

Carbon dioxide partial pressure and ^{13}C content of north temperate and boreal lakes at spring ice melt

Abstract—Carbon dioxide (CO_2) accumulates under lake ice in winter and degasses to the atmosphere after ice melt. This large springtime CO_2 pulse is not typically considered in surface-atmosphere flux estimates, because most field studies have not sampled through ice during late winter. Measured CO_2 partial pressure ($p\text{CO}_2$) of lake surface water ranged from 8.6 to 4,290 Pa (85–4,230 μatm) in 234 north temperate and boreal lakes prior to ice melt during 1998 and 1999. Only four lakes had surface $p\text{CO}_2$ less than or equal to atmospheric $p\text{CO}_2$, whereas 75% had $p\text{CO}_2 > 5$ times atmospheric. The $\delta^{13}\text{C}_{\text{DIC}}$ ($\text{DIC} = \Sigma\text{CO}_2$) of 142 of the lakes ranged from -26.28‰ to $+0.95\text{‰}$. Lakes with the greatest $p\text{CO}_2$ also had the lightest $\delta^{13}\text{C}_{\text{DIC}}$, which indicates respiration as their primary CO_2 source. Finnish lakes that received large amounts of dissolved organic carbon from surrounding peatlands had the greatest $p\text{CO}_2$. Lakes set in noncarbonate till and bedrock in Minnesota and Wisconsin had the smallest $p\text{CO}_2$ and the heaviest $\delta^{13}\text{C}_{\text{DIC}}$, which indicates atmospheric and/or mineral sources of C for those lakes. Potential emissions for the period after ice melt were $2.36 \pm 1.44 \text{ mol CO}_2 \text{ m}^{-2}$ for lakes with average $p\text{CO}_2$ values and were as large as $13.7 \pm 8.4 \text{ mol CO}_2 \text{ m}^{-2}$ for lakes with high $p\text{CO}_2$ values.

North temperate and boreal regions of the world have high densities of lakes that are covered by ice during winter. About 10% of the total land area of Finland is occupied by 190,000 lakes and ponds larger than 0.05 ha in area; 56,000 of them are larger than 1 ha (Raatikainen and Kuusisto 1990). Several regions of northern North America, Europe, and Asia have similarly large numbers of lakes. Decomposition of plant and animal debris, respiration, and other biogeochemical processes result in the accumulation of dissolved carbon gases under ice in these lakes during winter. The accumulated gases are released to the atmosphere shortly after ice melt, during what is commonly the largest lake-gas emission event of the year (Michmerhuizen et al. 1996; Striegl and Michmerhuizen 1998). The carbon dioxide partial pressure ($p\text{CO}_2$) of lake surface water preceding ice melt is an indicator of net lake respiration and of net hydrologic exchange of CO_2 that occur under ice during winter. At Williams Lake, Minnesota, Anderson et al. (1999) observed that decrease of $p\text{CO}_2$ of lake surface water also correlates well with decrease of lake CO_2 storage during the days after ice melt. If this were to hold true for several lakes, regional estimates of springtime CO_2 flux could be made from surface measurements of lake $p\text{CO}_2$ rather than from loss-of-storage calculations requiring $p\text{CO}_2$ versus depth profiles and depth versus volume data (e.g., Anderson et al. 1999).

The ^{13}C content of dissolved inorganic carbon (DIC) is an indicator of the carbon sources that contribute to the overall lake C budget and of the biogeochemical processes that occur in lake water and sediment. Lake $\delta^{13}\text{C}_{\text{DIC}}$ can also be directly related to the $\delta^{13}\text{C}$ signature of autochthonous car-

bonates and organic matter that settle from the water column and are stored in bottom sediment (Talbot 1990). Assessment of the change over time of the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of carbonates in lake sediment is a useful tool for inferring paleoclimate and paleohydrology (Schwalb et al. 1995). However, contemporary variability of $\delta^{13}\text{C}_{\text{DIC}}$ within and among lakes is not well documented, and quantitative relationships among lake $p\text{CO}_2$, $\delta^{13}\text{C}_{\text{DIC}}$, hydrology, ecology, and geological setting are not well understood. Little is known about the distribution of $p\text{CO}_2$ across a range of lakes at ice melt, and no surveys of $\delta^{13}\text{C}_{\text{DIC}}$ under ice have previously been reported.

Lakes commonly are supersaturated with CO_2 relative to the atmosphere (Kling et al. 1991, 1992; Cole et al. 1994), and, for much of the year, import plus in situ production of CO_2 exceeds export plus within-lake use of CO_2 (Striegl and Michmerhuizen 1998). Consequently, many lakes have net annual loss of CO_2 across the water-air interface. Additional carbon loss of CH_4 is also well documented (e.g., Michmerhuizen et al. 1996). Allochthonous carbon sources of the emitted CO_2 and CH_4 include hydrologic inputs of DIC derived from dissolution of carbonates and mineralization of organic carbon in the soil zone, and inputs of dissolved organic carbon (DOC) and particulate organic materials that are subsequently mineralized in the lake (Otsuki and Wetzel 1974; Kortelainen 1993; Striegl and Michmerhuizen 1998; del Giorgio et al. 1999).

Carbon gas storage in seasonally ice-covered lakes is typically greatest during late winter, just prior to ice melt (Striegl and Michmerhuizen 1998; Striegl et al. 2000). Most of this gas is lost to the atmosphere in a short time after ice melt (Michmerhuizen et al. 1996; Anderson et al. 1999). Late winter is an important period to study C-gas cycling in lakes for other reasons. First, it is the time when interlake comparisons are most feasible, because all lakes have similar water temperature, and ice has sealed them off from air-water interaction for several months. This also allows for isotopic evaluation of C sources under comparable conditions. Second, surveys of lakes in late winter (Michmerhuizen et al. 1996; Striegl et al. 2000) indicate that annual C-gas flux is probably greater than would be suggested by studies conducted only during open water periods (Kling et al. 1991; Cole et al. 1994). Finally, if factors such as the wind effect on lake mixing and primary production are minimized, it may be possible to relate gas exchange and C source to hydrological, ecological, and geological setting for a wide range of lakes.

We hypothesized that potential springtime CO_2 flux from lakes could be estimated by $p\text{CO}_2$ under ice shortly before breakup, that it would be greatest in lakes with relatively large hydrologic inputs of DOC, and that late winter $p\text{CO}_2$ for those lakes would exceed previously reported $p\text{CO}_2$ values for north temperate lakes. We also hypothesized that the

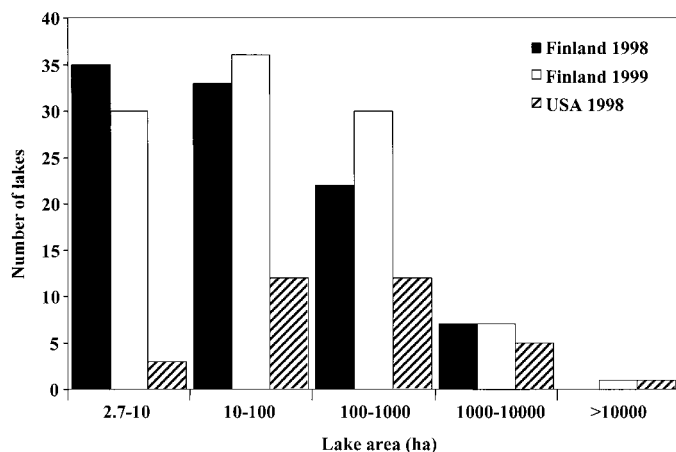


Fig. 1. Surface area (in hectares) of lakes sampled in the United States and Finland prior to the spring ice melts of 1998 and 1999.

$\delta^{13}\text{C}_{\text{DIC}}$ of the lakes would decrease as lake $p\text{CO}_2$ increased and that $\delta^{13}\text{C}_{\text{DIC}}$ would plateau at a constant minimum negative value representative of the terrestrial C source.

This article discusses the results of $p\text{CO}_2$ and $\delta^{13}\text{C}_{\text{DIC}}$ measurements at 34 lakes in Wisconsin and Minnesota and 98 lakes in Finland prior to ice melt in 1998, of $p\text{CO}_2$ measurements at an additional 102 Finnish lakes in 1999, and of $\delta^{13}\text{C}_{\text{DIC}}$ measurements of a subset of 11 of the 1999 lakes with $p\text{CO}_2 > 1,000$ Pa. Estimates of potential CO_2 emission that used surface $p\text{CO}_2$ data are validated by measurements of surface $p\text{CO}_2$ versus CO_2 storage under ice at 29 lakes in Wisconsin and Minnesota during late winter 1997 and 1998. Whole-lake (volume weighted) $\delta^{13}\text{C}_{\text{DIC}}$ was also measured four times during the open-water season at Williams and Shingobee lakes, Minnesota (Schwalb et al. 1995; Winter and Averett 1997; Striegl and Michmerhuizen 1998), to assess seasonal and within-lake variability of lake water $^{13}\text{C}_{\text{DIC}}$.

The 34 U.S. lakes (latitude 46° – 49°N) represent ranges in lake size, hydrologic position on the landscape, and hydraulic residence in a carbonate till setting in north-central Minnesota, a noncarbonate bedrock setting in northeastern Minnesota, and a noncarbonate till setting in Wisconsin (Michmerhuizen et al. 1996; Striegl et al. 2000). Of the 200 Finnish lakes sampled (latitude 60° – 69°N), 175 were selected that statistically represent the entire lake population of Finland. Twenty-five lakes having total phosphorus concentration in the upper 5% of Finnish lakes were also sampled. Most lakes in Finland are set in noncarbonate bedrock or in noncarbonate till; carbonate deposits are not common. Peat deposits cover till in many areas of Finland (Niemi et al. 1993) and contribute DOC to many lakes (Kortelainen 1993). The size distribution of the lakes sampled is shown in Fig. 1.

Methods— $p\text{CO}_2$ was directly measured on water samples collected from auger holes cut through the ice near the deepest point of each lake. All samples were collected a safe time before breakup of ice cover, usually ~ 2 – 3 weeks. Ten lakes in Lapland, northern Finland, were sampled ~ 6 weeks before ice melt in 1999. Early ice melt had been predicted for those lakes because of a warm April, but the early melt

did not occur. After augering, 30 ml of bubble-free water was collected at 0.2 m depth by use of a 60-ml polypropylene syringe. Fifteen milliliters of the sample was injected from the syringe, through a disposable 15-mm diameter Whatman GF/A syringe filter, and into a 37-ml serum bottle with nitrogen headspace and 1 g carbonate-free KCl preservative. Three 0.5-ml replicates of equilibrated headspace were analyzed by use of a LICOR 6252 CO_2 analyzer fitted with a sample injection port and nitrogen carrier. Headspace CO_2 concentration was taken as the average of the three measurements, and lake $p\text{CO}_2$ was calculated by use of the appropriate Henry's Law constant, corrected for temperature and atmospheric pressure (Plummer and Busenberg 1982). Identical replicate samples were acidified to convert DIC to CO_2 , and the headspace was analyzed by gas chromatography–isotope mass spectrometry to determine $\delta^{13}\text{C}_{\text{DIC}}$ (per mil relative to Pee Dee Belemnite; Fritz and Fontes 1980). DOC ($\text{mg L}^{-1}\text{C}$) and water color ($\text{mg L}^{-1}\text{Pt}$) were also measured on samples collected from lakes in Finland. Lake CO_2 storage and whole-lake $\delta^{13}\text{C}_{\text{DIC}}$ values were determined by volume-averaging measured concentrations of samples collected from the entire depth profile (Michmerhuizen et al. 1996; Striegl and Michmerhuizen 1998).

Results and discussion—Surface water $p\text{CO}_2$ ranged from 8.6 Pa at White Sand Lake, Wisconsin, to 4,290 Pa at Vähä-Meltosjärvi, Finland, averaging 452 Pa. U.S. lakes ranged from 8.6 to 514 Pa, averaging 139 Pa, and Finnish lakes ranged from 78 to 4,290 Pa, averaging 506 Pa. Under the assumption of an atmospheric CO_2 concentration of 37 Pa ($365 \mu\text{atm}$), this is ~ 0.23 to 116 times the atmospheric concentration (Fig. 2A). $p\text{CO}_2$ maxima and means, especially those from Finland, were greater than those reported elsewhere for northern lakes during ice-free periods (Kling et al. 1991; Cole et al. 1994). On average, Finnish lakes sampled during 1999 had larger $p\text{CO}_2$ values than lakes sampled in 1998 (Fig. 2A). This was assumed to be due to a large number of lakes in flat peat-rich coastal areas in the 1999 sampling and not to interannual variability. The 11 Finnish lakes with $p\text{CO}_2 > 1,000$ Pa were in catchments with a high proportion of peatland or agricultural fields. Three Wisconsin lakes set in noncarbonate till and one Minnesota lake in crystalline bedrock had $p\text{CO}_2 \leq 37$ Pa, which suggests few terrestrial C inputs to these clearwater lakes. $p\text{CO}_2$ decreased with increased lake area in U.S. lakes ($r^2 = 0.54$), which is consistent with earlier observations for CH_4 in Minnesota and Wisconsin lakes (Michmerhuizen et al. 1996). This pattern was not observed for Finnish lakes, possibly because of the large variability in $p\text{CO}_2$ observed for small Finnish lakes. Peatlands cover as much as one third of the land area of Finland, and the $p\text{CO}_2$ of small lakes set in peatlands or adjacent to wetlands is strongly influenced by DOC inputs from those areas (Kortelainen 1993; Hope et al. 1996). Actual DOC inputs to these lakes are determined by biogeochemical and hydrological conditions that vary greatly among lakes. Correlation coefficients for $p\text{CO}_2$ versus DOC and for $p\text{CO}_2$ versus water color (which covaries with DOC) for Finnish lakes were 0.51 and 0.58, respectively. As with large U.S. lakes, large Finnish lakes had small $p\text{CO}_2$.

The $\delta^{13}\text{C}_{\text{DIC}}$ of the 132 lakes sampled during 1998 ranged

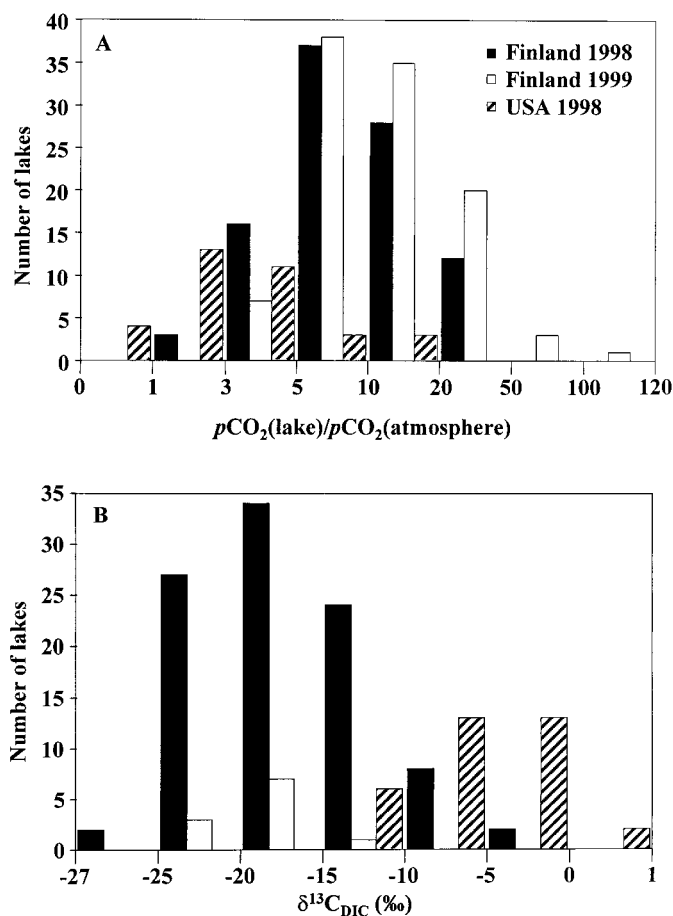


Fig. 2. Number of lakes sampled in the United States and Finland prior to the spring ice melts of 1998 and 1999 that reside within the ranges of (A) $p\text{CO}_2$ and (B) $\delta^{13}\text{C}_{\text{DIC}}$ indicated on the horizontal axes. Lake $p\text{CO}_2$ is in multiples of atmospheric $p\text{CO}_2$, assumed to be 37 Pa (365 μatm), and $\delta^{13}\text{C}_{\text{DIC}}$ is in per mil relative to Pee Dee Belemnite.

from -26.28‰ to $+0.95\text{‰}$ (Fig. 2B), averaging -13.75‰ . $\delta^{13}\text{C}_{\text{DIC}}$ was inversely related to $p\text{CO}_2$, with the lightest DIC found in lakes that had the greatest $p\text{CO}_2$ (Fig. 3A). This suggests that respiration of DOC and decomposition of organic sediments are the primary sources of CO_2 for those lakes. Provided that respiration was the primary source of the CO_2 , it was hypothesized that $\delta^{13}\text{C}_{\text{DIC}}$ values would plateau at some minimum negative value as $p\text{CO}_2$ continued to increase. This was the case for the 11 Finnish lakes that had $p\text{CO}_2 > 1,000$ Pa in 1999. However, those $\delta^{13}\text{C}_{\text{DIC}}$ values, which ranged from -23.85‰ to -13.70‰ , were slightly more positive than would have been expected from the 1998 data alone (Fig. 3B). This was probably due to the enrichment of $\delta^{13}\text{C}_{\text{DIC}}$ caused by methanogenesis (Clark and Fritz 1997). Vähä-Meltojärvi, the lake with the greatest $p\text{CO}_2$ value, had a surface CH_4 concentration of 280 μmol , compared with median and mean concentrations of 0.7 and 10.8 μmol CH_4 at the 102 Finnish lakes sampled during 1999 (Striegl unpubl. data). Many other factors could contribute to an increase in $\delta^{13}\text{C}_{\text{DIC}}$, including a heavier source of organic material available for respiration, isotopic mixing with

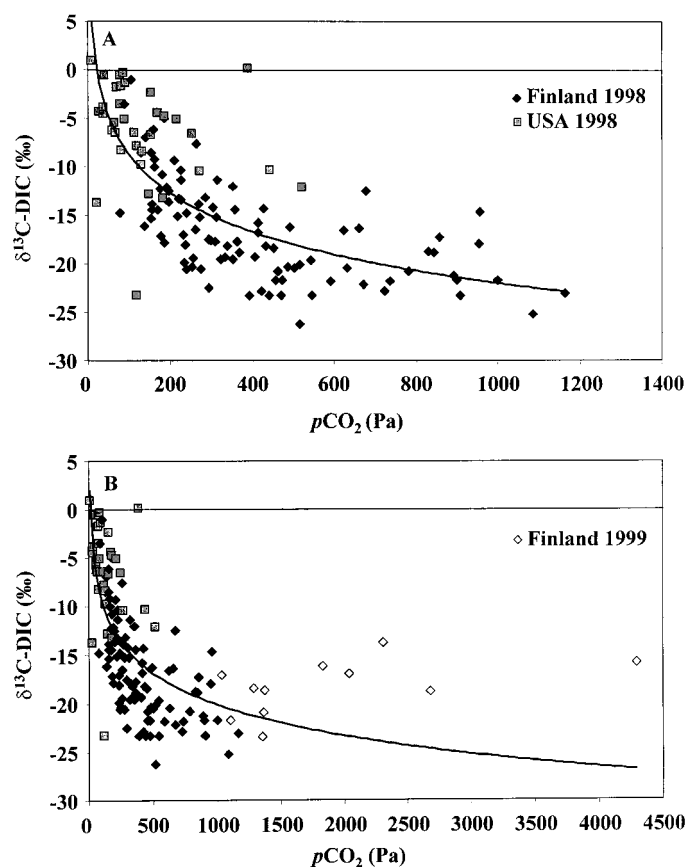


Fig. 3. Relationship between $p\text{CO}_2$ and $\delta^{13}\text{C}_{\text{DIC}}$ in lakes sampled (A) prior to the spring ice melt of 1998 ($\delta^{13}\text{C}_{\text{DIC}} = -5.76 \times \ln p\text{CO}_2 + 17.8$; $r^2 = 0.54$; $P < 10^{-6}$); and (B) including 11 additional high- $p\text{CO}_2$ lakes sampled in Finland during 1999 ($\delta^{13}\text{C}_{\text{DIC}} = -4.66 \times \ln p\text{CO}_2 + 12.1$; $r^2 = 0.48$; $P < 10^{-6}$). Note the scale difference of the x-axis between panels A and B.

another DIC source such as ground water, or CO_2 uptake by photosynthesis under ice (Striegl and Michmerhuizen 1998).

Whole-lake $\delta^{13}\text{C}_{\text{DIC}}$ at Williams and Shingobee lakes was slightly more ^{13}C depleted than surface values at ice melt (Williams, -2.14‰ vs. -0.60‰ ; Shingobee, -10.66‰ vs. -10.43‰). This was attributed to the influence of lighter $\delta^{13}\text{C}_{\text{CO}_2}$ in bottom water resulting from respiration of organic debris in lake sediments (^{13}C of organic debris: Williams, -15.0‰ ; Shingobee, -26.8‰). From April to September, whole-lake $\delta^{13}\text{C}_{\text{DIC}}$ values increased by $+1.40\text{‰}$ at Williams Lake and by $+1.24\text{‰}$ at Shingobee Lake, because of photosynthetic uptake of lake CO_2 during summer (Striegl and Michmerhuizen 1998) and subsequent atmospheric equilibration.

Lakes with very enriched $\delta^{13}\text{C}_{\text{DIC}}$ values suggest atmospheric CO_2 (approximately -7.5‰ to -6.5‰) or carbonate mineral (approximately -4‰ to $+4\text{‰}$) sources of C (Clark and Fritz 1997; Fritz and Fontes 1980). Nine U.S. lakes and one Finnish lake had $\delta^{13}\text{C}_{\text{DIC}} > -3\text{‰}$. Six of these lakes are >240 ha in area (74% of lakes sampled have smaller area) and had $p\text{CO}_2 < 100$ Pa (92% of lakes had greater $p\text{CO}_2$). Three of the others are closed-basin lakes, and the fourth has a surface-water outlet but no inlet. Large lakes and closed-

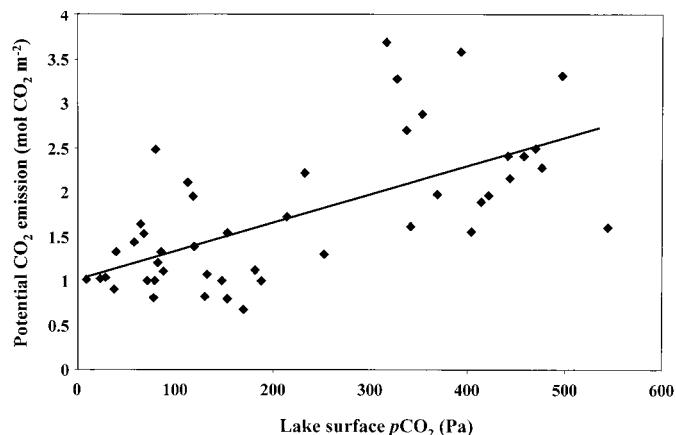


Fig. 4. Relationship between $p\text{CO}_2$ and potential CO_2 emission at 29 Wisconsin and Minnesota lakes ($\text{mol CO}_2 \text{ m}^{-2} = p\text{CO}_2 \times 0.0032 + 1.025$; $r^2 = 0.42$; $\text{SE} = 0.61$; $P = 1.3 \times 10^{-6}$).

basin lakes tend to have long hydraulic residence times and to have less CO_2 than small open-basin lakes in midsummer, because photosynthetic demand commonly exceeds hydrologic inputs of CO_2 and bioavailable DOC. Photosynthetic depletion of lake $p\text{CO}_2$ below atmospheric concentrations results in periods when relatively heavy atmospheric CO_2 influxes to the lakes during the open-water period. Selective uptake of $^{12}\text{CO}_2$ by photosynthesis results in further ^{13}C enrichment of the lake CO_2 pool during open water and under ice. Although dissolution of carbonate minerals can also contribute to heavy $\delta^{13}\text{C}_{\text{DIC}}$, dissolution is thought to be less important than atmospheric influx or photosynthesis, because most of the lakes studied were not set in carbonate terrain. More exact determination of the relative importance of atmospheric versus carbonate sources is not possible without additional measurement of ^{14}C (Deevey et al. 1954).

Loss of CO_2 from lakes after ice melt can take many days and is most accurately measured by tracking exponential decrease in lake CO_2 storage with time or by direct measurement of flux by use of the eddy covariance technique (Anderson et al. 1999). Boundary layer, surface renewal, and tracer methods that require monitoring of the gas partial pressure gradient across the water-air interface, wind, temperature, and other environmental factors are also useful for the calculation of CO_2 flux across the water-air interface (e.g., Liss and Slater 1974; Smith 1985; Soloviev and Schuessel 1994; Cole and Caraco 1998). However, none of these methods have been applied to lakes after ice melt, nor are they useful for calculating total CO_2 loss with use of a single point measurement.

Figure 4 shows potential CO_2 emission versus lake surface $p\text{CO}_2$ measured on 46 occasions at 29 Wisconsin and Minnesota lakes during 1997 and 1998. Potential emission is calculated as the measured gas storage per unit lake area minus gas storage when the lake is at equilibrium with the atmosphere (Michmerhuizen et al. 1996). Depending on mixing conditions, most of this gas is emitted to the atmosphere (Michmerhuizen et al. 1996; Anderson et al. 1999). High $p\text{CO}_2$ in bottom water allows for potential emission even when $p\text{CO}_2$ is less than atmospheric CO_2 pressure at

the surface (Striegl and Michmerhuizen 1998). Extrapolation of the regression line in Fig. 4 gives a range in potential emission from $1.1 \pm 0.67 \text{ mol CO}_2 \text{ m}^{-2}$ for the Wisconsin lake with 8.6 Pa $p\text{CO}_2$ to $13.7 \pm 8.4 \text{ mol CO}_2 \text{ m}^{-2}$ for the Finnish lake with 4,290 Pa. We have no way to validate the upper estimate, because CO_2 storage was not measured at the Finnish lakes.

Application of the regression equation in Fig. 4 to lakes with average $p\text{CO}_2$ gives potential emissions of 1.44 ± 0.88 and $2.52 \pm 1.54 \text{ mol CO}_2 \text{ m}^{-2}$, respectively, for U.S. and Finnish lakes and $2.36 \pm 1.44 \text{ mol m}^{-2}$ for all lakes sampled. Under the assumption of total lake areas of $3.4 \times 10^6 \text{ ha}$ for Finland and $1.6 \times 10^8 \text{ ha}$ globally for seasonally frozen lakes (Meybeck 1995), we speculate a maximum springtime flux of $\sim 8.6 \times 10^{10} \pm 5.2 \times 10^{10} \text{ mol CO}_2$ for Finnish lakes and $3.8 \times 10^{12} \pm 2.3 \times 10^{12} \text{ mol CO}_2$ for all seasonally frozen lakes at ice melt.

The 27.23‰ range observed in lake $\delta^{13}\text{C}_{\text{DIC}}$ indicates the complexity of the many biotic and abiotic interactions that control C cycling in lakes. Similar ranges are undoubtedly present in the various other lake inorganic and organic C components (Oana and Deevey 1960; Stuiver 1975; Schindler et al. 1997). Differences in $\delta^{13}\text{C}$ among lakes are linked to lake hydrology and setting. Small open-basin lakes with short hydraulic residence time and that are thought to receive relatively large inputs of DOC tended to have high $p\text{CO}_2$ and light $^{13}\text{C}_{\text{DIC}}$. Closed-basin lakes and large lakes with long hydraulic residence time tended to have lower $p\text{CO}_2$ and heavier $^{13}\text{C}_{\text{DIC}}$. A change in lake hydrology, whether initiated by climate change or by some other factor, is reflected in the ^{13}C history of lakes (Talbot 1990; Schwalb et al. 1995). Some effects of change may be counteractive. For instance, drying of peatlands could result in larger CO_2 emission from the peatlands as they dry and oxidize and in smaller CO_2 emission and more positive $\delta^{13}\text{C}$ at nearby lakes that formerly received isotopically light and oxidizable DOC peatland leachate. Conversely, decreased hydrologic input of nutrients to lakes could result in decreased lake productivity, less depletion of lake $p\text{CO}_2$ by photosynthesis, and more negative lake $\delta^{13}\text{C}$ (Schindler et al. 1997). Such hydrologic factors need to be considered on a lake-by-lake basis, whether interpreting current lake $p\text{CO}_2$ and $\delta^{13}\text{CO}_2$ status or the depositional history of ^{13}C in lake sediments.

Robert G. Striegl¹

United States Geological Survey
Box 25046, MS 413
Denver, Colorado 80225-0046

Pirkko Kortelainen

Finnish Environment Institute
P.O. Box 140
FIN-00251 Helsinki, Finland

Jeffrey P. Chanton

Department of Oceanography
Florida State University
Tallahassee, Florida 32306-4340

¹ Corresponding author (rstriegl@usgs.gov).

Kimberly P. Wickland

United States Geological Survey
Box 25046, MS 413
Denver, Colorado 80225-0046

Glynnis C. Bugna

Department of Oceanography
Florida State University
Tallahassee, Florida 32306-4340

Miitta Rantakari

Finnish Environment Institute
P.O. Box 140
FIN-00251 Helsinki, Finland

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