

SEASONALITY OF METHANE EMISSIONS  
FROM FIVE LAKES AND ASSOCIATED  
WETLANDS OF THE COLORADO ROCKIES

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**Abstract.** Methane emissions were measured over a 15-month interval for five lakes and five associated wetland sites in the Rockies of Colorado at elevations between 2800 and 3600 m. Three of the five lakes accumulated dissolved methane under ice; accumulation was as high as 53-fold above ice-free water column concentrations in the shallowest lake. The combination of high dissolved oxygen and low dissolved inorganic nitrogen concentrations within the water column during ice breakup suggests that methane emissions rather than methane oxidation led to the substantial loss of dissolved methane from the shallowest lake at the time of spring thaw. A pulsed release of methane to the atmosphere at the time of ice breakup within lakes may be widespread at high latitudes and may play a role in the observed increase in tropospheric methane concentrations in the northern hemisphere. During the ice-free season, the mean emission rate was

1.6 mmol m<sup>-2</sup> d<sup>-1</sup> over open water for the five lakes, but the mean was much higher (13 mmol m<sup>-2</sup> d<sup>-1</sup>) over the *Nuphar lutea* beds located in one of the lakes. Open water emissions occurred primarily through diffusion rather than bubbling. For wetlands near the lakes, average lake emissions ranged from negligible to almost 6 mmol m<sup>-2</sup> d<sup>-1</sup>; the average across all sites was 2.1 mmol m<sup>-2</sup> d<sup>-1</sup> during the warm season. There was no measurable emission during the winter months. Surface dissolved methane explains 40% of the variation in emissions from the open water sites; the combination of soil organic C content and soil temperature explains 40% of variation in emissions from the wetland sites. The data from the Southern Rockies and information that has accumulated on other lake types over the last 15 years indicate that lakes may be a larger source strength of methane than reported estimates.

#### INTRODUCTION

Methane is a radiatively important trace gas. Although its concentration is considerably lower than that of tropospheric carbon dioxide (circa 1.75 ppm versus 350

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ppm) [Wuebbles and Edmonds, 1991], methane is more effective on a molar basis than carbon dioxide in causing radiative heating [Ramanathan et al., 1985]. According to recent estimates, tropospheric methane concentrations have been increasing at a rate of about 1% per year over the last decade [Blake and Rowland, 1988], but the source of this increase in methane is yet to be identified conclusively. Neither anthropogenic sources (livestock, rice paddies, biomass burning, natural gas production) nor biogenic sources (wetlands, termites, lakes) have been quantified with sufficient accuracy to support rigorous estimates of global emissions from these sources.

Using a meager data set, Ehhalt [1974] made the first estimates of global anthropogenic and biogenic methane sources. Ehhalt identified wetlands as an important methane source comprising 30-40% of the total biogenic source. Since Ehhalt's publication, new measurements of biogenic methane emissions from wetlands have accumulated [Baker-Blocker et al., 1977; Harriss et al., 1982, 1985, 1988; Sebacher et al., 1986; Crill et al., 1988; Chanton and Martens, 1988; Whalen and Reeburgh, 1990; Roulet et al., 1992], but published data on methane emissions from subalpine and alpine wetlands are scarce. These habitats are potentially a source of methane because they store water during the winter and remain saturated during most or all of the warm season. Their high water content leads to low soil oxygen concentrations that would allow the production of methane.

In contrast to wetlands, freshwater lakes are reported to be an insignificant source of tropospheric methane [Khalil and Rasmussen, 1983; Cicerone and Oremland, 1988]. However, this conclusion is not well documented. The authors of recent global budgets have relied upon the estimates of Ehhalt [1974] for methane emitted by lakes, even though (1) Ehhalt's estimates were

based upon only two data sets, (2) the estimates include only ebullition (bubbling) rather than total emissions across the air/water interface, and (3) Ehhalt's assumptions for extrapolating the lake data to a global scale were probably incorrect.

The purpose of this study is to quantify methane emissions from lakes and wetlands of the subalpine and alpine regions in Colorado and to attempt to relate emissions to environmental variables. Methane emissions from five lakes and their associated wetlands located in the Southern Rocky Mountain region were measured over a 15-month period. In addition, measurements were made of environmental variables that potentially influence methane emissions: soil temperature [Baker-Blocker et al., 1977; Svensson and Rosswall, 1984; Moore and Knowles, 1987; Crill et al., 1988], soil moisture [Svensson, 1976], depth of water [Sebacher et al., 1986; Harriss et al., 1982; Bartlett et al., 1988], and soil organic carbon [Harriss and Sebacher, 1981; Kelly and Chynoweth, 1981]. The data analysis deals with variability of emissions among sites and, through correlation analysis, identifies environmental factors that appear to influence methane emission.

#### STUDY SITES

The five study sites are located in the Front Range of the Southern Rocky Mountains within the subalpine (2500-3200 m) and alpine (3200-3884 m) zones (Table 1, Figure 1). Lake Dillon was formed in 1963 by impoundment of the Blue River; an extensive data set is available for it [Lewis et al., 1984; Morris, 1985, 1990]. The lake was sampled at depths  $\leq 10$  m, which represents about 34% of the lake's surface area. Lake Dillon has extensive wetlands only at its upper end, where stands of *Carex utriculata*, *C. athrostachya*, *Poa palustris*, and *Beckmannia syzigachne* are found.

Red Rock and Long Lakes are both natural lakes located within the Boulder Creek watershed. Red Rock

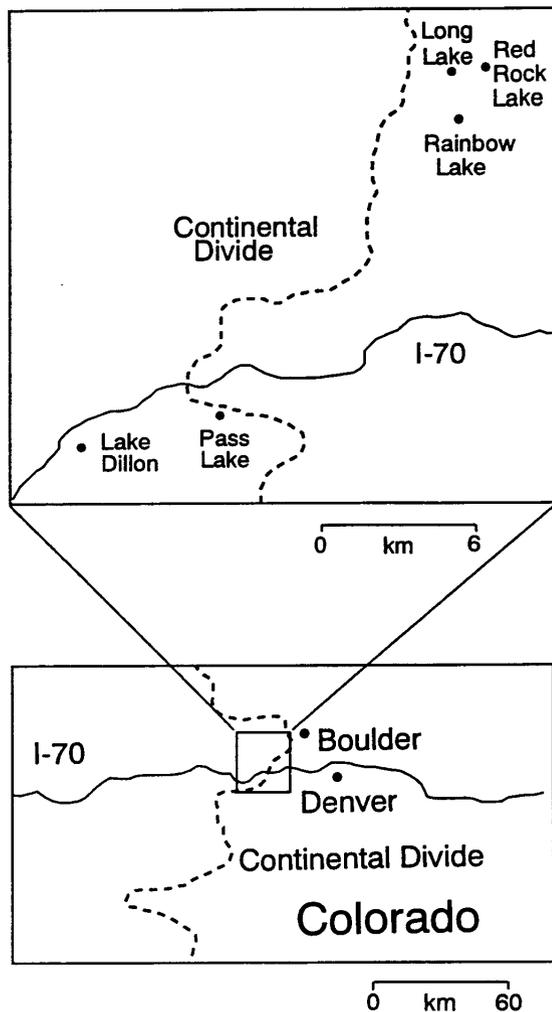


Fig. 1. Location of the five sampling sites.

Lake is shallow, is located at a slightly lower elevation, and has an extensive population of the rooted floating-leaved macrophyte, *Nuphar lutea*, (ssp. *polysepala*)

that covers about 60% of its surface area from July to October. The wetlands surrounding Red Rock Lake contain primarily sedge (*Carex aquatilis*). An extensive willow (*Salix*) community extends upstream toward Long Lake. Red Rock Lake is protected from high winds by conifers (*Picea engelmannii* and *Abies lasiocarpa*) that surround the lake, while Long Lake is more exposed to winds. The wetlands surrounding Long Lake are more extensive than those found at Red Rock Lake. The wetter depressions contain *Carex aquatilis*, and the higher, drier regions contain a diverse assemblage of vascular plants: *Clementsia rhodantha*, *Deschampsia cespitosa*, *Psychrophila leptosepala* (*Caltha leptosepala*), *Erigeron*, *Agrostis variabilis*, *Pedicularis groenlandica*, *Ranunculus adoneus*, *Mertensia lanceolata*, and *Persicaria maculata*.

Rainbow Lake, which is located two watersheds to the south of Red Rock Lake and Long Lake, is the lowest in elevation of a series of five interconnected lakes. It is similar to Red Rock Lake in elevation, size, and degree of protection from the wind, but the vegetation around its shores is more diverse (*Deschampsia cespitosa*, *Eleocharis acicularis*, *Carex aquatilis* and *Salix*); it does not contain floating leaved macrophytes.

Pass Lake, the highest of the five lakes, is located on the Continental Divide directly below the tree line. The wetlands are occupied by *Carex*, *Chondrophylla aquatica* (*Ciminalis fremontii*),

TABLE 1. Characteristics of the Five Lakes

Lake	Elevation, m	Area, ha	Depth, m
Dillon	2750	1300	57
Red Rock	3095	2.1	1
Rainbow	3109	1	1
Long	3208	16	7.5
Pass	3608	1.6	3.5

See Figure 1 for locations. Depth refers to the maximum depth.

*Pedicularis*, *Amerosedum lanceolatum* (*Sedum lanceolatum*), *Castilleja*, *Primula parryi*, and *Psycrophila leptosepala* (*Caltha leptosepala*).

Weber [1976] was used to identify plant species. Synonymous species names that are more commonly used in other regions of the United States [Weber and Wittmann, 1992] are shown in parentheses following the plant names.

#### METHODS

The static chamber method was used to measure methane emissions from the lakes and wetlands [Dacey and Klug, 1979; Miller and Oremland, 1988]. Sampling was most intensive at Red Rock Lake, where measurements spanned a 15-month period (monthly in 1989 and biweekly in 1990 during the ice-free period). Measurements were made monthly at the other sites over a 13 or 14 month period.

Methane emissions from the lakes were measured with a plastic chamber (40 cm diameter, 12 cm height) equipped with a floatation collar; two chambers were deployed per sampling date. Once the chamber was sealed, duplicate gas samples were removed through a septum with 5-cm<sup>3</sup> glass syringes equipped with three-way stopcocks. Gas samples were collected every 20 to 30 min over a 1.5-hour period. To prevent loss of gas from the syringes after sampling, the syringe barrels were filled with distilled water. At the end of the sampling period, a known quantity of ethane was added to each sampling chamber so that the headspace volume could be calculated. The gas samples were analyzed within 24 hours on an Hewlett-Packard model 5840A gas chromatograph equipped with a flame ionization detector. The samples were injected onto a 3.2-mm stainless steel column (3 m) packed with Haysep A (80/100 mesh); the carrier gas was ultrapure helium set at a flow rate of 20 mL/min, and the oven temperature was 40°C. The level of precision is ±2%, and the lower limit of detection is 0.5

ppm methane. The minimum detectable flux at the meadow sites is 0.008 mmol CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup>, and at the lake sites is 0.02 mmol CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup>. All sample concentrations were corrected for differences in elevation and air temperature between sampling locations and the laboratory.

At the end of the sampling period water depth was measured, and water temperatures were measured at increments of 0.5 m with a thermistor. Surface and bottomwater samples were collected with a Van Dorn sampler. Duplicate subsamples were removed from the water sampler with 60-cm<sup>3</sup> syringes equipped with three-way stopcocks and needles. These samples were analyzed for dissolved methane by the technique of McAuliffe [1971]. In addition, duplicate samples for dissolved oxygen were analyzed by the Winkler method [Carpenter, 1965]. Sediment cores were collected at the beginning of the project from each lake with a piston corer (4 cm diameter). The cores were sectioned at 2-cm intervals in the field and returned to the laboratory where the sections were dried at 50°C to constant weight. The dried samples were ground and replicate subsamples were analyzed for organic carbon and nitrogen content on a Carlo Erba model 1106 elemental analyzer.

Emission rates were also measured from the *Nuphar lutea* community located in Red Rock Lake. Chambers were placed over one or two floating leaves. Emissions from the lakes are classified as either open water (all lakes) or macrophyte (*Nuphar lutea*, Red Rock Lake only).

In the meadows, two boxes were placed on the higher, drier ground and two boxes were placed on the lower, wetter ground. The emissions were measured in the same manner as for the lakes, except that the sampling chambers consisted of aluminum frames (30 x 30 x 7 cm) equipped with removable lids. The frames were inserted into the soils and left uncovered for about 1 hour to allow

methane emitted by disturbance of the soil to dissipate into the atmosphere. The frames were then sealed with lids containing a closed-cell neoprene gasket mounted along the edges; wing nuts secured the lids to the frames. Temperature was monitored in the sampling boxes.

At the end of the sampling period, soil temperature was taken within each sample box with a mercury thermometer inserted to a depth of 5 cm. The depth of standing water in the chamber was noted, and a soil sample (6-cm depth) was collected with a soil corer. The soil samples were returned to the laboratory, where large organic debris was removed, wet weight was measured and the samples were dried to constant weight at 50°C and reweighed as a means of quantifying soil moisture content. The soil samples were also analyzed for carbon and nitrogen as described above.

During the winter, methane emissions were not measured from the lakes. However, concentrations of dissolved oxygen and methane were monitored periodically by sampling the water column through a hole augured out of the ice. Methane emissions from the wetlands were measured once at each site during the period of snow cover. Two approaches were used to measure the emissions: (1) snow was removed from the ground, and the boxes were sealed onto frozen soils, and (2) the boxes were placed on top of the snow. Samples were collected and analyzed as described above.

## RESULTS

**Lakes.** Table 2 summarizes the environmental characteristics measured in conjunction with the emission measurements from the 5 lake sites. All lakes retained oxygen; the lowest mean concentration was for Red Rock Lake (64% saturation). Average open water dissolved methane concentrations ranged from 0.07  $\mu\text{M}$  at Long Lake to 1.59  $\mu\text{M}$  at Red Rock Lake. The lakes varied substantially in sediment C content. Relative to the average dissolved methane concentrations during the ice-free period (Table

TABLE 2. Summary of the Environmental Characteristics Measured at the Five Lake Sites

Site	Sampling Depth, cm	Temperature, °C	Oxygen, mg $\ell^{-1}$	Dissolved Methane, $\mu\text{M}$	Carbon, $\mu\text{mol mg}^{-1}$ dry	Nitrogen, $\mu\text{mol mg}^{-1}$ dry
Dillon	239 (125-315)	12.7 (7.5-15.4)	8.13 (6.93-9.97)	0.74 (0.24-1.14)	7.9 (7.0-8.4)	0.55 (0.31-0.68)
Long	224 (180-280)	9.3 (7.0-10.7)	6.97 (6.19-7.94)	0.10 (ND-0.27)	5.3 (5.0-5.4)	0.44 (0.40-0.50)
Pass	224 (130-325)	6.6 (2.3-9.8)	7.41 (6.36-8.39)	0.65 (0.29-1.20)	1.6 (0.8-3.0)	0.18 (0.03-0.32)
Red Rock	90 (75-112)	9.2 (1.5-10.9)	5.07 (3.88-7.72)	1.46 (0.83-2.37)	22.3 (21-24)	1.43 (1.37-1.48)
	83 (65-100)	10.6 (1.5-13.5)	4.84 (3.88-7.23)	1.77 (0.67-2.56)	24.2 (23-26)	1.55 (1.28-1.81)
Rainbow	72 (40-100)	10.4 (3.3-14.5)	7.41 (5.73-9.61)	1.02 (0.31-2.07)	12.1 (11-13)	0.86 (0.81-0.97)

The values indicate the mean of the data collected during the ice-free period, and the parentheses show the range in the data. The first line for Red Rock Lake is the open-water data, and the second line is the data collected from the macrophyte zone. ND means not detectable.

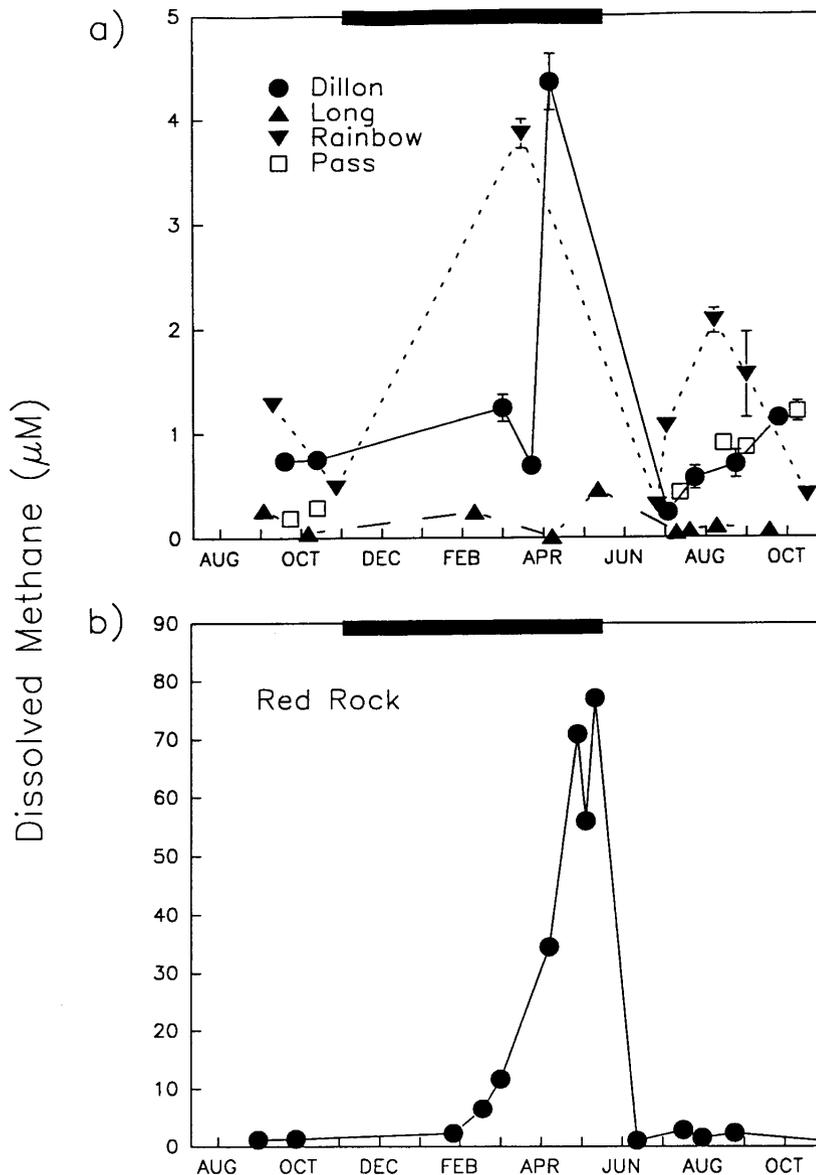


Fig. 2. Dissolved methane concentrations (mean of two surface water samples  $\pm$  standard deviation) for (a) four of the study lakes and (b) for Red Rock Lake, where measurements were made more frequently. The thickened portion of the upper abscissa indicates the period of ice cover. Winter data for Pass Lake are not shown because the lake froze completely to the sediments.

2), there was a fourfold increase in dissolved methane concentrations in Rainbow Lake, a sixfold increase in Lake Dillon, and a 53-fold increase in Red Rock Lake under the winter ice cover (Figure 2), even though oxygen concentrations remained relatively high (4-8 mg

$l^{-1}$ ). Methane concentrations remained low and oxygen concentrations remained high in Long Lake throughout the winter. Water column methane concentrations could not be measured during the winter at Pass Lake, which froze completely to the bottom sediments.

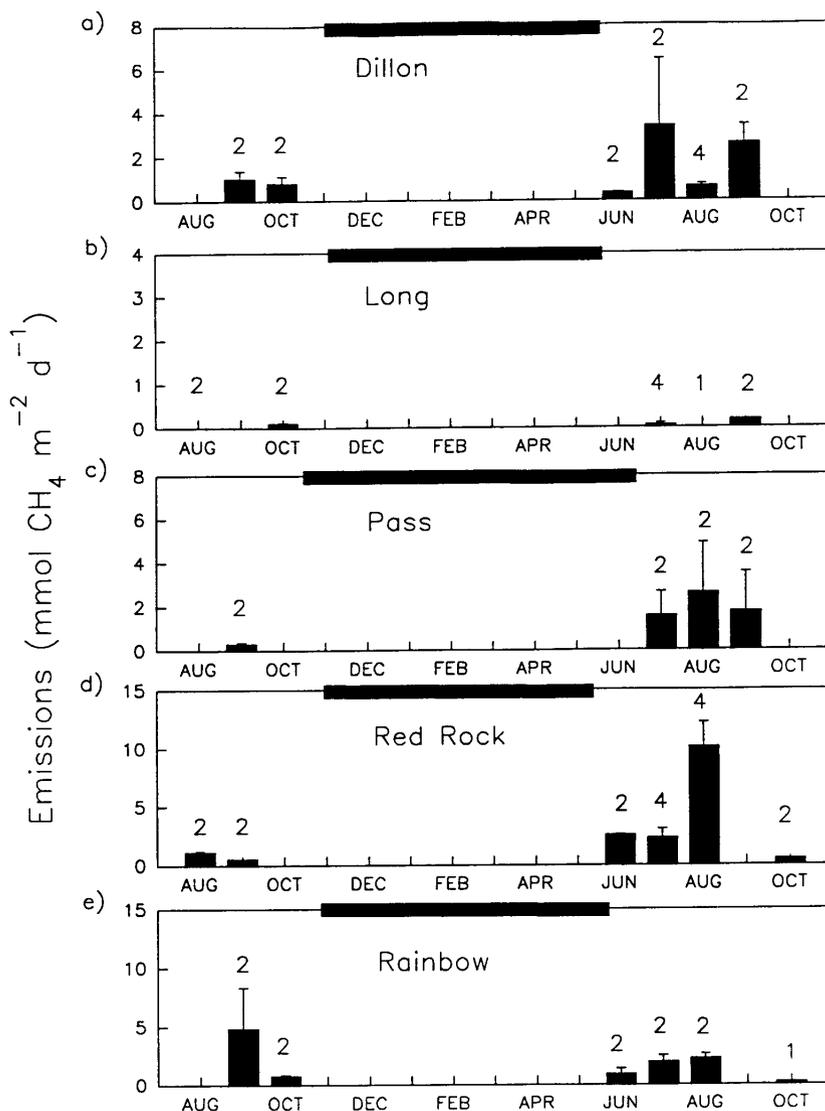


Fig. 3. Mean monthly methane emissions from the open water portion of the five study lakes (error bars indicate one standard deviation; sample size indicated above the average monthly emission rates). In some cases where emissions were either zero or too low to appear on the figure only the sample size is shown. The thickened portion of the upper abscissa indicates the period of ice cover.

Thaw began in the last half of May at Dillon, Long, Red Rock, and Rainbow Lakes and in late June at Pass Lake. After thaw, the lakes began emitting methane. Positive emissions were observed throughout the summer and early fall (Figure 3). The emissions from Long Lake, which deviated from this general seasonal pattern, were low throughout the ice-free period

(range: 0 to 0.17 mmol CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup>, Figure 3). In Red Rock Lake, large temporal variability in the quantity of methane emitted by the macrophyte community was observed between July and October (Figure 4).

Average lake-wide emissions during the ice-free periods are shown in Table 3. In the case of Lake Dillon, the emission data

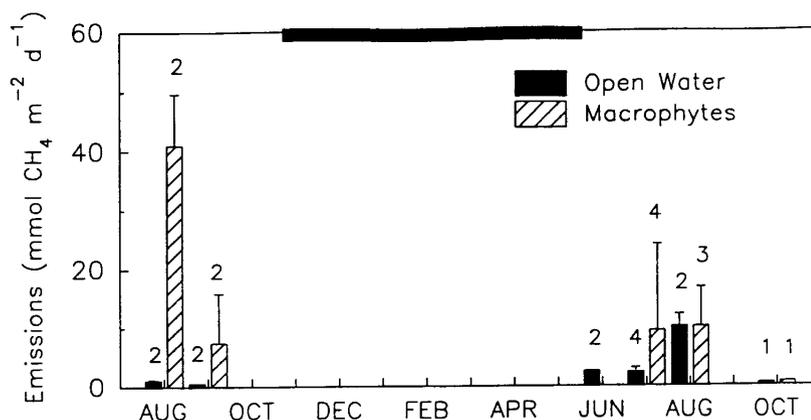


Fig. 4. Mean monthly methane emissions from the open water portion (solid bars) and *N. lutea* zone (hatched bars) of Red Rock Lake. Symbols are as in Figure 3.

represent fluxes from depths of  $\leq 10$  m, which constitute about 34% of the total lake surface area. Average openwater emissions across the 5 lakes varied by a factor of about 40. A one-way analysis of variance (ANOVA) detected a significant difference in mean emissions from the 5 open water sites ( $p < 0.05$ ). A Student-Newman-Keuls (SNK) test indicated that Red Rock Lake and Long Lake emitted significantly different quantities of methane, but no difference could be detected among the other three lakes. The most striking feature

of Table 3 is the high emissions observed for the *Nuphar lutea* community of Red Rock Lake. Emissions from the macrophytes were significantly greater than the average emissions from all five of the openwater sites (ANOVA analysis,  $p < 0.05$ ; SNK,  $p < 0.05$ ).

In general, relationships of environmental variables with methane emissions were weak (bivariate correlation analysis and multiple correlation analysis). However, dissolved methane concentration of surface water explained about 40% of the

TABLE 3. Mean and Standard Error of Methane Emissions During the Ice-Free Period From the Lakes (Open Water), Wetlands, and *Nuphar lutea* Community

Site	Open Water	Meadow	
Dillon	1.34 $\pm$ 0.38 (14) <sup>a</sup>	0.01 $\pm$ 0.01 (23)	
Long	0.07 $\pm$ 0.02 (10)	0.86 $\pm$ 0.19 (23)	
Pass	1.76 $\pm$ 0.55 (10)	0.10 $\pm$ 0.04 (21)	
Red Rock	2.94 $\pm$ 0.93 (13)	5.46 $\pm$ 0.55 (34)	12.6 $\pm$ 4.7 (12) <sup>b</sup>
Rainbow	1.80 $\pm$ 0.51 (13)	2.40 $\pm$ 0.35 (27)	

Units are in mmol m<sup>-2</sup> d<sup>-1</sup>. The numbers in parentheses indicate the sample size.

<sup>a</sup>Emissions are representative of about 34% of the lake's surface area.

<sup>b</sup>*Nuphar lutea* community.

TABLE 4. Summary of the Environmental Characteristics Measured at the Five Wetland Sites

Site	Water Depth, cm	Temperature, °C	Soil Moisture, % water, by weight	Carbon, μmol mg <sup>-1</sup> DW	Nitrogen, μmol mg <sup>-1</sup> DW
Dillon	0.7 (0-4)	11.9 (9.5-15.0)	58.2 (36.0-78.0)	8.5 (3.6-16.6)	0.55 (0.25-1.02)
Long	0.7 (0-3)	12.0 (6.0-15.0)	81.2 (76.6-86.8)	26.7 (20.4-34.5)	1.22 (0.97-1.54)
Pass	0.7 (0-4)	10.9 (7.0-17.0)	70.6 (48.8-84.3)	20.2 (8.1-30.9)	0.98 (0.38-1.36)
Red Rock	1.2 (0-4)	11.9 (6.0-16.0)	83.6 (77.5-87.0)	36.7 (31.9-44.0)	1.50 (0.68-2.33)
Rainbow	0.3 (0-3)	12.4 (6.0-17.5)	74.4 (69.9-82.3)	24.3 (17.1-38.2)	1.20 (0.80-1.78)

Snow-free period only; parentheses show the range in data.

variability in methane emissions ( $r^2 = 0.38$ ,  $n = 60$ ,  $p < 0.001$ ). Surface methane concentrations were positively correlated with the organic C ( $r^2 = 0.49$ ,  $p < 0.001$ ) content of the lake sediments and negatively correlated with dissolved oxygen in the surface waters ( $r^2 = 0.33$ ,  $p < 0.001$ ) and sampling depth ( $r^2 = 0.19$ ,  $p < 0.001$ ).

**Wetlands.** Table 4 summarizes the environmental characteristics measured in conjunction with the emission measurements from the five wetland sites. The wetlands surrounding Red Rock Lake were more waterlogged than the others. Soil porosity was lowest at Lake Dillon, as was the organic C and N content of the soil. In contrast, the soil of Red Rock Lake was particularly rich in organic C. Methane emissions were zero while the ground was frozen and were positive following snowmelt except in one case. At Long Lake (Figure 5b), a negative flux was observed. For Lake Dillon (Figure 5a), emissions from the wetland soils were zero on nearly every occasion.

Average emissions across the five wetland sites varied by a factor of about 550 (Table 3). ANOVA detected a significant difference in mean emissions among the five wetland sites ( $p < 0.001$ ); an SNK test indicated that the wetlands of Red Rock Lake emitted significantly higher quantities of methane than the other wetlands ( $p < 0.05$ ). Average emissions were significantly higher for *N. lutea* (Red Rock Lake) than for the wetlands or open water sites (ANOVA,  $p < 0.001$ ); there was no significant difference between the mean emission rates from the open water and wetlands (ANOVA,  $p > 0.05$ ). A multiple regression showed that the combination of organic C content of the sediments and soil temperature explains 40% of the variability in emissions from the wetlands ( $r^2 = 0.38$ ,  $n = 74$ ,  $p < 0.0001$ ).

#### DISCUSSION

**Lakes.** Methane emissions from lakes can occur by molecular

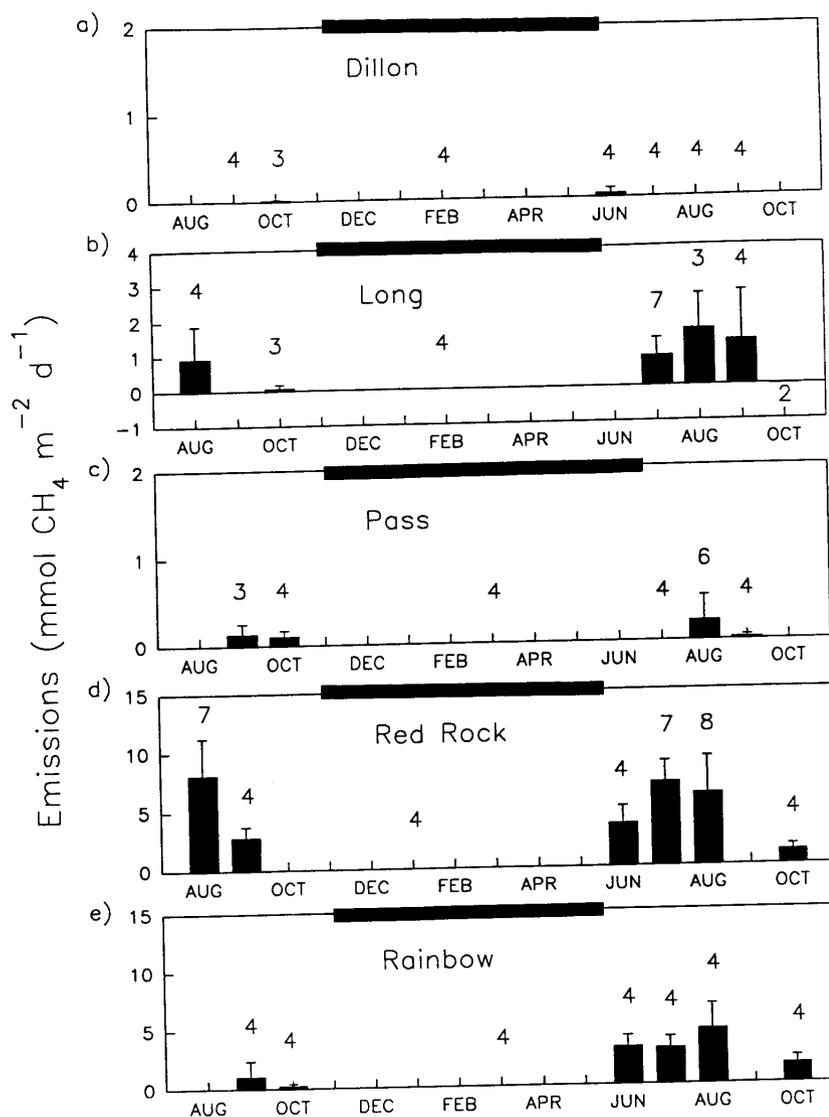


Fig. 5. Mean monthly methane emissions from the five wetland sites. Symbols are as in Figure 3.

diffusion, ebullition, and through the aerenchyma of vascular plants [Schütz et al., 1991]. When ebullition occurs, concentration changes occur in a stepwise manner as methane-rich bubbles break apart upon reaching the air-water interface [Crill et al., 1988; Miller and Oremland, 1988]. The chamber measurements indicate that efflux of methane from the open water sites was by diffusion, because changes in methane concentrations within the chambers were always linear over time. In

lakes, where diffusion is the major route of efflux, emissions are dependent upon surface methane concentrations [Rudd and Hamilton, 1978]. This explains why surface water methane concentrations explained about 40% of the variability in emissions from the five lakes.

Methane production in lakes originates almost exclusively in the sediments, where the environment can be strongly reducing [Rudd and Taylor, 1980]. Plant detritus, root exudates

[Schütz et al., 1991], and particulate organic material settling out of the mixed surface layer [Kelly and Chynoweth, 1981] supply the carbon required by methanogenic bacteria to support methane production. This explains the significant correlation between dissolved methane concentration in the surface water and organic C content of the lake sediments. As methane diffuses upward through the water column, its concentration is modified by methane oxidation. Consequently, both sampling depth and oxygen concentration can influence surface methane concentrations in lakes. Although methane production rates can also be influenced by sediment temperatures [Kelly and Chynoweth, 1981], we did not find a significant correlation between methane emissions and lake temperature, probably because the temperature range was small.

Methane emissions from the zone of *Nuphar lutea* located in Red Rock Lake were probably dominated by active transport through the aerenchymous tissue of the plant. Sebacher et al. [1985] demonstrated that this group of rooted floating-leaved macrophytes exhibits the highest emissions of methane from vascular plants. The emissions from the *Nuphar* zone in Red Rock Lake were about 4 times higher than the open water zone (Table 3), presumably because the conduits provided by the macrophytes prevented methane from being oxidized as it traveled from the sediments to the atmosphere [Chanton and Dacey, 1991]. Emissions vary with leaf age [Dacey, 1981]. This could explain the high variability in the mean emissions from the *Nuphar* for each sampling date, as the flux boxes were randomly deployed over the macrophytes, and leaf age was not taken into account.

The quantity of methane emitted from the open water and macrophyte regions of Red Rock Lake varied greatly between the two years (Figure 4). In 1989, direct transport through macrophytes represented about 99% of the lakewide emissions. In contrast,

diffusion from the open water region (49%) and transport through the macrophytes (51%) were essentially balanced in 1990. It is likely that the difference in the quantity of methane contributed by the macrophytes in 1989 and 1990 was due to leaf damage. A violent hailstorm on July 11, 1990, shredded the leaves of the macrophytes, and the plants did not fully recover before fall.

Methane produced within lake sediments can be stored within the water column under ice, as shown by the accumulation of dissolved methane under the ice, especially in Red Rock Lake (Figure 2). It is surprising that oxygen concentrations remained high under the ice because anoxia usually develops in conjunction with methane oxidation either at the time of fall overturn [e.g., Rudd and Hamilton, 1978], or during the winter [Bédard and Knowles, 1991]. An increase in gaseous species under the ice has been noted in a number of Arctic lakes. For example, Kling et al. [1991] observed that dissolved carbon dioxide concentrations below the ice in four Arctic lakes were up to 10 times greater than expected from ambient air concentrations. However, to the best of our knowledge, this is the first time that increases in dissolved methane under the ice have been reported for lakes that remain aerobic throughout the winter.

When bacteria are dependent upon nitrogen fixation as a sole source of nitrogen for their metabolism, dissolved oxygen concentrations greater than  $1 \text{ mg l}^{-1}$  render methane oxidizers ineffective [Rudd and Taylor, 1980]. For example, in Lake 227, Rudd et al. [1976] observed that methane oxidizing bacteria remain active in the presence of oxygen if dissolved inorganic nitrogen ( $\text{DIN} = \text{NH}_4^+ + \text{NO}_3^- + \text{NO}_2^-$ ) is available as a nitrogen source, such as during fall and spring overturn. This cannot explain the variation in the methane accumulation patterns in Rocky Mountain lakes because DIN is extremely low in all of these lakes throughout the year (W. Lewis,

unpublished data, 1991). Clearly, a better understanding of the process of methane accumulation under ice is required as a basis for prediction of annual methane evasion from lakes.

When ice breakup begins in lakes, loss of accumulated dissolved methane can occur by two mechanisms: (1) rapid dissolution of methane, which is highly insoluble in water [Yamamoto et al., 1976], and subsequent elevated emission rates to the troposphere, and/or (2) increased rates of methane oxidation in response to invasion of oxygen from the atmosphere and redistribution of DIN during overturn. Direct methane emission measurements were not made on Red Rock Lake at the time of thaw. However, methane oxidation was probably minimal during thaw because dissolved oxygen concentrations remained high throughout the ice-over and breakup period (4 - 8 mg l<sup>-1</sup>), and because concentrations of DIN are low throughout the year in these alpine lakes. If we assume that the loss of dissolved methane in Red Rock Lake resulted principally from methane evasion during the first 24 hours of ice-out, emission rates could have been as high as 8 mmol m<sup>-2</sup> d<sup>-1</sup>, or about 2 times higher than the emissions that were measured in early June. Therefore we conclude that the rapid decrease of stored dissolved methane observed in Red Rock Lake (77.1 μM to 1.02 μM) was primarily a result of direct emission of methane to the troposphere.

Increases in tropospheric methane concentrations during the spring have been observed at Cape Meares, Oregon [Khalil and Rasmussen, 1983] and at the Olympic Peninsula, Washington [Quay et al., 1991]. The sudden release of methane from lakes at the time of spring thaw may contribute to the spring increase in tropospheric methane mixing ratios.

**Wetlands.** Methane emissions from the wetlands were highly variable, as is common in wetlands [Svensson and Rosswall, 1984; Crill et al., 1988; Bartlett et al., 1989; Whalen

and Reeburgh, 1990; Roulet et al., 1992]. A number of investigators have observed a significant statistical relationship between methane emissions and environmental factors, including soil temperature [Baker-Blocker et al., 1977; Moore and Knowles, 1987; Crill et al., 1988], depth of the water table [Sebacher et al., 1986; Moore et al., 1990], and soil moisture content [Svensson and Rosswall, 1984]. In these studies, field sites were generally sampled repeatedly over a single summer season. When methane emissions are sampled over a large geographical range [e.g., Whalen and Reeburgh, 1990] or over one or more years [e.g., Harriss et al., 1988, 1990; Yavitt et al., 1990], as in the present study, correlation analyses have revealed very weak relationships between emissions and environmental characteristics. For our study, despite a geographical range spanning about 60 km and a time span of more than 1 year, the combination of organic carbon and soil temperature explains 40% of the variability in the emissions of methane across the five wetland sites. The relationship between carbon and methane emission rates suggests that carbon may limit methane production in alpine wetlands, where the growing season is short and biomass production is low. For example, Whiting et al. [1991] found a significant correlation between methane emissions and plant biomass and/or photosynthesis. The quantity or the quality of organic carbon produced over the summer season may limit methanogenesis.

The wetlands surrounding Lake Dillon do not contain as much organic carbon as the older, natural wetlands (Table 4), perhaps as a result of the relatively recent flooding of upland soils due to impoundment. Carbon limitation may explain the low methane emissions at Lake Dillon, which may be the case with many reservoirs. Data from reservoirs are lacking, but our results suggest that methane emissions from impoundments may be different than natural wetlands.

TABLE 5. Comparison of Methane Emissions From Open Water and Macrophyte Regions of Lakes as Reported in the Literature.

	Mean	SE	Maximum	n	Source
Open Water					
Arctic					
small lakes	1.3	--	8.2	6	1
Temperate					
Florida					
freshwater lakes	2.1	0.29	--	46	2
CA & NV					
freshwater lakes	10.0	5.3	70	16	3
saline lakes	0.3	0.04	4.8	25	3
CO Front Range					
small lakes	1.6	0.3	12	60	4
Schefferville, Quebec					
ponds, Capricorn					
fen	2.1 <sup>a</sup>	2.0	--	--	5
Tropical					
Amazon					
low water	4.6	0.9	72	116	6
low water	2.5 <sup>b</sup>	0.8	--	40	7
high water	1.7	0.3	6.9	41	8
high water	5.5 <sup>b</sup>	1.9	--	36	7
Orinoco					
high water	1.3	0.3	37	76	9
falling water	3.1	0.9	46	45	9
Macrophytes					
Temperate					
Red Rock L., CO	12.6	4.7	47	12	4
Duck L., MI	10	--	--		10
Tropical					
Amazon					
low water	12.6	2.2	100	85	6
low water	8.2 <sup>b</sup>	2.9	--	28	7
high water	14.4	4.5	187	55	8
high water	24.4 <sup>b</sup>	6.9	--	27	7
Orinoco					
high water	1.1	0.4	8.3	36	9
falling water	12.2	3.9	97	36	9

Units are in  $\text{mmol CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ . The range in emissions is essentially zero to the maximum; n denotes the sample size.

References: 1, Whalen and Reeburgh [1990]; 2, Barber et al. [1988]; 3, Miller and Oremland [1988]; 4, this study; 5, Moore et al. [1990]; 6, Bartlett et al. [1988]; 7, Devol et al. [1990]; 8, Bartlett et al. [1990], 9, L.K. Smith and W.M. Lewis, Jr. [1992]; 10, Dacey and Klug [1979].

<sup>a</sup>Calculated from a transfer model.

<sup>b</sup>Corrected values from 1985 data reported in the work of Devol et al. [1988].

*Global methane source strength of lakes.* Table 5 summarizes the published methane emission data for lakes. Most emission data for lakes are from tropical floodplain lakes; few data are from temperate or arctic lakes. Surprisingly, emissions from lakes do not seem to vary greatly with latitude. Excluding the data of Oremland and Miller [1988], the average emission rate across all studies is 2.6 mmol CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> and the standard error is only 0.5. Regardless of latitude, emissions are higher over macrophytes than open water by a factor of about 4. Emission rates from macrophytes located in tropical lakes and the two temperate lakes shown in Table 5 average 11.9 ± 2.3 mmol CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup>.

An estimate for the global source strength of methane from lakes can be calculated using the average emission rates derived from Table 5. Lakes cover about 2.5 x 10<sup>6</sup> km<sup>2</sup> of the Earth's surface area [Wetzel, 1983]. A conservative estimate of the total surface area that is productive in terms of methane is 10% (as used in Ehhalt's [1974] estimate). If we assume an even mix of open-water and macrophytes within the productive zone, the total source strength of lakes would be about 11 x 10<sup>12</sup> g CH<sub>4</sub> yr<sup>-1</sup>. It is possible that lakes emit methane over more than 10% of their total surface area. For example, we found that methane was emitted across the total surface area of Red Rock Lake, Rainbow Lake, and Pass Lake. If we assume that 50% of the surface area of lakes emits methane, the total source strength of methane from lakes would be about 55 x 10<sup>12</sup> g CH<sub>4</sub> yr<sup>-1</sup>.

From Ehhalt [1974], Cicerone and Oremland [1988] report that freshwaters contribute 1 - 25 x 10<sup>12</sup> g CH<sub>4</sub> yr<sup>-1</sup>, which could be substantially less than the actual source strength. Our revised estimate is based upon actual emission rates rather than ebullition rates as used by Ehhalt [1974]. A refined global estimate of the areal extent of freshwater lakes grouped by mean depth is probably the most urgently needed

information to further constrain the source strength estimate for freshwater lakes in the tropospheric methane budget.

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#### REFERENCES

- Baker-Blocker, A., T. M. Donahue, and K. H. Mancy, Methane flux from wetland areas, *Tellus*, 29, 245-250, 1977.
- Barber, T. R., R. A. Burke, Jr., and W. M. Sackett, Diffusive flux of methane from warm wetlands, *Global Biogeochem. Cycles*, 2, 411-425, 1988.
- Bartlett, K. B., P. M. Crill, D. I. Sebacher, R. C. Harriss, J. O. Wilson and J. M. Melack, Methane flux from the central Amazon floodplain, *J. Geophys. Res.*, 93, 1571-1582, 1988.
- Bartlett, D. S., K. B. Bartlett, J. M. Hartman, R. C. Harriss, D. I. Sebacher, R. Pelletier-Travis, D. D. Dow, and D. P. Brannon, Methane emissions from the Florida Everglades: Patterns of variability in a regional wetland ecosystem, *Global Biogeochem. Cycles*, 3, 363-374, 1989.
- Bartlett, K. B., P. M. Crill, J. A. Bonassi, J. E. Richey, and R. C. Harriss, Methane flux from the Amazon River floodplain: Emissions during rising water, *J. Geophys. Res.*, 95, 16,773-16,788, 1990.
- Bédard, C., and R. Knowles, Hypolimnetic O<sub>2</sub> consumption, denitrification, and methanogenesis in a thermally stratified lake, *Can. J. Fish. Aquat. Sci.*, 48, 1048-1054, 1991.

- Blake, D. R., and F. S. Rowland, Continuing worldwide increase in tropospheric methane, 1978 to 1987, *Science*, 239, 1129-1131, 1988.
- Carpenter, J. H., The Chesapeake Bay Institute technique for the Winkler dissolved oxygen method, *Limnol. Oceanogr.*, 10, 141-143, 1965.
- Chanton, J. P., and C. S. Martens, Seasonal variations in ebullitive flux and carbon isotopic composition of methane in a tidal freshwater estuary, *Global Biogeochem. Cycles*, 2, 289-298, 1988.
- Chanton, J. P., and J. W. H. Dacey, Effects of vegetation on methane flux, reservoirs, and carbon isotopic composition, in *Trace Gas Emissions by Plants*, edited by T. D. Sharkey, E. A. Holland, and H. A. Mooney, pp. 65-91, Academic, San Diego, Calif., 1991.
- Cicerone, R. J., and R. S. Oremland, Biogeochemical aspects of atmospheric methane, *Global Biogeochem. Cycles*, 2, 299-327, 1988.
- Crill, P. M., K. B. Bartlett, R. C. Harriss, E. Gorham, E. S. Verry, D. I. Sebacher, L. Madzar, and W. Sanner, Methane fluxes from Minnesota peatlands, *Global Biogeochem. Cycles*, 2, 371-384, 1988.
- Dacey, J. W. H., and M. J. Klug, Methane efflux from lake sediments through water lilies, *Science*, 203, 1253-1255, 1979.
- Dacey, J. W. H., Pressurized ventilation in the yellow waterlily, *Ecology*, 62, 1137-1147, 1981.
- Devol, A. H., J. E. Richey, B. R. Forsberg, and L. A. Martinelli, Seasonal dynamics in methane emissions from the Amazon River floodplain to the troposphere, *J. Geophys. Res.*, 95, 16,417-16426, 1990.
- Ehhalt, D. H., The atmospheric cycle of methane, *Tellus*, 26, 58-70, 1974.
- Harriss, R. C., and D. I. Sebacher, Methane flux in forested freshwater swamps of the southeastern United States, *Geophys. Res. Lett.*, 8, 1002-1004, 1981.
- Harriss, R. C., D. I. Sebacher, and F. P. Day, Methane flux in the Great Dismal Swamp, *Nature*, 292, 673-674, 1982.
- Harriss, R. C., E. Gorham, D. I. Sebacher, K. B. Bartlett, and P. A. Flebbe, Methane flux from northern peatlands, *Nature*, 315, 652-654, 1985.
- Harriss, R. C., D. I. Sebacher, K. B. Bartlett, D. S. Bartlett, and P. M. Crill, Sources of atmospheric methane in the South Florida environment, *Global Biogeochem. Cycles*, 2, 231-243, 1988.
- Kelly, C. A., and D. P. Chynoweth, The contributions of temperature and of the input of organic matter in controlling rates of sediment methanogenesis, *Limnol. Oceanogr.*, 26, 891-897, 1981.
- Khalil, M. A. K., and R. A. Rasmussen, Sources, sinks and seasonal cycles of atmospheric methane, *J. Geophys. Res.*, 88, 5131-5144, 1983.
- Kling, G. W., G. W. Kipphut, and M. C. Miller, Arctic lakes and streams as gas conduits to the atmosphere: Implications for tundra carbon budgets, *Science*, 251, 298-301, 1991.
- Lewis, W. M., Jr., J. F. Saunders III, D. W. Crumpacker, Sr., and C. Brendecke, *Eutrophication and Land Use: Lake Dillon, Colorado*, *Ecol. Stud.* Vol. 46, pp. 1-202. Springer-Verlag, New York, 1984.
- McAuliffe, C., Gas chromatographic determination of solutes by multiple phase equilibrium, *Chem. Technol.*, 1, 46-51, 1971.
- Miller, L. G., and R. S. Oremland, Methane efflux from the pelagic regions of four lakes, *Global Biogeochem. Cycles*, 2, 269-277, 1988.
- Moore, T. R., and R. Knowles, Methane and carbon dioxide evolution from subarctic fens, *Can. J. Earth Sci.*, 67, 77-81, 1987.
- Moore, T., N. Roulet, and R. Knowles, Spatial and temporal variations of methane flux from subarctic/northern boreal forests, *Global Biogeochem. Cycles*, 4, 29-46, 1990.
- Morris, D. P., Nutrient limitation of phytoplankton in selected Colorado lakes, M.A. thesis,

- Univ. Colo., Boulder, 1985.
- Morris, D. P., Regulation of bacterioplankton production in Lake Dillon, Colorado, Ph.D. thesis, Univ. Colo., Boulder, 1990.
- Quay, P. D., S. L. King, J. Stutsman, D. O. Wilbur, L. P. Steele, I. Fung, R. H. Gammon, T. A. Broen, G. W. Farwell, P.M. Grootes, and F.H. Schmidt, Carbon isotopic composition of atmospheric  $CH_4$ : Fossil and biomass burning source strengths, *Global Biogeochem. Cycles*, 5, 24-47, 1991.
- Ramanathan, V., R. J. Cicerone, H. B. Singh, and T. Kiehl, Trace gas trends and their potential role in climate change, *J. Geophys. Res.*, 90, 5547-5566, 1985.
- Roulet, N. T., R. Ash, and T. R. Moore, Low boreal wetlands as a source of atmospheric methane, *J. Geophys. Res.*, 97, 3739-3749, 1992.
- Rudd, J. W. M., A. Furutani, R. J. Flett, and R. D. Hamilton, Factors controlling methane oxidation in shield lakes: The role of nitrogen fixation and oxygen concentration, *Limnol. Oceanogr.*, 21, 357-364, 1976.
- Rudd, J. W. M., and R. D. Hamilton, Methane cycling in a eutrophic shield lake and its effects on whole lake metabolism, *Limnol. Oceanogr.*, 23, 337-348, 1978.
- Rudd, J. W. M., and C. D. Taylor, Methane cycling in aquatic environments, *Adv. Aquat. Environ.*, 2, 77-150, 1980.
- Sebacher, D. I., R. C. Harriss, and K. B. Bartlett, Methane emissions to the atmosphere through aquatic plants, *J. Environ. Qual.*, 14, 40-46, 1985.
- Sebacher, D. I., R. C. Harriss, K. B. Bartlett, S. M. Sebacher, and S. S. Grice, Atmospheric methane sources: Alaskan tundra bogs, an alpine fen, and a subarctic boreal marsh, *Tellus Ser. B.*, 38, 1-10, 1986.
- Schütz, H., P. Schröder, and H. Rennenberg, Role of plants in regulating the methane flux to the atmosphere, in *Trace Gas Emissions by Plants*, edited by T. D. Sharkey, E. A. Holland, and H. A. Mooney, pp. 29-63, Academic, San Diego, Calif., 1991.
- Svensson, B. H., Methane production in tundra peat, in *Microbial Production and Utilization of Gases ( $H_2$ ,  $CH_4$ ,  $CO$ )*, edited by H. G. Schlegel, G. Gottschalk, and N. Pfennig, pp. 135-139, E. Goltze, Göttingen, 1976.
- Svensson, B. H. and T. Rosswall, In situ methane production from acid peat in plant communities with different moisture regimes, *Oikos*, 43, 341-350, 1984.
- Weber, W. A., *Rocky Mountain Flora*, Colorado Associated University Press, Boulder, 1976.
- Weber, W. A., and R. C. Wittmann, *Catalog of the Colorado Flora: A biodiversity baseline*, University of Colorado Press, Boulder, 1992.
- Wetzel, R. G., *Limnology*, Saunders College, Philadelphia, Pa., 1983.
- Whalen, S. C. and W. S. Reeburgh, A methane flux transect along the trans-Alaska pipeline haul road, *Tellus, Ser. B*, 42, 237-249, 1990.
- Whiting, G. J., J. Chanton, D. Bartlett, and J. Happell, Methane flux, net primary production, and biomass relationships in a subtropical grassland community, *J. Geophys. Res.*, 96, 13,067-13,071, 1991.
- Wuebbles, D. J. and J. Edmonds, *Primer on Greenhouse Gases*, Lewis Publishers, Chelsea, Mich., 1991.
- Yamamoto, S., J. B. Alcauskas, and T. E. Crozier, Solubility of methane in distilled water and seawater, *J. Chem. Eng. Data*, 21, 78-80, 1976.
- Yavitt, J. B., G. E. Lang, and A. J. Sexstone, Methane fluxes in wetland and forest soils, beaver ponds, and low-order streams of a temperate forest ecosystem, *J. Geophys. Res.*, 95, 22,463-22,474, 1990.

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