

## Potential methane emission from north-temperate lakes following ice melt

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### *Abstract*

Methane, a radiatively active “greenhouse” gas, is emitted from lakes to the atmosphere throughout the open-water season. However, annual lake CH<sub>4</sub> emissions calculated solely from open-water measurements that exclude the time of spring ice melt may substantially underestimate the lake CH<sub>4</sub> source strength. We estimated potential spring CH<sub>4</sub> emission at the time of ice melt for 19 lakes in northern Minnesota and Wisconsin. Lakes ranged in area from 2.7 to 57,300 ha and varied in littoral zone sediment type. Regression analyses indicated that lake area explained 38% of the variance in potential CH<sub>4</sub> emission for relatively undisturbed lakes; as lake area increases potential CH<sub>4</sub> emission per unit area decreases. Inclusion of a second term accounting for the presence or absence of soft organic-rich littoral-zone sediments explained 83% of the variance in potential spring CH<sub>4</sub> emission. Total estimated spring CH<sub>4</sub> emission for 1993 for all Minnesota lakes north of 45° with areas ≥ 4 ha was 1.5 × 10<sup>8</sup> mol CH<sub>4</sub> assuming a 1 : 1 ratio of soft littoral sediment to hard littoral sediment lakes. Emission estimates ranged from 5.3 × 10<sup>7</sup> mol assuming no lakes have soft organic-rich littoral sediments to 4.5 × 10<sup>8</sup> mol assuming all lakes have soft organic-rich littoral sediments. This spring CH<sub>4</sub> pulse may make up as much as 40% of the CH<sub>4</sub> annually emitted to the atmosphere by small lakes.

Increasing atmospheric concentrations of methane (CH<sub>4</sub>), a radiatively active gas implicated in global atmospheric warming, have led to the detailed study of the global CH<sub>4</sub> budget. Freshwater environments contribute >70% of the natural source and >20% of the total global source of CH<sub>4</sub> to the atmosphere (Khalil and Shearer 1993). Although wetlands are the most important component of this source (Khalil and Shearer 1993; Khalil and Rasmussen 1983; Cicerone and Oremland 1988), lakes are also important sources that can emit CH<sub>4</sub> to the atmosphere continually during ice-free periods (Smith and Lewis 1992; Kling et al. 1992; Miller and Oremland 1988; Dacey and Klug 1979). Lakes also have the capacity to produce and store CH<sub>4</sub> under ice cover during winter (Smith and Lewis 1992; Miller and Oremland 1988), creating the potential for release of most of that stored CH<sub>4</sub> to the atmosphere following ice melt.

The annual CH<sub>4</sub> budget of lakes is controlled by complex interactions of CH<sub>4</sub> production in bottom sediments, oxidation in the water column, and loss to the atmosphere by diffusion and ebullition (Kuivila et al. 1988; Iversen et al. 1987; Rudd and Hamilton 1978; Reeburgh and

Heggie 1977; Rudd et al. 1974), as well as potential inputs from hydrologic sources such as inflow of CH<sub>4</sub>-rich groundwater (Freeze and Cherry 1979) and surface water (de Angelis and Lilley 1987). Annual CH<sub>4</sub> storage in cold dimictic lakes is characterized by two cycles of CH<sub>4</sub> loss and buildup. Periods of loss immediately follow spring and fall turnover with interim periods of buildup during summer stratification and under winter ice cover. At the time of spring ice melt, the CH<sub>4</sub> concentration gradient to the atmosphere is very steep and, if oxidative losses are small, loss in storage immediately following spring turnover is essentially the loss to the atmosphere.

Methane, as an end product of anaerobic decomposition, is directly related to carbon loading. Consequently, lakes with high sediment organic content have been observed to produce more CH<sub>4</sub> than lakes with low sediment organic content (Smith and Lewis 1992). Lakes with extensive littoral macrophyte communities tend to have more organic-rich sediments than lakes without littoral zone macrophytes, and the death and decomposition of macrophytes in these lakes may result in greater CH<sub>4</sub> emission. The extent that littoral zone macrophyte communities can affect dissolved CH<sub>4</sub> concentrations depends on the size and depth of the lake. Small lakes with large ratios of littoral zone area to lake area are more influenced by littoral zone carbon contributions than large lakes with smaller ratios of littoral zone area to lake area. Most of the world's lakes are small, with morphologies conducive to productive littoral zones (Wetzel 1983).

There are few estimates of CH<sub>4</sub> emission from various lake types within climatic regions. In temperate North America, Miller and Oremland (1988) measured pelagic CH<sub>4</sub> flux to the atmosphere (mol m<sup>-2</sup> d<sup>-1</sup>) from four lakes

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Table 1. Locations, surface areas, and littoral-zone sediment types of the 19 study lakes. Lakes with sandy or rocky littoral zones are categorized as hard sediment.

| Lake*                | N lat  | W long | Area (m <sup>2</sup> ) | Sediment type |
|----------------------|--------|--------|------------------------|---------------|
| <b>SRHA</b>          |        |        |                        |               |
| Little Shingobee (1) | 46°59' | 94°41' | 27,120                 | soft          |
| Williams (2)         | 46°57' | 94°40' | 370,900                | soft          |
| Shingobee (3)        | 47°00' | 94°41' | 655,100                | soft          |
| 11th Crow Wing (4)   | 46°48' | 94°44' | 2,997,000              | soft          |
| Leech (5)            | 47°    | 94°    | 573,400,000            | soft          |
| <b>LTER</b>          |        |        |                        |               |
| Crystal (6)          | 46°00' | 89°37' | 378,900                | hard          |
| Allequash (7)        | 46°02' | 89°37' | 1,612,000              | hard          |
| Big Muskellunge (8)  | 46°01' | 89°37' | 3,841,000              | hard          |
| Trout (9)            | 46°02' | 89°40' | 15,610,000             | hard          |
| <b>SNF</b>           |        |        |                        |               |
| Glacier Pond (10)    | 47°57' | 91°34' | 72,300                 | hard          |
| Tofte (11)           | 47°58' | 91°35' | 506,100                | hard          |
| Jasper (12)          | 47°58' | 91°33' | 758,300                | hard          |
| Ojibway (13)         | 47°57' | 91°33' | 1,521,000              | soft          |
| Snowbank (14)        | 48°00' | 91°25' | 20,040,000             | hard          |
| <b>MMA</b>           |        |        |                        |               |
| Hiawatha (15)        | 44°55' | 93°14' | 217,000                | soft          |
| Nokomis (16)         | 44°54' | 93°14' | 805,500                | disturbed     |
| Harriet (17)         | 44°55' | 93°18' | 1,195,000              | disturbed     |
| Calhoun (18)         | 44°57' | 93°18' | 1,720,000              | disturbed     |
| Minnnetonka (19)     | 44°55' | 93°35' | 53,010,000             | soft          |

\* SRHA—Shingobee River headwaters area; LTER—long-term ecological research area; SNF—Superior National Forest; MMA—Minneapolis metropolitan area. Numbers correspond to Fig. 2.

in California and Nevada, Smith and Lewis (1992) studied CH<sub>4</sub> flux from five alpine lakes in Colorado, Rudd and Hamilton (1978) calculated CH<sub>4</sub> flux from a eutrophic lake on the Canadian Shield, and Fallon et al. (1980) estimated CH<sub>4</sub> flux from Lake Mendota, Wisconsin. In addition, there have been estimates of CH<sub>4</sub> flux from Arctic (Kling et al. 1992; Whalen and Reeburgh 1990) and tropical lakes (Bartlett et al. 1988; Devol et al. 1990; Bartlett et al. 1990; Smith and Lewis 1992), but no comparative studies of lake CH<sub>4</sub> emission have previously been made for broad regions such as the glacial lake regions of the northern U.S., Canada, or northern Europe.

Our study relates the magnitude of potential springtime CH<sub>4</sub> emission to the atmosphere from north-temperate lakes to easily measured lake characteristics. We hypothesized that emission would be inversely proportional to lake area because lakes with large surface area tend to have smaller ratios of littoral-zone area to total lake area and that lakes with soft organic-rich littoral sediments would emit more CH<sub>4</sub> to the atmosphere than lakes without such sediments. For this interlake comparison we sought similar antecedent conditions for all lakes studied so that variable conditions such as thermal control of CH<sub>4</sub> production or wind-driven losses of dissolved gas could be discounted. Our sampling therefore focused on determining the CH<sub>4</sub> loss from lakes immediately after early spring breakup of ice cover.

## Methods

*Study lakes*—We selected 19 lakes in four geographic locations in northern Minnesota and Wisconsin (Table 1). The five lakes sampled in north-central Minnesota are in the Shingobee River headwaters area (SRHA) in Hubbard County. Two of these, Williams Lake and Shingobee Lake, have extensive historical data sets (Siegel and Winter 1980; LaBaugh et al. 1981; Carter et al. 1993; Rosenberry et al. 1993; McConnaughey et al. 1994). Lakes in the SRHA are set in carbonate-rich calcareous glacial sediments, have abundant littoral macrophytes, and soft organic-rich littoral zone sediments (soft sediments, Table 1). The lakes are primarily used for recreation, and there are some seasonal and year-around residences along their shores.

Four lakes were sampled at the NSF north-temperate lakes Long-Term Ecological Research (LTER) area in Vilas County, Wisconsin. These lakes are set in noncalcareous glacial sediments and have predominantly sandy littoral zone sediments (hard sediments, Table 1). Use of the LTER lakes is similar to that of the SRHA lakes except that they have fewer residences along their shores than the SRHA lakes.

Five lakes were selected in the Superior National Forest (SNF) in Lake County, Minnesota. Lakes in the SNF are mostly set on the Precambrian Shield and typically have

rocky littoral zones (hard sediments, Table 1). One of the five lakes, Ojibway Lake, has extensive macrophyte growth and soft organic-rich littoral zone sediments. Use of most of the SNF lakes is highly regulated for recreational use with no development along shorelines other than a few campsites.

Five lakes were sampled in the Minneapolis metropolitan area (MMA). These are soft sediment lakes that receive mixtures of urban, suburban, and agricultural runoff. They are used intensively for recreation and are typically surrounded by permanent residences. Lakes Nokomis, Harriet, and Calhoun have littoral zones that have been disturbed along most of their shoreline by macrophyte harvesting, application of herbicides to control macrophyte growth, and (or) bank stabilization.

*Depth profiles of CH<sub>4</sub> concentration*—Preliminary CH<sub>4</sub> data were collected at Williams Lake (SRHA) in 1992. In 1993, surveys of the 19 lakes were conducted twice in spring—once before ice melt and once after—to ensure that peak concentrations of dissolved CH<sub>4</sub> were quantified. We hypothesized that turbulent conditions at breakup may incorporate CH<sub>4</sub> from bottom sediments into the water column causing whole-lake CH<sub>4</sub> storage to be greater at spring turnover than before ice melt. The larger of the two measured storage values was used to calculate potential CH<sub>4</sub> emission to the atmosphere. For all lakes, water samples were collected at the deepest accessible part of the lake or lake basin. In 1992 we collected samples every meter. Based on the smooth profiles of CH<sub>4</sub> concentration vs. depth obtained in 1992, we limited the 1993 sampling to four depths: just under ice or at the water surface if ice was melted, one-third of the depth of the lake, two-thirds of the depth of the lake, and 1 m above the bottom of the lake.

Samples were pumped directly from the lakes into 50-ml polypropylene syringes equipped with three-way nylon stopcocks. The sample water was never in contact with ambient air. Filled syringes were subsequently discharged until they held 25 ml of bubble-free water. Samples were chilled during transport to the laboratory.

In the laboratory, 25 ml of nitrogen gas was added to the syringes. Samples were equilibrated with the headspace by shaking vigorously for 3 min. Headspace gases were then analyzed on a gas chromatograph equipped with a flame ionization detector and a Porapak-N column, using nitrogen as the carrier gas. Gas analyses were done no more than 6–8 h after samples were collected. The concentration of CH<sub>4</sub> in the water samples was calculated with the Bunsen adsorption coefficient for CH<sub>4</sub> (Yamamoto et al. 1976) at the appropriate equilibration temperature.

*Lake CH<sub>4</sub> storage and potential emission*—Potential CH<sub>4</sub> emission for a lake is the area-adjusted maximum dissolved CH<sub>4</sub> available for release to the atmosphere. Profiles of CH<sub>4</sub> concentration vs. depth were integrated with volume vs. depth data obtained by digitizing lake contour maps to calculate CH<sub>4</sub> storage within depth in-

tervals. Horizontal mixing was assumed. The sum of the CH<sub>4</sub> stored in all depth intervals was whole-lake storage (mol CH<sub>4</sub>). Whole-lake CH<sub>4</sub> excess (mol CH<sub>4</sub>) was calculated as the total measured lake storage of CH<sub>4</sub> minus the storage of CH<sub>4</sub> if the lake was at equilibrium with the atmosphere (we assumed 1.75 ppm CH<sub>4</sub> by volume). To adjust for differences in lake areas, we divided whole-lake CH<sub>4</sub> excess by lake surface area to obtain potential CH<sub>4</sub> emission per unit area of lake surface (mmol CH<sub>4</sub> m<sup>-2</sup>).

*CH<sub>4</sub> oxidation and production measurements*—Hanging-bottle experiments were conducted at Williams Lake after ice melt in spring 1993 to determine the importance of CH<sub>4</sub> oxidation or production at that time. In addition to the three syringe samples from each depth that were used to determine initial CH<sub>4</sub> concentration, two 1-liter bottles were filled and capped. The filling tube was placed at the bottom of the bottles and the bottles were overfilled without bubbling or splashing to prevent the exchange of gases to or from the water sample. Once full, the bottles were tied onto a weighted rope and suspended in the lake at the depth from which they were collected. After 24 h, bottles were retrieved and put into a cooler of ice for transport to the laboratory. Sample water was taken from the bottles with the same type of syringes used for the initial profile. Extraction and measurement protocols were identical to those used in determining the initial CH<sub>4</sub> concentration profile. Methane concentrations in the bottles were averaged to obtain oxidation or production values for each sample depth. The difference between the initial CH<sub>4</sub> concentrations and the concentrations in the bottles after the 24-h incubation period indicated either oxidation (a negative change) or production (a positive change). Total CH<sub>4</sub> oxidation in the lake was calculated on a volume-weighted basis by the method previously explained for determination of whole-lake CH<sub>4</sub> storage.

*Statistical analysis*—Potential CH<sub>4</sub> emission and lake area were log-transformed to obtain a normal distribution of data. The data were analyzed by a simple linear regression of log potential CH<sub>4</sub> emission vs. log lake area to determine whether lake area was a significant predictor of potential CH<sub>4</sub> emission. Subsequently, the data were reanalyzed without the three disturbed MMA lakes to assess the relationship between potential CH<sub>4</sub> emission and lake area in relatively undisturbed lakes. A third analysis was performed to determine whether a model including lake area and a dummy variable for the presence or absence of soft littoral sediments could explain more of the variability in potential CH<sub>4</sub> emission (Weisberg 1985; SAS/STAT user's guide, release 6.03 ed.). Disturbed lakes were not included as a category because there were too few of them and their areas did not span a large enough range to identify a specific trend.

*Regional estimate*—We estimated regional emission using the relationship for potential lake CH<sub>4</sub> emission as a function of lake area and littoral zone sediment type and using the frequency distribution of lake size for more

than 12,000 lakes >4 ha in Minnesota north of 45° latitude. The Minnesota Conservation Department (MCD 1968) lists the number of lakes in each county and divides the lakes into 12 size categories ranging from 4 to 400,000 ha. For lake areas >60 ha, the ranges for each category are progressively larger (see MCD 1968). Our regional estimate assumes that the median lake area for each size category adequately describes the mean potential emission per lake in that category. We calculated the actual mean area for the largest size category because there were only 47 lakes in that category and the range in area was large (2,000–400,000 ha). Although our field measurements were taken from lakes as small as 2.7 ha, lakes <4 ha are not included in the MCD (1968) report and were not included in our estimate of regional CH<sub>4</sub> emission. We could not locate a similar report listing the surface area of all lakes in Wisconsin, so our regional estimate is limited to northern Minnesota. Potential CH<sub>4</sub> emission for the median lake area of each lake size category was obtained by means of regression equations (see results). The potential CH<sub>4</sub> emission (mmol m<sup>-2</sup>) was multiplied by the median lake area to obtain median CH<sub>4</sub> excess per lake for each size category. The moles of excess CH<sub>4</sub> per lake were then multiplied by the number of lakes in the particular size category to estimate total CH<sub>4</sub> excess for all lakes in the category. The regional CH<sub>4</sub> emission is the sum of CH<sub>4</sub> excess in all lake size categories.

In order to apply our model to all Minnesota lakes north of 45° we assumed that the ratio of soft littoral sediment lakes to hard littoral sediment lakes was 1:1, identical to the ratio in our sample of 16 lakes. However, because we did not know the actual ratio of soft to hard littoral sediment lakes we also calculated a range in regional CH<sub>4</sub> emission. The maximum regional estimate assumes that all lakes in the region have soft littoral sediments and the minimum estimate assumes that no lakes in the region have soft littoral sediments.

## Results

In 1992, the dissolved CH<sub>4</sub> storage in Williams Lake decreased from 78,900 mol under ice to 26,600 mol the day after ice melt, and 11,700 mol 2 d after ice melt. Methane storage continued to decrease until at least 20 May when whole-lake storage was only 2,010 mol (Fig. 1). This amounts to a 97% loss in whole-lake CH<sub>4</sub> storage by 20 May with the first 85% lost within 48 h of ice melt. Methane storage increased after 20 May and continued to increase through summer until fall turnover (Fig. 1).

The calculated potential spring CH<sub>4</sub> emission for the 19 lakes sampled in 1993 ranged from 0.4 to 185 mmol CH<sub>4</sub> m<sup>-2</sup> (Table 2). Small lakes had greater potential CH<sub>4</sub> emission per unit surface area than large lakes, and lakes with soft littoral sediments had greater potential CH<sub>4</sub> emission than lakes without such sediments (Fig. 2). Lakes Nokomis, Harriet, and Calhoun—urban lakes with disturbed littoral zones—had uniformly small potential CH<sub>4</sub> emission (Fig. 2).

Methane oxidation was negligible in the upper 5 m of

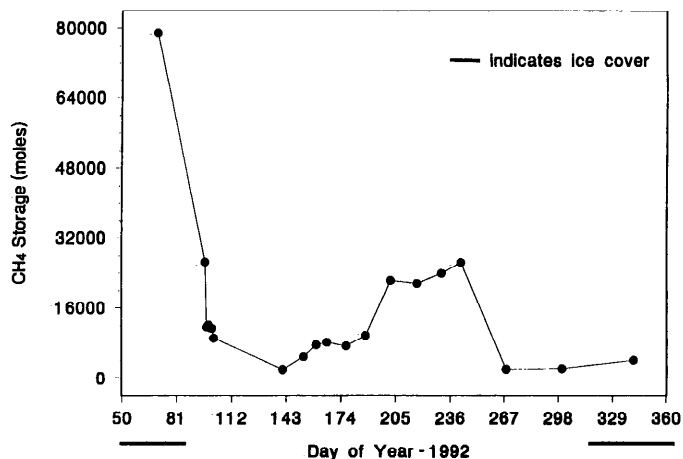


Fig. 1. Whole-lake CH<sub>4</sub> storage in Williams Lake, March–December 1992. Decreases in CH<sub>4</sub> storage are rapid both in early spring and late fall at about the time of turnover.

Williams Lake on 21 April 1993 as indicated by no measurable change in concentration in our incubation bottles. Measured oxidation at depths below 5 m totaled 870 mol CH<sub>4</sub> d<sup>-1</sup>. This compares to a minimum measured whole-lake oxidation rate of 400 mol d<sup>-1</sup> in January 1992 and a maximum rate of 10,500 mol d<sup>-1</sup> in August 1992 (Striegl unpubl. data). The importance of CH<sub>4</sub> oxidation relative to CH<sub>4</sub> emission increases as CH<sub>4</sub> storage decreases (870 mol d<sup>-1</sup> consumes 1.1% of the CH<sub>4</sub> storage measured in Williams Lake in 1992 under ice, 3.3% of the storage the day of ice melt, and 7.4% of the storage 2 d after ice melt). Loss of storage attributable to oxidation at the time of ice melt is therefore small relative to the 85% loss of total storage observed in the 2 d following ice melt.

Table 2. Potential spring CH<sub>4</sub> emissions (mmol m<sup>-2</sup>) from the 19 study lakes.

| Lake             | Potential CH <sub>4</sub> emission |
|------------------|------------------------------------|
| Little Shingobee | 185.0                              |
| Williams         | 94.7                               |
| Shingobee        | 83.2                               |
| 11th Crow Wing   | 38.3                               |
| Leech            | 9.1                                |
| Crystal          | 7.2                                |
| Allequash        | 11.5                               |
| Big Muskellunge  | 9.3                                |
| Trout            | 0.4                                |
| Glacier Pond     | 18.6                               |
| Tofte            | 24.1                               |
| Jasper           | 6.8                                |
| Ojibway          | 54.7                               |
| Snowbank         | 1.6                                |
| Hiawatha         | 104.0                              |
| Nokomis          | 0.9                                |
| Harriet          | 1.5                                |
| Calhoun          | 2.3                                |
| Minnnetonka      | 5.3                                |

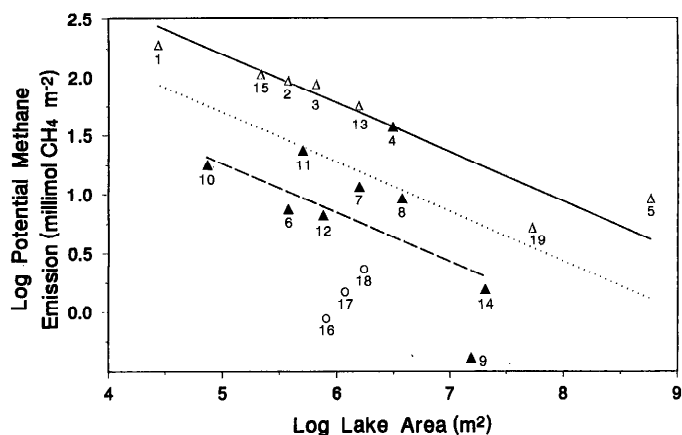


Fig. 2. Log potential emission vs. log lake area for the 19 lakes. Numbers correspond to those in Table 1. Lakes with soft sediments— $\Delta$ ; lakes without soft sediments— $\blacktriangle$ ; the three disturbed lakes— $\circ$ . Solid line—regression equation 2 when  $S1 = 0$  (soft sediment lakes); dashed line—regression equation 2 when  $S1 = 1$  (hard sediment lakes), model  $r^2 = 0.83$ ; dotted line—simple regression equation 1 that assumes a 1:1 mix of soft and hard sediment types ( $r^2 = 0.38$ ). The three disturbed lakes were not included in the regression analysis.

On the basis of linear regression, log lake area explained 24% of the variance in log potential  $\text{CH}_4$  emission for all 19 lakes (SAS/STAT users guide, release 6.03 ed.;  $P = 0.03$ ). Log lake area explained an additional 14% of the variance ( $r^2 = 0.38$ ,  $P = 0.01$ ) if the three MMA lakes having disturbed littoral zones are excluded from the data set. This model is

$$\text{log potential emission} = 3.68 - (0.40 \times \text{log area}) \quad (1)$$

where emission is in mol  $\text{CH}_4$  and lake area is in  $\text{m}^2$ . Inclusion of a term for sediment type results in the model

$$\text{log potential emission} = 4.30 - (0.93 \times S1) - (0.42 \times \text{log area}) \quad (2)$$

where  $S1 = 0$  if a lake has soft littoral sediments and  $S1 = 1$  if it does not. The two resulting regression lines (Fig. 2) are parallel with significantly different intercepts ( $r^2 = 0.83$ ,  $P = 0.0001$ ).

Regional spring  $\text{CH}_4$  emission from Minnesota lakes north of  $45^\circ$  was  $1.5 \times 10^8$  mol in 1993 assuming that the mix of lake sediment types is 1:1. More than half of the total emission came from lakes between 4 and 80 ha (Fig. 3). The remainder came from lakes between 80 and 400,000 ha. The range of regional spring  $\text{CH}_4$  emission for 1993 was from  $5.3 \times 10^7$  mol (assuming no lakes have soft sediments) to  $4.5 \times 10^8$  mol (assuming all lakes have soft sediments).

## Discussion

Lakes are direct sources of  $\text{CH}_4$  to the atmosphere and as such need to be considered when evaluating global climate change scenarios. Although recent global budgets

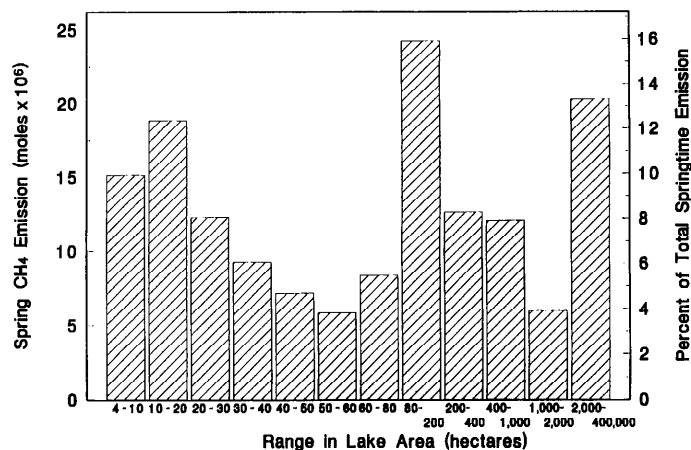


Fig. 3. Spring  $\text{CH}_4$  emission from MCD (1968) lake categories in Minnesota (north of  $45^\circ$ ). Left axis indicates spring  $\text{CH}_4$  emission from each category. Right axis shows the percent of the total  $\text{CH}_4$  emission from northern Minnesota lakes coming from each category. Note the increasing range of lake area encompassed by categories as size increases.

treat lakes as minor sources of  $\text{CH}_4$  when compared to wetlands (Khalil and Shearer 1993), many studies may underestimate annual lake  $\text{CH}_4$  emission. Most  $\text{CH}_4$  emission measurements from lakes have been made during summer (Roulet et al. 1992; Whalen and Reeburgh 1990; Miller and Oremland 1988; Fallon et al. 1980) and exclude periods around ice melt or fall turnover.

We observed high concentrations of  $\text{CH}_4$  under ice and a subsequent rapid loss after ice melt in Williams Lake in 1992. A similar rapid loss was observed in Williams Lake after fall turnover. The low  $\text{CH}_4$  oxidation rates measured at the time of ice melt suggest that most  $\text{CH}_4$  storage under ice was released to the atmosphere and not oxidized in the lake. Smith and Lewis (1992) found a similar decrease in  $\text{CH}_4$  concentration at spring ice melt in Red Rock Lake in Colorado; they also attributed the decrease to release to the atmosphere. The annual  $\text{CH}_4$  emission estimated for a beaver pond in boreal Canada ( $45^\circ\text{N}$ ,  $<10$  ha) was  $475 \text{ mmol m}^{-2} \text{ yr}^{-1}$  (Roulet et al. 1992). This estimate did not include emission following ice melt. The potential  $\text{CH}_4$  emission at ice melt for Little Shingobee Lake ( $46^\circ\text{N}$ , 2.7 ha) was  $185 \text{ mmol CH}_4 \text{ m}^{-2}$  (Table 2), or 40% of the total annual estimate for the beaver pond. Thus, spring emission of  $\text{CH}_4$  from lakes may be a much more important component of annual  $\text{CH}_4$  emission than previously thought.

Methane is an important end product of carbon cycling in lakes (Rudd and Hamilton 1978; Kuivila et al. 1988). Carbon used for methanogenesis comes from accumulated organic matter settled on lake bottoms. The inverse relationship between potential  $\text{CH}_4$  emission and lake area suggests that the littoral zone is an important contributor of organic matter to the  $\text{CH}_4$  cycle. Our findings support this because the greatest potential spring  $\text{CH}_4$  emission came from lakes having productive organic-rich

littoral-zone sediments. With increasing lake area, the ratio of littoral-zone area to whole-lake area generally decreases, and the influence of littoral productivity on the whole lake decreases (Wetzel 1983). Potential CH<sub>4</sub> emission also decreases with increased lake area. Lakes without soft organic-rich sediments follow the same general pattern, but have smaller potential CH<sub>4</sub> emission. Although littoral zone productivity is still apparently important to the CH<sub>4</sub> cycle in these lakes, the amount of organic matter available for decomposition is smaller than in lakes with highly productive littoral zones. Under warming conditions littoral zone productivity would be expected to increase in both hard and soft sediment lakes. This increase in productivity would provide additional organic matter for CH<sub>4</sub> production and lake CH<sub>4</sub> emission would likely increase. Increased CH<sub>4</sub> emission from lakes could provide a positive feedback to global warming mechanisms by further contributing to the increase of atmospheric CH<sub>4</sub> concentration.

Potential spring CH<sub>4</sub> emission from relatively undisturbed lakes is best described by the model that includes lake area and littoral sediment type. Of the 16 relatively undisturbed lakes in our study, eight had soft sediments and eight did not. Based on this, we estimated the regional CH<sub>4</sub> emission in the spring to be  $1.5 \times 10^8$  mol. Although the model has been applied only to spring turnover, when oxidative losses are small, it holds promise for extrapolation to annual emission. In a study of CH<sub>4</sub> flux from Alaskan lakes measured over 6 weeks during the ice-free period, Bartlett et al. (1992) estimated the average daily flux rate from small lakes to be 25 times higher than the average daily flux from large lakes. This finding suggests that the pattern of decreased CH<sub>4</sub> emission with increased lake area may be consistent throughout the ice-free period.

The spring regional CH<sub>4</sub> emission estimate may be conservative in three ways. First, lakes with surface area <4 ha, which have the highest potential CH<sub>4</sub> emission per unit area, were not included. Second, continued CH<sub>4</sub> buildup under ice cover after we first measured lake CH<sub>4</sub> storage and before ice melt may have caused us to underestimate potential spring CH<sub>4</sub> emission for some lakes. Finally, our emission estimates are based solely on CH<sub>4</sub> dissolved in the water column at the time of our measurements. Any loss of CH<sub>4</sub> from sediment by ebullition is not included in our estimate.

MMA lakes having disturbed littoral zones did not fit our observed pattern of higher CH<sub>4</sub> emissions associated with soft littoral sediment lakes. Macrophyte harvesting and the application of herbicides decrease the biomass of plant material, thus reducing the amount of organic matter available for decomposition. Physical and chemical disturbances associated with macrophyte control may also inhibit methanogenesis. Bank stabilization (i.e. building a wall where the lake edge once was) disrupts the littoral zone and may also inhibit macrophyte growth and subsequent methanogenesis. We cannot verify, without further study, whether the lakes we measured are representative of other lakes disturbed by lake management practices.

In 10 of the 19 lakes we measured potential lake CH<sub>4</sub> emission was greater shortly after ice melt than before ice melt. We were not able to determine whether this increase was due to continued CH<sub>4</sub> production under ice cover after our first measurement or to mixing of stored CH<sub>4</sub> from the sediments into the water column. However, it seems likely that windy conditions at ice melt may cause the release of CH<sub>4</sub> stored in sediment into the water column. Under such conditions the maximum potential CH<sub>4</sub> emission actually occurs shortly after ice melt.

We do not know whether the observed relations among lake size, sediment type, and potential spring CH<sub>4</sub> emission extend to other climatic or seasonal conditions or whether they can be extrapolated to smaller bodies of water. In addition, it seems that estimates of annual lake CH<sub>4</sub> emission are conservative because of a lack of measurements at and around the time of turnover. Our measurements at this time indicate that most of the regional spring CH<sub>4</sub> emission from northern Minnesota lakes in 1993 came from small lakes. Because there are so many small lakes and ponds, estimates of global lake CH<sub>4</sub> emission need to be weighted to small lakes. Consideration of littoral-zone sediment type and productivity would also improve the accuracy of predicted CH<sub>4</sub> emission. Additional estimates of annual CH<sub>4</sub> emission for larger regions and a wider variety of lake types, based on more complete early spring and late fall CH<sub>4</sub> measurements, are needed to improve our understanding of lake-atmosphere interactions.

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