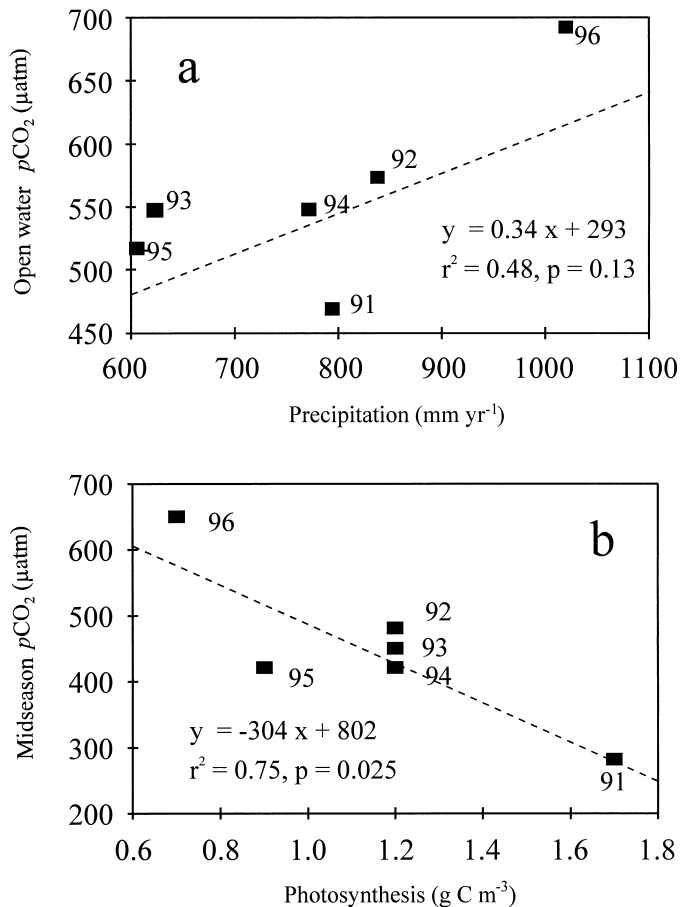

Fig. 3. (a) Annual precipitation and annual open water pCO_2 averages for Lake 240, 1991 through 1996. Dotted line = linear trend line, not significant ($p = 0.13$). (b) Photosynthetic $^{14}CO_2$ fixation, on an areal basis, and pCO_2 averages for the midsummer period (15 June to 15 August) in Lake 240, 1991 through 1996. Dotted line = linear trend line, not significant ($p = 0.025$)

(up to 34,700 ha), there appeared to be no major differences in pCO_2 among the lakes that were smaller than 5,000 ha (Table 1). In the two larger NOLSS lakes (Sydney Lake and Trout Lake), average open water pCO_2 values were consistently lower than in the smaller lakes (Table 1), but linear regression analysis of pCO_2 against size did not result in a statistically significant trend. When this data set was expanded to include the much larger Lake Nipigon (484,800 ha) and Lake Superior (8,220,000 ha), as well as two smaller lakes at ELA (less than 2.4 ha), there was a significant negative linear relationship between pCO_2 and the logarithm of the lake area ($r^2 = 0.80$, $p < 0.001$; Fig. 5).

Measurements of DOC concentration showed a positive relationship between DOC and pCO_2 (Fig. 6a). For the six NOLSS lakes, plus Lake 240, the positive trend between pCO_2 and DOC concentration was not statistically significant (Fig. 6a, closed symbols), but it was significant when 11 lakes were included ($r^2 = 0.65$, $p = 0.0027$; Fig. 6a, all symbols). The DOC concentrations were also negatively related to the logarithm of water residence time ($r^2 = 0.70$, $p = 0.0013$; Fig. 6b).

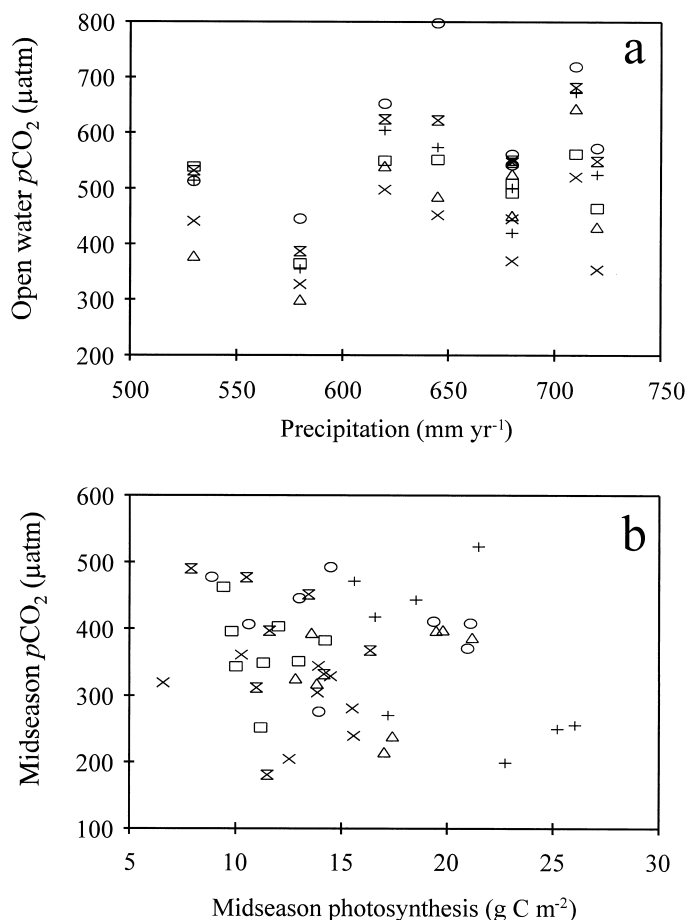Other patterns observed, when all 11 lakes were consid-

Fig. 4. (a) Annual precipitation and annual open water pCO$_2$ averages for the six NOLSS lakes, 1988 through 1995. Symbols as in Fig. 2. (b) Photosynthetic CO$_2$ fixation (measured by ^{14}C incorporation) and pCO$_2$ averages for the midsummer period (15 June to 15 August) in the six NOLSS lakes, 1988 through 1995.

ered, were a positive linear correlation between pCO$_2$ and the ratio of the area of epilimnetic sediments to the volume of the epilimnion (A_e/V_e) in each lake ($r^2 = 0.87$, $p = 0.0001$; Fig. 7) and a negative relationship with mean depth ($r^2 = 0.46$, $p = 0.02$; Table 1).

Discussion

Hypothesis 1, that spatial variability of surface water CO$_2$ concentrations does not increase with lake size, was supported. Spatial variability was no greater in Lake Nipigon and Trout Lake than in Lake 240, even though they are approximately 10,000 and 1,000 times larger than Lake 240 (Table 1). On some sampling dates variability was much lower than on others (Table 2), possibly related to the recent wind history. Because of this low spatial variability, one sampling site should be adequate to determine if a lake is above or below equilibrium with the atmosphere on a given date, even in lakes with complicated shoreline and island configurations. Additional sites may be necessary if there are bays in the lake where circulation with the rest of the lake is restricted, and/or these bays receive stream inflow. For
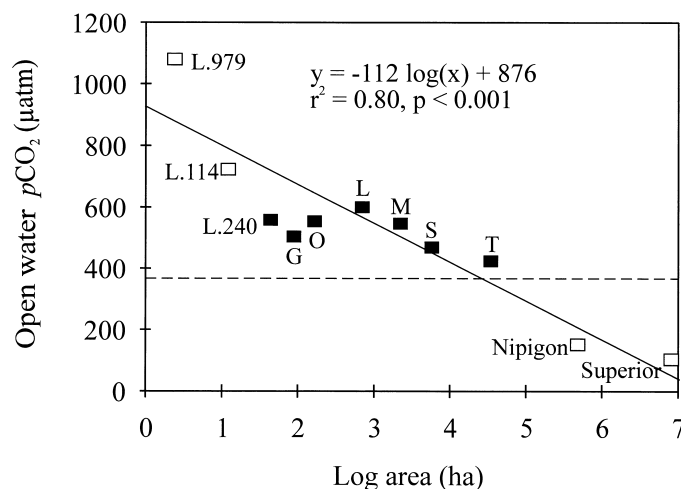

Fig. 5. Open water pCO$_2$ values, averaged over all study years for each lake, and lake sizes (surface areas) for the six NOLSS lakes and Lake 240 (closed symbols: G = Green, O = Orange, L = Linge, M = Musclow, S = Sydney, T = Trout) and for Lake 979, Lake 114, Lake Nipigon, and Lake Superior (open symbols).
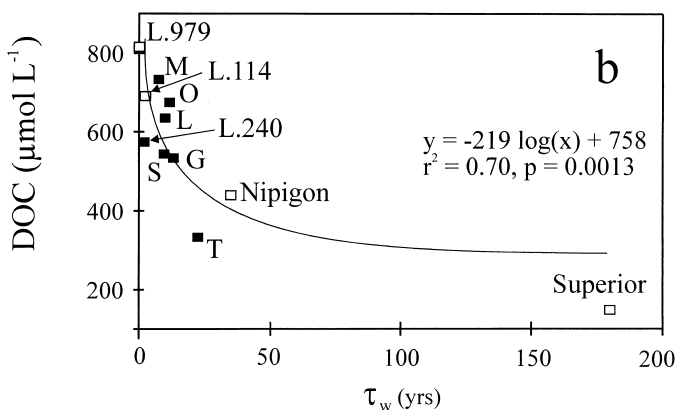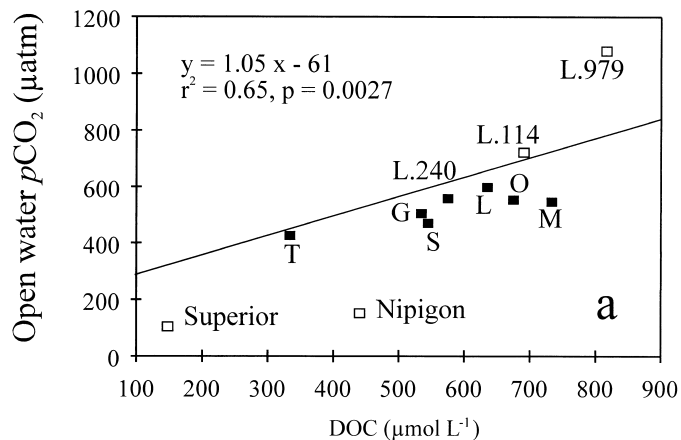

Fig. 6. (a) Dissolved organic carbon (DOC) concentrations, averaged over all study years, and lake sizes (surface areas) for the six NOLSS lakes and Lake 240 (closed symbols: G = Green, O = Orange, L = Linge, M = Musclow, S = Sydney, T = Trout) and for Lake 114, Lake 979, Lake Nipigon, and Lake Superior (open symbols). (b) Relationship between the average DOC concentration and the open water pCO$_2$ values for the same lakes as in (a).
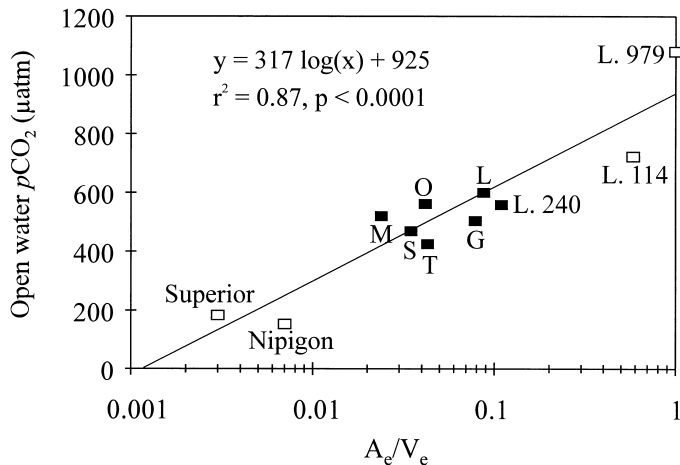
Fig. 7. Relationship between open water pCO_2 and A_e/V_e (log scale), for the six NOLSS lakes and Lake 240 (closed symbols; G = Green, O = Orange, L = Linge, M = Musclow, S = Sydney, T = Trout) and for Lake 979, Lake 114, Lake Nipigon, and Lake Superior (open symbols).

example, in Lake Nipigon, the only two sites with pCO_2 values above saturation (24–26 July 1989) were in bays near inflows.

Hypothesis 2, that temporal variability in surface water pCO_2 does not increase with lake size, was also supported. In fact, the reverse appeared to be true, with temporal variability within the year being *lower* in larger lakes because Lake Nipigon and Lake Superior had the most consistent pCO_2 values throughout the open water period (Fig. 1b,c). However, the longer period of ice break-up that occurs in larger lakes made it difficult to access Lake Nipigon during the early spring period when pCO_2 values may have been higher. Lake Superior is usually ice-free year round and therefore is not subject to the buildup of CO_2 that normally occurs during the winter in the other lakes. The fall (late August through October) increase in pCO_2 observed in all lakes except the two largest (Fig. 2) is due to the entrainment of thermocline and hypolimnetic water that has accumulated $CO_{2(aq)}$ from decomposition during the summer period. Larger lakes have deeper mixing depths (Fee et al. 1996), and so entrained deep water is mixed into a larger volume, causing less effect on epilimnetic chemistry. Also, the entrained water itself may have lower concentrations of CO_2 in the larger lakes because as hypolimnetic decomposition proceeds, the CO_2 produced is diluted into a comparatively larger volume of water.

Hypothesis 3, that annual variability is significant because of linkages between CO_2 processes and weather patterns, was supported in that year-to-year variation in pCO_2 was statistically significant. This year-to-year synchrony of pCO_2 values in all the lakes (Fig. 2) is difficult to explain by anything other than changes in regional weather patterns from one year to another. Evidence for the effect of particular weather factors such as rainfall and sunlight on pCO_2, however, is weak or lacking. A link between annual pCO_2 averages and precipitation might be expected. DOC export from watersheds is positively related to precipitation (Schindler et al. 1992; Dillon and Molot 1997), and a portion of

the DOC in lakes is decomposed to CO_2 (e.g., Tranvik and Hofle 1987; Graneli et al. 1998). Also, CO_2 generated in soils may be carried into the lakes in runoff and stream waters (e.g., Kling et al. 1991). There was a weak link between annual levels of precipitation and pCO_2 (Figs. 3a and 4a), and the very high pCO_2 seen in the wettest year (1996, Fig. 3a) is evidence that precipitation may affect pCO_2. These results suggest that it would be worthwhile, when evaluating CO_2 data collected from a lake for only one to a few years, to look at whether the years sampled were representative of the range of precipitation levels for that site.

A link between annual pCO_2 averages and sunlight might also be expected, through an effect on photosynthetic CO_2 fixation. However, although sunlight obviously affects rates on a daily basis and with depth within a water column (e.g., Fee 1990), annual average sunlight was not related to annual average photosynthesis (data not shown). Part of the explanation may be the degree to which incident light penetrates the water column. For example, Lake 240 had its lowest photosynthesis rate and highest incident PAR in 1996. High precipitation in this year brought in large quantities of colored DOC, which diminished light penetration. Even if there had been a meteorological link with photosynthesis, it might not have mattered to variability in pCO_2 because measured photosynthetic activity had slight (Fig. 3b) or no (Fig. 4b) influence on interannual pCO_2 variability.

The poor linkage between either precipitation or sunlight and pCO_2 suggests that a single weather-related factor, by itself, did not exert a strong enough control to show an observable effect on pCO_2. Thus, if weather was the cause of the synchrony among lakes with respect to pCO_2, the specific mode of action was unclear, probably because "weather" is a complex combination of many factors, including the timing of changes within each year.

Hypothesis 4, that average pCO_2 values are *not* related to lake size, was not supported. The larger lakes had lower pCO_2 values (Fig. 5), and even though pCO_2 values changed from year to year, there was a tendency for the ranking of lakes to be maintained (Fig. 2). However, size (surface area) itself was not likely a causative factor. This conclusion is derived from examining the set of NOLSS lakes, separate from the others. These lakes were chosen particularly so that the main difference among them was surface area (Fee and Hecky 1992), with other characteristics being as similar as possible. For example, they have a similar geologic setting (Canadian Shield), hydrology (stratified lakes with water residence times greater than 5 yr), and productivity (27 to 49 g C m^{-2} yr^{-1}). Within this group the decrease in average open water pCO_2 with increasing size was only slight (solid squares, Fig. 5).

The purpose of including Lake Nipigon, Lake Superior, and the smaller ELA lakes in this study was to increase the total size range to six orders of magnitude. Photosynthetic rates and the ratio of drainage area to lake surface area (A_d/A_0) for most of these additional lakes were not different from the range found in the six NOLSS lakes (Table 1). However, water residence time (τ_w) and the ratio of epilimnetic area to epilimnetic volume (A_e/V_e) were definitely outside the NOLSS range. A_e/V_e decreased with size, whereas τ_w increased (Table 1). Also, the two smallest lakes (Lake 114

and Lake 979) have adjacent peatlands, which have been identified as a contributor to higher pCO_2 in lakes (Hope et al 1996; Kelly et al. 1997; Kratz et al. 1997; Riera et al. 1999). Thus, when interpreting data from the two extreme ends of the size spectrum, we must keep in mind that other factors covaried with size. Although the types of covariance seen here are probably common, e.g., increased τ_w due to increased depth and volume with increased area, they are not universal.

The trend of decreasing pCO_2 with increasing size (Fig. 5) is probably best explained by the decreasing trend in DOC concentration (Table 1) because photosynthetic rates did not increase with lake size (Table 1; *see also* Fee et al. 1992). A relationship between pCO_2 and DOC, seen in our data set (Fig. 6a), has also been observed in Wisconsin lakes (Hope et al. 1996) and presumably occurs because DOC is a source of carbon for respiration, which produces CO_2. High DOC inputs may also be accompanied by high concentrations of CO_2 coming from the same soils or peat that contribute the DOC (Kling et al. 1991).

What is the reason for the negative relationship of DOC concentration with lake size in our set of lakes? In similar geologic settings, allochthonous DOC *input* rate, per unit area of lake surface, should be related to the ratio of drainage area (A_d) to lake surface area (A_0), and A_d/A_0 has been correlated with DOC and pCO_2 in a set of Wisconsin lakes (Hope et al. 1996). However, in our data set, A_d/A_0 did not show a significant relationship with DOC concentration, except that the lake with the largest A_d/A_0 also had the highest DOC concentration (Table 1). Although A_d/A_0 affects the DOC input per unit area, water residence time (τ_w) will affect the input of allochthonous DOC per unit volume of lake water, i.e., the DOC concentration (Curtis and Schindler 1997). In our set of lakes, mean depth increased as area increased, with a corresponding increase in lake volume and τ_w, and a decrease in DOC (Fig. 6b). If the larger area lakes had not also been deeper, we would probably not have seen the decrease in pCO_2 with increasing size.

The general lack of support for hypothesis 5, that average pCO_2 values are negatively related to photosynthetic rates because photosynthesis removes CO_2, was probably the most surprising result of this study (Fig. 4b). The method used here for photosynthesis measurement has been extensively tested, including a comparison with measurements made by ^{14}C addition to a whole lake (Bower et al. 1987). However, phytoplankton photosynthesis measured by ^{14}C uptake is a rate for the daylight period only, and its relationship to net CO_2 uptake for both the daytime and for the 24-h period is uncertain (Peterson 1980). Therefore its net effect on pCO_2 is uncertain.

To investigate this further, we made estimates of average net epilimnetic CO_2 fixation, or net epilimnetic production (NEP), over 24-h periods by calculating (1) net CO_2 flux across the air–water interface, which is supported by net production or uptake of CO_2 due to all processes ($\Delta CO_{2(\text{all processes})}$), and (2) subtracting the contribution of CO_2 production estimated to occur from DOC degradation ($\Delta CO_{2(\text{DOC allochthonous})}$):

$$\Delta CO_{2(\text{NEP})} = \Delta CO_{2(\text{all processes})} - (\Delta CO_{2(\text{DOC allochthonous})}). \quad (2)$$

A negative sign indicates net fixation (removal) of CO_2, and

$\Delta CO_{2(\text{NEP})}$ should be equal to photosynthetic fixation minus respiration, for the whole epilimnetic community. Changes in the bicarbonate pool can be ignored because these are small compared to the change in CO_2 when the driving reactions are photosynthesis and respiration (e.g., Park 1969).

The net flux of CO_2 across the air–water interface was estimated from the pCO_2 data, wind speed data, and the relationships of Wanninkhof (1992). Local average wind speeds, at 1 m height, were 2 m s^{-1} at ELA and 2.7 m s^{-1} at Red Lake and Lake Superior (Thunder Bay). For lakes up to the size of Trout Lake, we used gas exchange coefficients of 0.4 and 0.5 m d^{-1}, respectively, for these two average wind speeds (Wanninkhof 1992). We assumed a larger coefficient (1 m d^{-1}) for the two largest lakes because measurements of gas exchange in water bodies of different sizes, using SF$_6$, suggest that the value of k_{exch} is greater in larger bodies, even at the same wind speed (Wanninkhof 1992). The relationship of gas exchange to wind speed is a subject of continuing investigation, and the uncertainty in the approach used here is thought to be greater at lower wind speeds (Cole and Caraco 1998) and in larger lakes (Wanninkhof 1992). However, although the choice of gas exchange coefficients for the larger lakes affected the absolute values calculated, it did not change the overall trends.

The rate of DOC degradation to CO_2 was estimated from measured DOC concentration and from decomposition coefficients developed from ELA data by Curtis and Schindler (1997). We did these estimates for the midsummer period only, in order to focus on the period when surface water pCO_2 is least affected by mixing with deeper water.

The estimated daily net CO_2 fluxes (due to all processes) were much smaller than daylight photosynthetic rates (^{14}C uptake) and sometimes in the opposite direction (Table 4). This indicates that CO_2 fixation measured by ^{14}C uptake was largely offset, and sometimes exceeded, by CO_2 production. Allochthonous DOC degradation could account for only a part of this CO_2 production (Table 4), with the rest presumably coming from respiration of photosynthetically fixed carbon. The calculated NEP rates ranged from 20 to 60% of ^{14}C uptake (Table 4), similar to previous estimates of the relationship between net 24 h and daylight photosynthetic fixation (Berman and Pollingher 1974). NEP, however, is a *community* parameter, including the respiration of grazers, sediment bacteria, etc., and therefore is not the same as the term ''net photosynthesis,'' which refers only to the photosynthesis and respiration of the algae.

The variable nature of epilimnetic NEP compared to ^{14}C uptake (Table 4) means that ^{14}C uptake was a poor predictor of net CO_2 uptake in these lakes, and thus hypothesis 5, which proposes a negative relationship between photosynthetic activity and CO_2, was not supported. The relatively low magnitude of ^{14}C uptake in these lakes is important to note. Also, the estimates of NEP and allochthonous DOC degradation were similar in magnitude, making differences in either one important to the net effect on CO_2. In two experimentally fertilized lakes, where daytime photosynthetic rates were much higher than in these northwest Ontario lakes, pCO_2 values were significantly related to photosynthesis (Schindler et al. 1997).

The higher estimates for NEP/^{14}C uptake (Table 4) in the

Table 4. Estimate of midsummer (June 15–Aug 15) net epilimnetic CO_2 fixation (NEP). A negative sign indicates CO_2 uptake (NEP, ^{14}C) and flux into the lake from the atmosphere. **NOLSS lakes are shown in bold.**

	pCO$_2$ (μatm)	Gas exchange coefficient (m d^{-1})	CO$_2$ flux (mmol m^{-2} d^{-1})	Mixing depth (m)	DOC (μmol L^{-1})	Estimation of DOC degradation* (mmol m^{-2} d^{-1})	Estimation of NEP (mmol m^{-2} d^{-1})	Photosyn-thetic ^{14}C uptake (mmol m^{-2} d^{-1})	NEP/^{14}C uptake
Lake 240	452	0.4	0.76	5	575	2.9	−2.1	−14	0.15
Green	**367**	**0.5**	**−0.30**	**5.6**	**535**	**3.0**	**−3.3**	**−16**	**0.21**
Orange	**378**	**0.5**	**0.20**	**5.6**	**675**	**3.8**	**−3.6**	**−17**	**0.21**
Linge	**411**	**0.5**	**0.65**	**6.7**	**636**	**4.3**	**−3.6**	**−21**	**0.17**
Musclow	**354**	**0.5**	**−0.20**	**7.8**	**733**	**5.7**	**−5.9**	**−28**	**0.21**
Sydney	**334**	**0.5**	**−0.95**	**8.3**	**545**	**4.5**	**−5.5**	**−23**	**0.23**
Trout	**300**	**0.5**	**−1.45**	**11.7**	**334**	**3.9**	**−5.4**	**−18**	**0.30**
Nipigon	160	1	−8.45	9.3	441	4.1	−13	−27	0.46
Superior	183	1	−7.80	19	149	2.8	−11	−16	0.64

* Assuming a DOC degradation coefficient of 0.001 d^{-1} (Curtis and Schindler 1997).

epilimnia of the larger lakes caused us to consider *why* a greater proportion of the photosynthetically fixed carbon was not respired to CO_2. The larger lakes had longer residence times, which should allow more opportunity for respiration of fixed carbon within the lakes, not less. We considered the possibility that respiration rates were lower in the larger lakes because they are colder. However, the fact that rates of sediment respiration in epilimnetic sediments of Trout Lake were very similar to rates in Green Lake, even though Green Lake sediments were about 5° warmer (Ramlal et al. 1993), casts doubt on this explanation. We also considered grazing as a possible factor in NEP, but zooplankton biomass did not have a trend with lake size (Salki 1995). Also, the effect of grazing on CO_2 is likely an effect on photosynthesis, not respiration (Schindler et al. 1997).

One explanation for the size trend in NEP/^{14}C uptake is based on bathymetric characteristics. In our expanded data set the larger lakes have lower ratios of epilimnetic area to epilimnetic volume (A_e/V_e) than do the smaller lakes. A_e/V_e is mathematically equivalent to the probability that a sedimenting particle will encounter epilimnetic sediments rather than the thermocline, divided by the volume of epilimnetic

Fig. 8. Estimated fraction of photosynthetic ^{14}C uptake that remained fixed (NEP/^{14}C uptake), as a function of A_e/V_e. NEP = net epilimnetic production for the 24-h period as calculated in Table 4.

water into which any returning nutrients from the epilimnetic sediments would be diluted (Fee 1979). Thus, in lakes with high values of A_e/V_e there would be more return of CO_2 to epilimnetic waters because a smaller fraction of sedimenting particles would leave the epilimnion, and we observed higher CO_2 in lakes with high A_e/V_e (Fig. 7). Greater return of CO_2 means lower NEP/^{14}C uptake, and we also observed a strong negative trend in NEP/^{14}C uptake ($r^2 = 0.88$, $p = 0.00016$; Fig. 8) with log A_e/V_e. Thus, hypothesis 6, "that pCO_2 is positively related to A_e/V_e because the sediments are an important site of degradation of organic carbon," was supported.

The importance of A_e/V_e to the recycling of elements was previously shown by Fee (1979), who demonstrated the positive relationship between A_e/V_e and photosynthetic rates in ELA lakes and hypothesized that it was due to recycling of N and P in epilimnetic sediments. For carbon, greater recycling (to CO_2) at higher A_e/V_e values in smaller lakes means that even though daytime photosynthesis there might be higher, net 24-h community fixation (and drawdown of CO_2) will be lower. Fee et al. (1992, 1994) further showed that for lakes with the *same* A_e/V_e, a larger lake can sustain a higher rate of daytime photosynthesis, probably because turbulence (which clearly increases with lake size) enhances N and P recycling within the water column. The few data presented here do not appear to show the same degree of turbulence-related recycling for carbon, as the two largest lakes had the largest portion of photosynthetic carbon remaining fixed (*not* returned as CO_2, Table 4). This suggests that C is recycled less efficiently in the water column than N and P, as has been suggested for oceanic surface waters (Thomas et al. 1999).

We could not examine the role of epilimnetic sediments in this way if we had not first removed the contribution of DOC degradation to CO_2 (Eq. 2). This is because in this set of lakes A_e/V_e was linearly correlated ($r = 0.99$) to $1/Z_{mean}$, which is mathematically the same as A/V for the whole lake, and mean depth was correlated to τ_w. Increasing τ_w is expected to result in lower CO_2 because of the decreased input of degradable allochthonous DOC (Fig. 6; Curtis and Schindler 1997). Thus, when looking at total CO_2 flux and lake
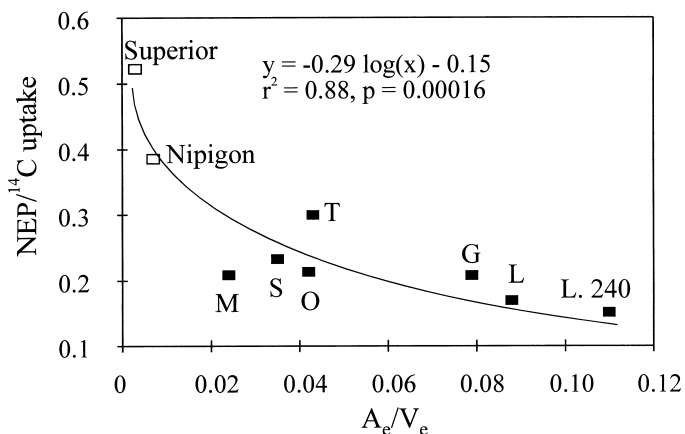
size, there is no need to invoke a role for the epilimnetic sediment area (A_e/V_e) in the negative relationship between pCO_2 and size (Fig. 5). However, the lower rate of recycling of daily photosynthesis (NEP/^{14}C) in the larger lakes cannot be explained by a longer τ_w (which should allow time for greater recycling), but the explanation based on lower A_e/V_e ratios in the larger lakes is very reasonable. This analysis is a demonstration of the value of searching for mechanistic relationships, rather than restricting analyses only to statistical correlations (Fee 1980).

The patterns of natural variability in pCO_2 levels in surface waters shown here, and the effect of lake size, were developed from a data set of north temperate, fairly oligotrophic lakes. Therefore, the sampling frequency and site recommendations given here may not apply to eutrophic and/or to tropical lakes. The relationships between pCO_2 and DOC concentration and the importance of water residence time and A_e/V_e, however, are factors that should be applicable to the understanding of CO_2 data and carbon cycling processes in all lakes. In addition, the lack of a relationship between daytime photosynthesis rates measured with ^{14}C and pCO_2 should be kept in mind in interpreting data from all surface waters, including the oceans.

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