Biogeochemistry **51:** 71–90, 2000.

Methane emissions from an Amazon floodplain lake: Enhanced release during episodic mixing and during falling water

DIANA ENGLE & JOHN M. MELACK
Department of Ecology, Evolution and Marine Biology, University of California, Santa Barbara, California, U.S.A.

Received 3 September 1999; accepted 10 January 2000

Key words: Amazon floodplain, episodic mixing, lakes, methane emission

Abstract. Methane fluxes to the troposphere were measured in Lake Calado, a dendritic floodplain lake located in the central Amazon Basin. Methane concentrations in the surface water of the lake were less than 0.5 μM during a period of high and rising water in April and May, except when episodic, deep mixing occurred and surficial concentrations reached as high as 4.8 μM. Diffusive fluxes ranged from ca. 2–20 mg CH_4 $m^{-2}d^{-1}$ (mean: 6.6 mg CH_4 $m^{-2}d^{-1}$) normally, but increased up to 220 mg CH_4 $m^{-2}d^{-1}$ during the passage of a rare cold front. During six weeks of rising water, the volume-weighted methane content of the lake increased during periods of stable thermal stratification (accumulation rates ranging from 16–1411 mg CH_4 $m^{-2}d^{-1}$) and decreased during episodes of partial mixing (rates of decrease ranging from 63–1792 mg CH_4 $m^{-2}d^{-1}$). Surface water methane concentrations during low and falling water in September varied by more than an order of magnitude (range, 0.3–9 μM), and diffusive fluxes ranged from 3–158 mg CH_4 $m^{-2}d^{-1}$ (mean, 54 mg CH_4 $m^{-2}d^{-1}$). During falling water in September, total methane flux from the lake to the troposphere measured with a floating chamber ranged from 53–328 mg CH_4 $m^{-2}d^{-1}$ (mean, 163 mg CH_4 $m^{-2}d^{-1}$). Ebullitive flux averaged 69% of total flux. Total methane flux was highest when thermal stratification was lost due to decreasing lake depth.

Introduction

Natural wetlands are an important source of atmospheric methane (Matthews & Fung 1987; Cicerone & Oremland 1988), and 41% of annual wetland methane emissions come from the tropics (Crill 1996). The highest wetland emissions occur in the tropics of the southern hemisphere (Aselmann & Crutzen 1989). Floodplains, with their mosaic of lakes, forested swamps and marshes, constitute most of the wetlands in the tropics of the Southern Hemisphere (Melack & Fisher 1990). The large floodplains of the Amazon Basin are a strong source of methane within this region, and are estimated to contribute about 5% of methane emissions from wetlands globally (Devol et

al. 1990) and ca. 2–14% of CH_4 emissions from tropical wetlands worldwide (Wassman & Martius 1997).

Methane emissions from the floodplain of the Amazon River are probably the most thoroughly studied among natural, tropical wetlands. Published values from the Amazon Basin include results from surveys of floodplain habitats conducted during high water (Bartlett et al. 1988, 1990; Devol et al. 1988) and low water (Devol et al. 1990), and time series measurements from individual sites (daily, Crill et al. 1988; monthly, Wassman et al. 1992). Open water areas of the Amazon floodplain generally release methane to the atmosphere at lower rates than inundated areas covered by floating macrophyte beds or flooded forest (Devol et al. 1994; Wassman & Martius 1997; Wassman et al. 1992).

During the inundation period, when floodplain lakes remain more than 5 m deep, thermal stratification is persistent (MacIntyre & Melack 1988), and methane is stored in the hypolimnia. Previous time series measurements of methane flux from an Amazon floodplain lake (Crill et al. 1988) were obtained during a period of low winds and a stable thermocline. However, during the high water season, frequent strong thunderstorms occur which can cause partial mixing of floodplain lakes. In addition, occasional cold fronts pass through the Amazon floodplain during high water, producing sustained high winds and cool temperatures for several days. These phenomena are reputed to cause lake turnover and fish kills (Brinkman & Santos 1974). During falling water, floodplain lakes eventually become shallow enough to lose their seasonal thermal stratification. Entrainment of hypolimnetic water into the mixed layer during these times poses the potential for large episodic releases of methane from the floodplain to the atmosphere.

In this study, we present measurements of methane emissions and methane content from an Amazon floodplain lake (L. Calado) made almost daily during a 40-day period of high and rising water (18 April–27 May, 1987), and a 10-day period of low and falling water in the same year (14–24 Sept., 1987). In only one previous study has methane been measured with similar frequency in an Amazon floodplain lake (21 July–29 Aug., 1985; Crill et al. 1988). Our measurements during high water were affected by several strong thunderstorms and the arrival of a cold front with sustained strong winds, which caused partial mixing of the lake. Our low-water measurements spanned the period during which thermal stratification was lost owing to decreasing lake depth. These time series data in conjunction with related limnological and meteorological measurements suggest the importance of episodic emissions of methane associated with mixing events on the Amazon floodplain.

Study area

The floodplain along the 2800 km of the main stem Amazon River in Brazil, which is called the Solimões River above its confluence with the Negro River, is composed of open water (lakes), floating macrophyte mats (floating meadows) and forest (Junk & Piedade 1997). The total floodplain fringing the mainstem Amazon River in Brazil occupies about 92,000 km^2 and an additional 62,000 km^2occurs along the lower 400 km of the Japura, Purus, Negro, and Madeira tributaries within Brazil (Sippel et al. 1992). In the central basin near Manaus, the river stage varies about 10 m seasonally with highest levels in May to July and lowest levels usually in October through December (Richey et al. 1988).

The floodplain reach on the Solimões River between the Purus and Negro rivers is about 4400 km^2in area and contains 333 lakes (Sippel et al. 1992). Our principal study site, Lake Calado, (3°15′S, 60°34′W) is located on the north side of the Solimões River 80 km upriver from its confluence with the Negro River. The lake is primarily narrow and dendritic, but its southern end is about 1 km wide and is strongly influenced by the Solimões River. The lake's maximum depth varies from 1 to 12 m in concert with the yearly rise and fall of the Solimões River (Lesack 1988). Persistent thermal and chemical vertical stratification commenses when depth exceeds 6 m and continues for 6 to 9 months each year (MacIntyre & Melack 1988).

Methods

Samples of methane and measurements of limnological conditions were obtained in the middle of the southern portion of L. Calado at the location described in Setaro and Melack (1984), Melack and Fisher (1983), and Crill et al. (1988). Methane was sampled in lake water by stripping dissolved methane from water samples via agitation with air. Surficial water was sampled with a syringe inserted into the upper ca. 2 cm of water; vertical profiles were obtained by sampling every 0.5 m with a Van Dorn bottle. In each case, a water sample of 30 ml was taken into a 60 ml plastic syringe fitted with a three-way valve. An equal volume of ambient air was introduced into the syringe and the sample shaken vigorously for 2 minutes (McAuliffe 1971). A gas sample from the air space in the syringe was immediately transferred to a 4 ml serum bottle previously filled with distilled water and sealed with a rubber stopper and aluminum crimp. The gas sample was transferred through a hypodermic needle into the inverted vial, simultaneously expelling the water via a second needle. The serum bottles were returned to the U.S. for analysis with a Shimadzu Mini-2 gas chromatograph equipped with a

flame ionization detector. Concentrations were corrected for temperature and ambient air methane concentration (see Crill et al. 1988 for further details).

The combined diffusive and ebullitive methane flux from open water in L. Calado was determined using a floating chamber made of aluminum, with vertical walls 0.2 m high and covering an area 0.25 m^2. Samples of gas were removed from the chamber by syringe through a three-way valve every 5 minutes during the 20 minute deployments. After collection, samples were transferred to serum bottles, returned to the U.S. and analyzed as described above.

Lake temperature profiles were measured with a thermistor and Wheatstone bridge readable to 0.1 °C and calibrated against a mercury thermometer accurate to 0.1 °C. Dissolved oxygen was measured with a Clark polarographic electrode with submersible stirrer to a precision of 0.2 mg L^{-1}. The thermocline was defined as the depth of the maximum temperature gradient and was at least 0.1 °C per meter (MacIntyre & Melack 1988). The oxycline was determined as the depth at which dissolved oxygen first declined to 0.5 mg L^{-1} or less.

Meteorological measurements were made in the middle of the southern portion of the lake on a floating platform. During April and May, wind speed was measured at 4 m above the water with a three-cup anemometer whose threshold was 0.5 m s^{-1} and accuracy was ca. 0.1 m s^{-1}. Wind speed was registered every minute and stored in a solid state logger as hourly averages. During September wind speed was measured 2 m above the water with a three-cup totalizing anemometer read manually. Shaded air temperatures and surface water temperatures were measured manually with a mercury thermometer.

Diffusive flux estimates

Diffusive flux of methane from the lake surface to the atmosphere was estimated using the results of several recent empirical studies relating gas exchange parameters to water temperature and wind speed. Our procedure is outlined by the following five steps.

1. Schmidt numbers (Sc) for methane were calculated for each dissolved methane measurement using the surface water temperature (t) in °C and the following polynomial equation derived by Wannikhof (1992) for methane in freshwater:

$$\mathrm{Sc}_{\mathrm{CH4}} = 1897.8 - 114.28(t) + 3.2902(t^2) - 0.039061(t^3).$$

2. Wind speeds (U_z) measured at z = 4 m above the lake surface (April–May), or z = 2 m above the lake surface (Sept.), were converted to wind speeds at 10 m (U_{10}) using the following equation from Amorocho and DeVries (1980; eq. 21):

$$U_z = U_{10}[1 - (C_{10})^{1/2}\mathrm{K}^{-1}\ln(10/z)],$$

where C_{10} equals the surface drag coefficient for wind at 10 m (1.3×10^{-3}; Stauffer 1980), K equals the von Karman constant (0.41), and z = height of wind speed measurement in m above the water surface.

3. Cole and Caraco (1998) recently derived an empirical expression relating K_{600} (the piston velocity of CO_2 at 20 °C), and wind speed at 10 m above a lake surface (U_{10}). We used their model to calculate K_{600} (in cm hr^{-1}) for each wind speed in our study using U_{10} as obtained in Step 2:

$$K_{600} = 2.07 + 0.215(U_{10})^{1.7}.$$

4. Piston velocities for methane at each water temperature ($K_{CH4,t}$) were calculated using the following formula:

$$K_{600}/K_{CH4,t} = (Sc_{600}/Sc_{CH4,t})^{-n},$$

where Sc_{600} equals the Schmidt number for CO_2 at 20 °C (a constant), n = 2/3 when $U_{10} < 2$ m s^{-1}, n = 1/2 when $U_{10} \geq 2$ m s^{-1}, and using $Sc_{CH4,t}$ and K_{600} as calculated above.

5. Diffusive flux F was estimated using the expression:

$$F = K_{CH4,t}(C_w - \alpha C_a),$$

where C_w is the concentration of dissolved methane at the lake surface, C_a is the concentration of methane in air at the lake surface, and α = 0.02955, the Ostwald solubility coefficient for methane in freshwater (Wiesenburg & Guinasso 1979) for the average surface water temperature (27.6 °C) during our study. Because surface water temperature varied little in our study (by 3.4 °C during Apr.–May, and by 1.2 °C during Sept.) the maximum error in diffusive flux produced by using an average temperature to calculate α was <0.1%.

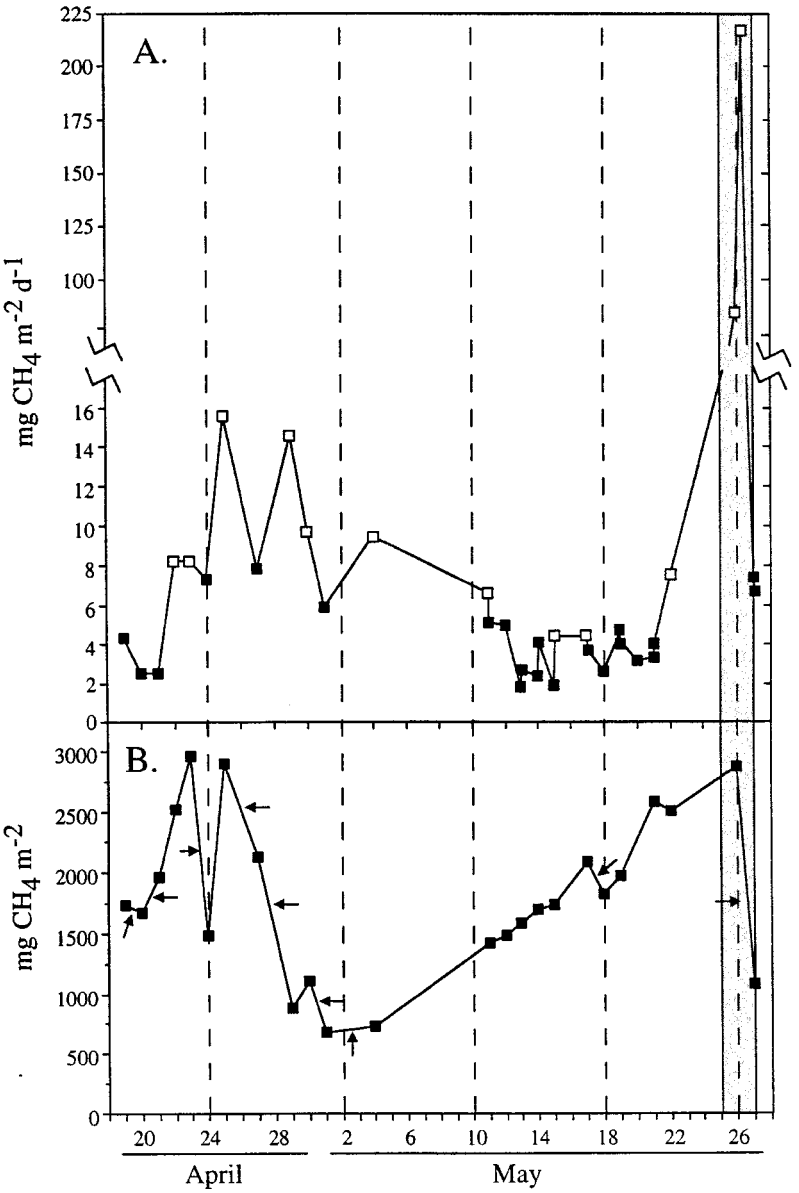

Figure 1. (A) Diffusive methane flux from the surface of L. Calado to the atmosphere over a 40-day period of rising water (19 April–27 May, 1987). Measurements were made shortly after dawn. Open squares mark when wind speed was higher than the average wind speed (>4.7 m s^{-1}) for the 40-day period. (B) Depth-integrated dissolved methane content of L. Calado during the same period. Arrows mark the intervals during which the lake's thermocline deepened to z = 6 m. The passage of the cold front is indicated by the shaded area. The lake increased in depth from 9.5 to 11 m during the period illustrated.

Table 1. Methane flux from L. Calado during rising water (April–May, 1987) and falling water (September 1987).

	mean + SE	range	*N*
April-May			
Surface water methane, excluding cold front (μM)	0.25 ± 0.02	(0.11–0.54)	46
Diffusive flux, excluding cold front (mg CH_4 m^{-2} d^{-1})	6.6 ± 0.67	(1.8–20.3)	44
Diffusive flux during cold front (mg CH_4 m^{-2} d^{-1})	83 and 220		2
Changes in depth-integrated lake methane content			
Accumulation rate (mg CH_4 m^{-2} d^{-1})	273 ± 90	(16–1411)	15
Loss rate (mg CH_4 m^{-2} d^{-1})	640 ± 228	(63–1792)	8
September			
Surface water methane (μM)	2.91 ± 0.73	(0.3–9.0)	13
Diffusive flux (mg CH_4 m^{-2} d^{-1})	53.9 ± 16.6	(3.4–157.4)	11
Ebullitive flux (mg CH_4 m^{-2} d^{-1})	110.9 ± 21.3	(21.0–258.3)	11
(as percent of total flux)	$69\% \pm 7\%$	(20%–95%)	11
Total flux (mg CH_4 m^{-2} d^{-1})	164.8 ± 30.5	(53.2–327.7)	11

Results and discussion

Methane emissions during rising water (April–May)

Dissolved methane concentrations in surficial waters of L. Calado ranged from 0.12 to 0.46 μM (n = 46, mean 0.25 μM) from 19 April to 22 May 1987. During the same period, diffusive methane fluxes from the lake to the troposphere ranged from 1.8 to 20.3 mg CH_4 m^{-2} d^{-1} (Figure 1, excluding two higher values obtained during unusual weather, see below) with a mean of 6.6 mg CH_4 m^{-2} d^{-1} (Table 1). Most of the measurements were made between 0600 and 0900 h, and were associated with wind speeds from 1.6–8.5 m s^{-1}(median, 4.3 m s^{-1}, Figure 2). Higher than average diffusive fluxes (i.e., $>$7 mg CH_4 m^{-2} d^{-1}, Table 1) were obtained at dawn on ten days between 19 April and 27 May. Eight of these measurements were accompanied by above average wind speed (Figure 1) and six of these measurements were accompanied by above average dissolved methane concentration in surface water.

Total methane flux from lakes includes both diffusive flux and bubble flux. Total methane fluxes were not measured during the rising water portion of our study, but can be estimated based on evidence from related studies. Bubbling occurred during one fifth of the total flux measurements made by Bartlett et al.

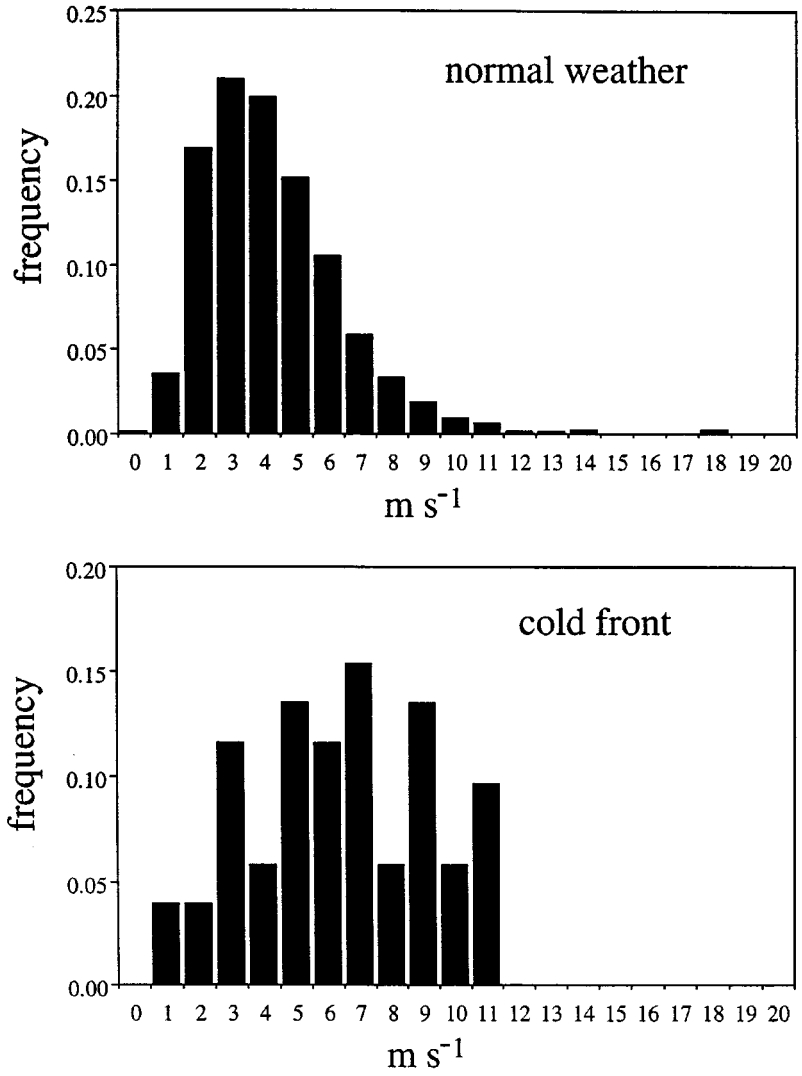

Figure 2. (Top) Frequency histogram for N = 911 hourly averages of wind speed measured with a three-cup anemometer 4 m above the surface of L. Calado. Wind speeds included in the analysis excluded those recorded during the passage of the cold front from 26–27 May (see text). (Bottom) Frequency histogram for N = 52 hourly averages of wind speed obtained during the passage of the cold front during 26–27 May, measured as described in A.

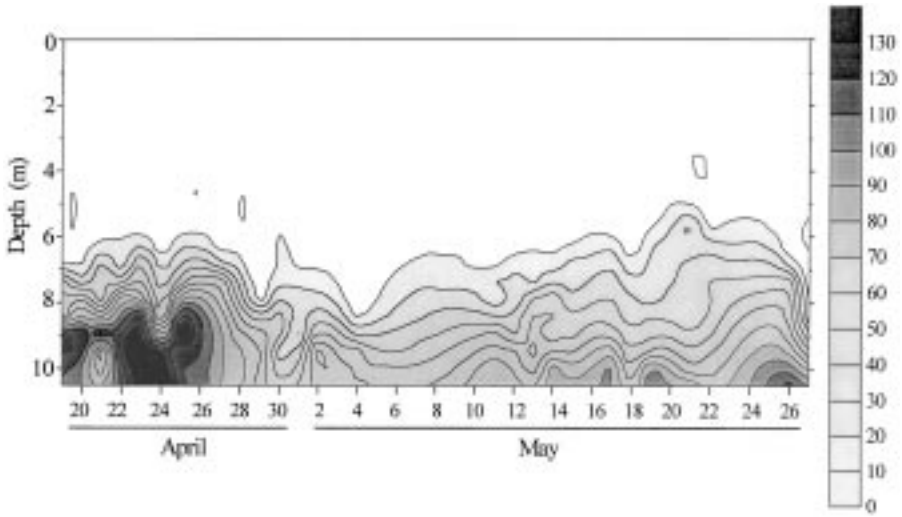

Figure 3. Vertical distribution of dissolved methane concentrations (units of shaded scale, μM) in L. Calado during the 40-day period of rising water from 19 April–27 May 1987.

(1990) in open water habitats (lakes and channels) on the Amazon floodplain during the same period as our study (April–May, 1987). They estimated that about 20% of the total flux of methane from open water during their study was delivered as bubbles (Bartlett et al. 1990). Applying this as representative percentage, we estimate a range for methane ebullition in L. Calado during Apr-May of 0.5–5.1 mg CH_4 m^{-2} d^{-1}, and a range for total flux of 2.3–25.4 mg CH_4 m^{-2} d^{-1}. This estimate, however, is lower than the average measured total flux of methane in open water of the floodplain (74 ± 14 mg CH_4 m^{-2} d^{-1}) obtained by Bartlett et al. (1990).

Although methane concentrations were normally very low near the surface of L. Calado during high water, methane concentrations increased up to 150 μM below the mixed layer, beginning at a depth of 5–6 m (Figure 3). These data indicate that the quantity of methane stored in the bottom waters of L. Calado varied during the 40 day study, and illustrate the potential for release of methane upon deep mixing. Lake bathymetry was used to integrate methane concentrations from the vertical profiles and to produce a time series for volume-weighted lake methane content expressed as mg CH_4 m^{-2} (Figure 1). When expressed in this way, it is seen that during this study, methane was alternately accumulating and decreasing in the lake.

Examination of lake temperature and oxygen profiles helps explain the timing of increases and decreases in methane content. Figure 4 shows the structure of the lake during two partial mixing events, the first occurring between 23–24 April, and the second occurring between 25–27 April. The

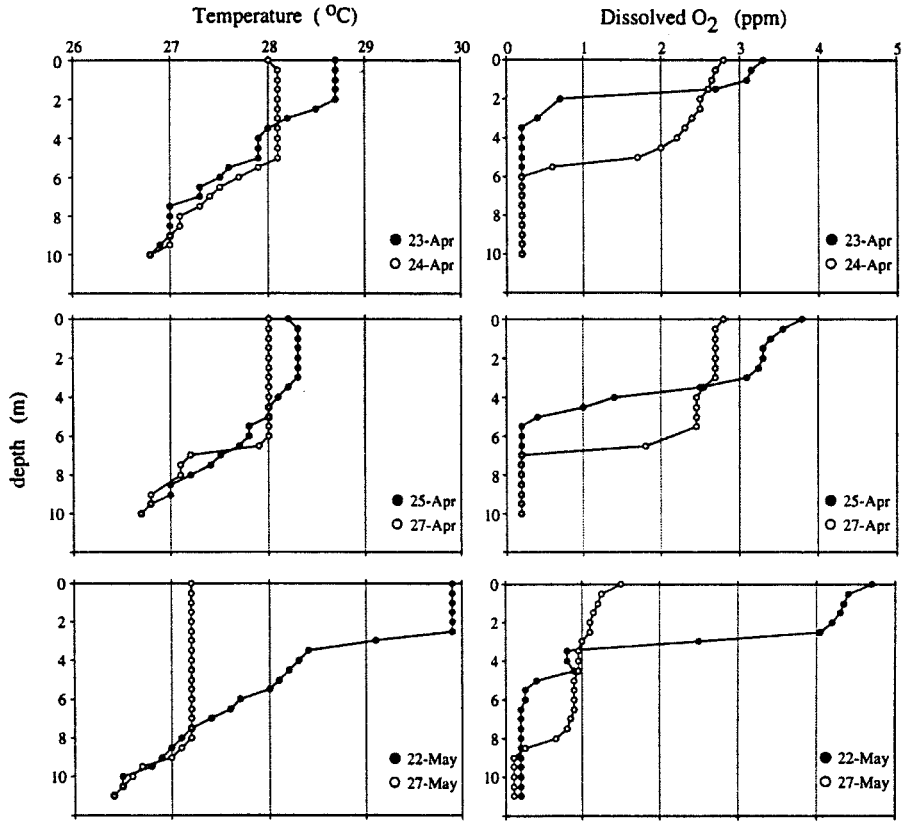

Figure 4. Temperature and dissolved oxygen profiles obtained before and after three partial mixing events during rising water in L. Calado. Measurements were made at dawn. Deepening of the thermocline and oxycline took place in response to stormy weather between 23–24 April and between 25–27 April, and during the passage of a strong cold front (*friagem*) between 25–27 May.

temperature and dissolved oxygen profiles for 23 and 25 April show the lake stratified with thermoclines and oxyclines close to the surface of the lake. These profiles were taken during periods of methane accumulation. The temperature and dissolved oxygen profiles for 24 April and 27 April were taken after stormy weather that caused partial mixing of the lake, deepening the thermocline from 3 to 6 m by 24 April, and from 5.5 to 7 m by 27 April. These partial mixing events were accompanied by drops in the methane content of the lake (–1470 mg CH_4 m^{-2} between 23–24 April, and –764 mg CH_4 m^{-2} between 25–27 April, Figure 1).

Overall, our data show an association between decreases in the methane content of the lake and periodic mixing to at least 6 m. Decreases in lake

methane content were observed on eight occasions during the high water portion of our study; in seven of these cases, the thermocline had deepened to $\geq$ 6 m during the 24 h preceding the measurement. During one four day period (30 April–4 May), the thermocline deepened from 3 m to 6 m, and remained below 6 m for three more days. During the first 24 h, the methane content of the lake decreased by 433 mg CH_4 m^{-2} (Figure 1). Although the thermocline remained below 6 m until May 3, further net decreases in methane content of the lake were not observed. On only one other occasion (21 April) did methane content fail to decrease when the thermocline deepened to $\geq$ 6 m.

In late May (25–27 May) a cool, windy meteorological condition, locally called a *friagem*, caused deep mixing in L. Calado (Figure 4). Such events, which usually last several days, are caused by northward displacement of cold fronts from southern South America. The *friagem* began in the evening of 25 May, with strong wind. Prior to this event, L. Calado was stratified close to the surface, with a mixed layer occupying only the top 2.5 m of the lake (Figure 4, 22 May profiles). From 25–27 May, sustained wind speeds were higher (median, 7 m s^{-1}, Figure 2(b)) than during the previous five weeks (Figure 2). As a result of high winds, persistent cloud cover, and cooler air temperatures (morning air temperatures of ca. 22 °C, versus normal morning air temperatures of ca. 26–28 °C), the mixed layer of the lake deepened from ca. 2.5 m to 6 m during the first night of the *friagem* and then to 8 m during the next 24 h (Figure 4, 27 May profiles). As a result of this deep mixing, surficial dissolved methane concentrations reached 4.8 μM, a diffusive flux as high as 220 mg CH_4 m^{-2} d^{-1} was observed, and lake methane content decreased by 1792 mg CH_4 m^{-2} between 26–27 May (Figure 1).

A comparable time series of methane depth profiles was measured at L. Calado during early falling water in 1985 (20 July–2 Sept. Crill et al. 1988). In their study, methane concentrations 6 m below the surface increased steadily over 40 days in July and August, rising from $<$80 μM to $>$210 μM, or an equivalent increase of 85 mg CH_4 m^{-2} d^{-1}. Based on measurements of methane gradients in sediment pore water, Crill et al. (1988) determined that the diffusion rate of methane from the bottom sediments into overlying water was in the range 80–115 mg CH_4 m^{-2} d^{-1}. The estimated flux from the sediments of L. Calado accounted for both the accumulation of methane in the hypolimnion and surface flux to the atmosphere in their study.

In our study of L. Calado, depth integrated lake methane content decreased on almost one-third of the days. The difference between the two studies seems to be related to mixing frequency. During the study of Crill et al. (1988), which coincided with the dry season, L. Calado decreased in depth over forty days from 8.8 m to $<$6.8 m. They reported that the thermocline was stable

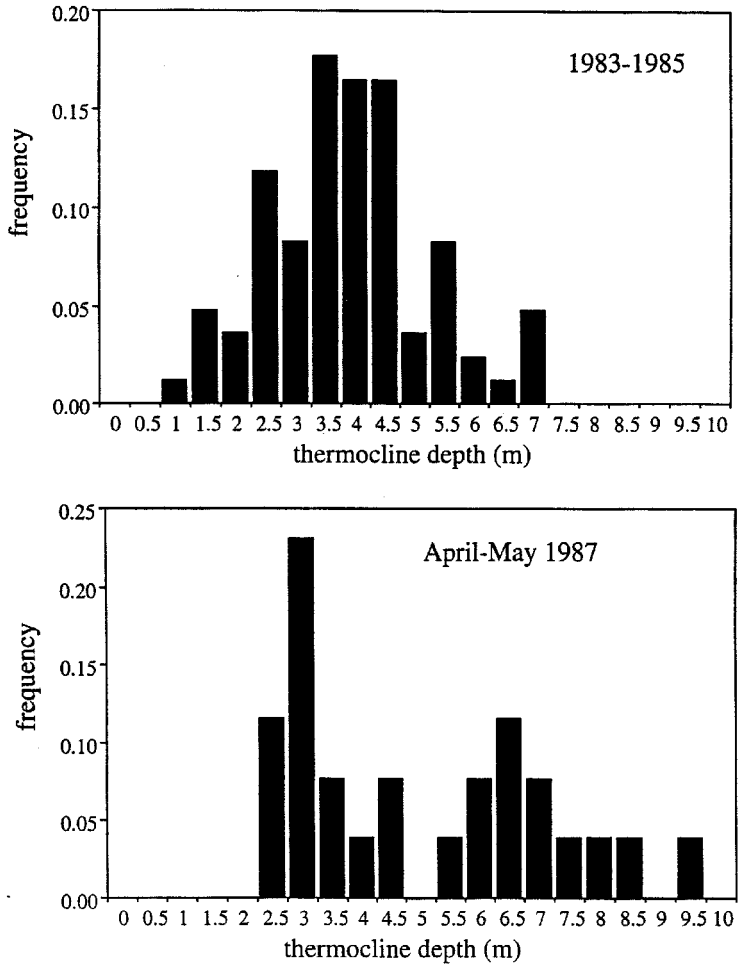

Figure 5. (Top) Frequency histogram of thermocline depths in L. Calado obtained during high water periods from 1983–1985 (N = 85). Thermocline depths were included only for dates on which the lake was >9 m deep. (Bottom) Frequency histogram of thermocline depths in L. Calado obtained during the high water portion of this study (April–May 1987, N = 26), during which the lake varied in depth from 9.5 to 11 m. Thermocline depth was selected as the bottom of the 0.5 m interval in the water column in which the rate of change of temperature was the highest.

during their study, did not go below 5 m, that wind speed hourly averages did not exceed 6 m s^{-1}, and that no intense storms or extended periods of rain and wind occurred. Average wind speed during their entire study (from totalizing anemometer) was 1.7 $\pm$ 0.7 m s^{-1} (mean $\pm$ SE, Crill et al. 1988). Our study took place during a windier and stormier period; hourly average

wind speed exceeded 6 m s^{-1} 24% of the time (Figure 2), and average wind speed (excluding the cold front) was 4.7 $\pm$ 0.07 m s^{-1}. The lake varied in depth during our study from 9.5 to 11 m. Thermoclines below 5 m occurred frequently during our study (Figure 5(b)).

In order to evaluate the frequency with which thermoclines $\geq$6 m deep occur in L. Calado, we used a daily record of temperature profiles obtained during three years (1983–1985) from the same sampling location in the lake (MacIntyre & Melack 1988). Including only dates for which total lake depth was at least 9 m, we generated a frequency histogram of thermocline depths (Figure 5(a)). In general, when the lake is at least 9 m deep, thermoclines of 6 m or deeper occur with a frequency of ca. 6%. The same analysis was done for the 40-day period in April and May from this study. Compared to the long term record, the results were different; thermoclines positioned at 6 m or below were observed 44% of the days (Figure 5(b)).

Table 1 contrasts the average diffusive flux, calculated from surface water methane concentrations, with the average net accumulation and loss rates in the water column, expressed in the same units. Loss rates estimated by decreases in methane content in the water column are in many cases 1–2 orders of magnitude higher than diffusive flux. It may be that peak diffusive fluxes from the lake produced by short-lived mixing events may not have coincided with the daily methane measurements. On at least one occasion, however, during the extended cold front, calculated diffusive fluxes were much higher than the average (Table 1), reflecting increased evasion of methane from the lake during thermocline deepening.

Methane oxidation in the water column probably accounts for some of the decrease in dissolved methane content during partial mixing events in Lake Calado. Methane may be consumed in the water column of lakes by both anaerobic and aerobic methane oxidizing bacteria. Aerobic methane oxidizing bacteria are methanotrophs: the oxidation of methane produces energy for growth. For growth to occur, these organisms must be positioned where both methane, oxygen and dissolved inorganic nitrogen are available; rates of aerobic methane oxidation are highest in the oxycline (Harrits & Hanson 1980). Most aerobic methanotrophs are also capable of nitrogen fixation when dissolved inorganic nitrogen supplies are low. However, because reduced oxygen tensions are required for nitrogen fixation by these bacteria, placement near the oxycline is critical for these organisms during nitrogen fixing conditions (Rudd et al. 1976).

Methanotrophic bacteria can significantly affect the methane budgets of stratified lakes. For example, methane oxidation in the oxic/anoxic boundary of Mono Lake, California, lowered dissolved methane concentrations by $>$98% (Oremland et al. 1987). Striegel and Michmerhuizen (1998) esti-

mated that 62% and 79% of the CH_4 produced in two dimictic lakes in Minnesota (L. Williams and L. Shingobee, respectively) was oxidized in the water column. The highest rate of methane oxidation in Shingobee Lake reported by Striegl and Michmerhuizen (1998) was equivalent to ca. 960 mg CH_4 $m^{-2}d^{-1}$. The highest rate of methane loss from the water column of L. Calado in April–May (1792 mg CH_4 $m^{-2}d^{-1}$) was observed during the cold front. Diffusive flux during the cold front ranged from 7 to 220 mg CH_4 $m^{-2}d^{-1}$, resulting in a minimum difference of ca. 1572 mg CH_4 $m^{-2}d^{-1}$ that may have been lost from the water column due to oxidation. Methane oxidation may significantly affect methane budgets even in oxygenated water columns. In large, shallow, unstratified L. Kasumiguara, Japan, 74% of dissolved methane in the water column was oxidized, rather than lost through the surface as diffusive flux (Utsumi et al. 1998); rates of methane oxidation reached as high as ca. 130 mg CH_4 $m^{-2}d^{-1}$.

In our study, decreases in the methane content of the water column were associated with partial mixing events in L. Calado. In these partial mixing events, the thermocline deepened from ca. 3–5 m to >6 m. With only one exception (22 May) decreases in the depth integrated methane content of the water column were accompanied by a deepening of the thermocline and the oxycline (Figure 1). As these partial mixing events took place, hypolimnetic water high in dissolved methane was entrained into the mixed layer, and oxygenated, providing appropriate conditions for methane oxidation in the water column.

Other investigators have obtained evidence of methane oxidation in Amazon floodplain lakes. Bacterial oxidation of methane results in ^{13}C enrichment of residual, unoxidized methane (Oremland et al. 1987). Devol et al. (1988) found that the $\partial^{13}C$ of methane dissolved in Amazon floodplain waters was higher than the $\partial^{13}C$ of methane sampled from bubbles in the sediment, providing evidence that bacterial oxidation had altered the isotope ratio of methane that diffused into the water column. During July through August 1985, Crill et al. (1988) estimated that only 15% at most of the methane produced by the sediments in L. Calado could have been oxidized, because the accumulation of methane in the hypolimnion over forty days under a stable thermocline plus measured flux to the atmosphere was essentially equivalent to the amount of methane produced by the sediment. However, during our study, the thermocline was not stable, and several partial mixing events occurred, providing opportunity for methane-rich hypolimnetic water to be entrained into the oxic mixed layer.

Another site for methane oxidation in Amazon floodplain lakes is the underwater portions of floating macrophyte beds. Although methane oxidation in the water column affects the concentration of dissolved methane, it

does not affect the rate of bubble flux from the sediment or the concentration of methane in bubbles rising through the water column (Martens et al. 1986). However, Chanton and Smith (1993) showed that methane-rich bubbles that originate in the sediment of Amazon floodplain lakes and become trapped underneath floating macrophyte beds are subject to methane oxidation. They measured the $\partial^{13}C$ of methane in bubbles sampled from floating macrophyte beds and methane captured from sediments and held experimentally in the underwater matrix of stems and roots of the floating macrophytes. In both cases, methane became enriched with ^{13}C relative to the methane in bubbles sampled directly from the sediment underneath macrophyte beds.

Wind driven mixing events may increase the importance of methane oxidation in the methane budgets of both temperate and tropical lakes. In ELA Lake 227, evasion rates were smaller than oxidation rates (Rudd & Hamilton 1978). During periods of thermal stratification, 11% of methane entering the water column was oxidized in the oxycline, 5% was lost to the atmosphere, and the remainder was stored in the hypolimnion. Both oxidation and evasion rates peaked during fall overturn, increasing by up to 10-fold. On an annual basis, methane oxidation removed ca. 65% of the methane generated by the lake. In L. Mendota, methane oxidation was estimated to account for 45% of the methane budget during stratified periods, and evasion from the lake surface was estimated to account for only 8% (Fallon et al. 1980). They attributed the greater role of methane oxidation in L. Mendota, compared to Lake 227, to differences in wind mixing during summer stratification; L. Mendota has a surface area about 780 times larger than Lake 227. Eddy diffusivities in the thermocline region of L. Mendota appear to be two orders of magnitude higher than those of Lake 227 (Fallon et al. 1980), which increases the turbulent mixing of oxygen from surface water down to depths where dissolved methane is concentrated. In L. Calado, the intensity of wind mixing appeared to determine whether the lake experienced net accumulation or net consumption of methane in the water column.

Methane emissions during falling water (September)

During an eleven day period in September 1987 water depth in L. Calado decreased from 4 m to 3 m, and vertical stratification of temperature and dissolved oxygen occurred near the bottom or was lacking (Figure 6). Dissolved methane concentrations in surface water ranged from 0.3 to 9.0 μM; the measurements were made between 0630 and 0940 (Table 1). Estimated diffusive methane fluxes were much lower (mean, 54 mg CH_4 $m^{-2}d^{-1}$) than the total fluxes measured with a floating dome (mean, 165 mg CH_4 $m^{-2}d^{-1}$, Figure 7). Ebullitive flux, calculated as the difference between total and diffusive flux, ranged from 20% to 95% of total flux, with an

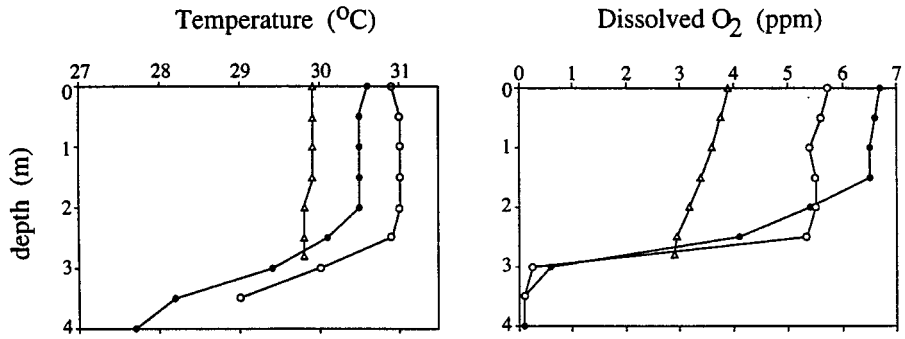

Figure 6. Temperature and dissolved oxygen profiles measured in L. Calado on 3 dates during falling water. Measurements were made at dawn on 14 Sept. (closed circles), 18 Sept. (open circles), and 24 Sept. (open triangles). The lake lost its seasonal thermal stratification between 18–24 Sept. due to decreasing lake depth.

average contribution of 69% (Table 1). This result is higher than that obtained by Barlett et al. (1988) in nearby lakes from 18 July to 2 Sept. 1985. In their study, an average of 49% of total methane flux in open water habitats occurred via bubbling. Other results are more similar to ours. Crill et al. (1988) observed that methane ebullition contributed 70% of total methane flux from L. Calado during July–August 1985; this number was later revised by Bartlett et al. (1990) to 73%. Wassman et al. (1992) observed that bubbling supplied 78% of total methane flux from L. Marchantaria, another central Amazon floodplain lake, during August–Sept. 1988.

Bartlett et al. (1990) compared values for total methane flux from L. Calado during rising water in 1987 (April to May) with those obtained by Bartlett et al. (1988) during falling water in 1985 (July to early Sept.), and concluded that seasonal differences in methane flux were not great in this lake. Devol et al. (1994) reported that, in general, methane fluxes from the Amazon floodplain were lower during low water (October–March) than during high water (April–Sept.); however, fluxes from open water areas did not show large seasonal differences and at all times of year were in the range 0–300 mg CH_4 $m^{-2}d^{-1}$. Wassman et al. (1992) measured higher methane fluxes in the open water of L. Marchantaria during low water than during high water. However, in their study site, anoxia persisted during the low water period and riverine flows imported oxygen to subsurface waters during high water period.

Our average total methane flux during September 1987 (mean, 163 mg CH_4 $m^{-2}d^{-1}$) was higher than that obtained by Bartlett et al. (1988) during falling water (18 July to 2 Sept.) in 1985 (mean, 27 mg CH_4 $m^{-2}d^{-1}$). Our measurements spanned the period in which L. Calado lost its thermal strat-

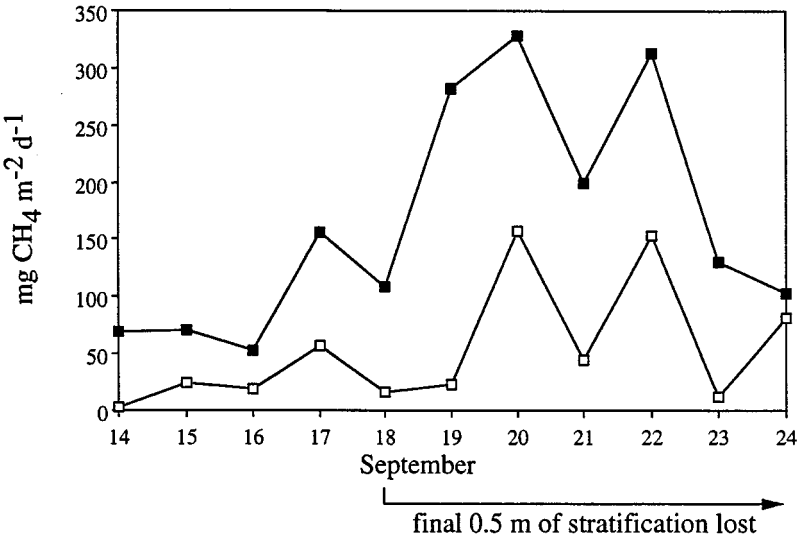

Figure 7. Total methane flux (solid squares) and diffusive methane flux (open squares) from L. Calado to the atmosphere during falling water. Total methane fluxes (diffusive plus ebullitive flux) were measured at dawn with a floating chamber. Diffusive fluxes were calculated via surface water methane concentrations obtained at the same time each day.

ification due to decreasing depth; after 18 Sept. the hypolimnion occupied only the bottom 0.5 m of the water column, and by 24 Sept. the lake was completely mixed (Figure 6). Total fluxes during our September study rose as this final mixing took place (Figure 7). After stratification was completely lost, and the bottom water became oxygenated, total methane flux dropped from 313 to 103 mg CH_4 $m^{-2}d^{-1}$ (Figure 7). In addition, bubbling accounted for $>$90% of total methane flux on six of eleven days in our study. Decreasing hydrostatic pressure may have increased the production of methane bubbles as the lake became increasingly shallow (Devol et al. 1988; Keller & Stallard 1994).

Conclusion

Our study illustrates the consequences of partial mixing events on the magnitude of methane release from an Amazon floodplain lake. Previous work at the same study site, conducted during a period of little rain, low winds and a stable thermocline, indicated that methane content of the floodplain lake increased over time, and that release of methane from the lake sediment could be accounted for by the sum of hypolimnetic storage plus methane flux from the lake surface to the atmosphere (Crill et al. l988). Additionally, during this

prior work, penetrative convection, rather than wind mixing, was judged to be responsible for the majority of surface renewal driving the diffusive flux of methane from the lake surface (Crill et al. l988). Our study took place during a windier period, owing to several strong afternoon thunderstorms and the passage of a strong cold front. These events, accompanied by wind-driven deepening of the thermocline, had contrasting consequences for methane flux from the floodplain. On one hand, these partial mixing events briefly elevated diffusive flux, by up to an order of magnitude during the cold front. On the other hand, these events reduced the methane content of the water column to a greater extent than could be explained by diffusive flux, or by diffusive plus ebullitive flux (the latter estimated). Methane oxidation during thermocline deepening was probably responsible for these reductions, and thus for decreasing the pool of methane ultimately available for export from the floodplain to the atmosphere. The advent of holomixis, toward the end of falling water, apparently also coincides with elevated rates of release of methane from the floodplain to the atmosphere. In our study, disappearance of the hypolimnion occured as the lake became $\leq$3 m deep, and was accompanied by a 2–3 fold increase in total methane flux for ca. 4 days.

Together, these results illustrate that estimates of methane emissions from the Amazon floodplain lakes should include the elevated rates accompanied by episodic mixing events, including the onset of destratification during falling water. The frequency and intensity of mixing events apparently determines whether net accumulation or net consumption of methane occurs in the water column of floodplain lakes. In addition, the data show that net methane flux to the atmosphere from surface waters is probably more variable over time than previously reported.

Acknowledgements

We thank K. Bartlett and P. Crill for analyses of methane samples and assistance in calculating fluxes from domes; and S. MacIntyre for guidance with estimates of diffusive flux. The manuscript was improved by suggestions from G. Kling, S. MacIntyre, and J. Chanton. This research was supported by NASA-ABLE2b and NASA-SIRB funds and grants from NSF, the California Space Institute, and the UCSB Academic Senate.

References

Amorocho J & DeVries JJ (1980) A new evaluation of the wind stress coefficient over water surfaces. J. Geophys. Res. 85: 433–442

Aselmann I & Crutzen PJ (1989) Freshwater wetlands: global distribution of natural wetlands and rice paddies, their net primary production, seasonality and possible methane emissions. J. Atmos. Chem. 8: 307–358

Bartlett KB, Crill PM, Sebacher DI, Harriss RC, Wilson JO & Melack JM (1988) Methane flux from the central Amazonian floodplain. J. Geophys. Res. 93: 1571–1582

Bartlett KB, Crill PM, Bonassi JA, Richey JE & Harriss RC (1990) Methane flux from the Amazon River floodplain: emissions during rising water. J. Geophys. Res. 95: 16,773–16,788

Brinkman WLF & de M Santos U (1974) The emission of biogenic hydrogen suflide from Amazonian floodplain lakes. Tellus 26: 261–267

Chanton JP & Smith LK (1993) Seasonal variations in the isotopic composition of methane associated with aquatic emergent macrophytes of the central Amazon basin. In: Oremland RD (Ed) Biogeochemistry of Global Change (pp 619–632). Chapman and Hall, New York

Cicerone RJ & Oremland RS (1988) Biogeochemical aspects of atmospheric methane. Global Biogeochem. Cycles 2: 299–327

Cole JC & Caraco NF (1998) Atmospheric exchange of carbon dioxide in a low-wind, oligotrophic lake measured by the addition of SF_6. Limnol. Oceanogr. 43: 969–675

Crill P (1996) Lattitudinal differences in methane fluxes from natural wetlands. In: Evans DD, Seitzinger SP & Crill P (Eds) Cycling of Reduced Gases in the Hydrosphere (pp 163–171). E Schweizerbart, Stuttgart

Crill PM, Bartlett KB, Wilson JO, Sebacher SI, Harriss RC, Melack JM, MacIntyre S & Lesack L (1988) Tropospheric methane from an Amazonian floodplain lake. J. Geophys. Res. 93: 1564–1570

Devol AH, Richey JE, Clark WA, King SL & Martinelli LA (1988) Methane emissions to the troposphere from the Amazon floodplain. J. Geophys. Res. 93: 1583–1592

Devol AH, Richey JE, Forsberg BR & Martinelli LA (1990) Seasonal dynamics in methane emissions from the Amazon River floodplain to the troposphere. J. Geophys. Res. 95: 16, 417–416, 426

Devol AH, Richey JE, Forsberg BR & Martinelli LA (1994) Environmental methane in the Amazon river floodplain. In: Mitsch WJ (Ed) Global Wetlands: Old World and New (pp 151–165). Elsevier Science B.V.

Emerson SE (1975) Gas exchange rates in small Canadian shield lakes. Limnol. Oceanogr. 20: 754–761

Fallon RD, Harrits S, Hanson RS & Brock TD (1980) The role of methane in internal carbon cycling in Lake Mendota during summer stratification. Limnol. Oceanogr. 25: 357–360

Harrits SM & Hanson RS (1980) Stratification of aerobic methane oxidizing organisms in Lake Mendota, Wisconsin. Limnol. Oceanogr. 25: 412–421

Junk WJ & Piedade MT (1997) Plant life in the floodplain with special reference to herbaceous plants. In: Junk WJ (Ed) The Central Amazon Floodplain. Ecology of a Pulsing System. Ecological Studies, Vol. 126 (pp 147–185). Springer Verlag

Lesack LFW (1988) Mass balance of nutrients, major solutes and water in an Amazon floodplain lake and biogeochemical implications for the Amazon Bazin. PhD Thesis. Univ.of California, Santa Barbara

Liss PS & Slater PG (1974) Flux of gases across the air-sea interface. Nature 247: 181–184

MacIntyre S & Melack JM (1988) Frequency and depth of vertical mixing in an Amazon floodplain lake (L. Calado, Brazil). Verh. Internat. Verein. Limnol. 23: 80–85

MacIntyre S, Wannikhof R & Chanton JP (1995) Trace gas exchange across the air-water interface in freshwater and coastal marine envirnments. Chapter 3. In: Matson PA &

Harriss RC (Eds) Methods in Ecology. Biogenic trace gases: measuring emissions from soil and water (pp 52–97). Blackwell Science, Cambridge

Martens CS, Blair NE, Green CD & DesMarais DJ (1986) Seasonal variations in the stable isotopic signature of biogenic methane in a coastal sediment. Science 233: 1300–1303

Matthews E & Fung I (1987) Methane emission from natural wetlands: global distribution , area, and environmental characteristics of sources. Global Biogeochem. Cycles 1: 61–86

McAuliffe C (1971) Gas chromatographix determination of solutes by multiple phase equililbrium. Chem. Technol. 1: 46–51

Melack JM & Fisher TR (1983) Diel oxygen variations and their ecological implication in Amazon floodplain lakes. Arch. Hydrobiol. 98: 422–442

Melack JM & Fisher TR (1990) Comparative limnology of tropical floodplian lakes with an emphasis on the central Amazon. Acta. Limnol. Brasil. 3: 1–48

Oremland RS, Miller LG & Whiticar MJ (1987) Sources and flux of natural gases from Mono Lake, California. Geochim. Cosmochim. Acta 51: 2915–2929

Peng T-S & Broecker W (1980) Gas exchange rates for three closed-basin lakes. Limnol. Oceanogr. 25: 789–796

Richey JE, Devol AH, Wofsy SC, Victoria R & Riberio MNG (1988) Biogenic gases and the oxidation and reduction of carbon in the Amazon River and floodplain waters. Limnol. Oceanogr. 33: 551–561

Rudd JWM, Furutani A, Flett RJ, & Hamilton RD (1976) Factors controlling methane oxidation in shield lakes: the role of nitrogen fixation and oxygen concentration. Limnol. Oceanogr. 231: 357–364

Rudd JWM & Hamilton RD (1978) Methane cycling in a eutrophic shield lake and its effects on whole lake metabolism. Limnol. Oceanogr. 23: 337–348

Setaro FV & Melack JM (1984) Responses of phytoplankton to experimental nutrient enrichment in an Amazon floodplain lake. Limnol. Oceanogr. 29: 972–984

Sippel SJ, Hamilton SK & Melack JM (1992) Inundation area and morphometry of lakes on the Amazon River floodplain, Brazil. Arch. Hydrobiol. 123: 385–400

Stauffer RE (1980) Windpower time series above a temperate lake. Limnol. Oceanogr. 25: 513–528

Striegl RG & Michmerhuizen CM (1998) Hydrologic influence on methane and carbon dioxide dynamics at two north-central Minnesota lakes. Limnol. Oceanogr. 43: 1519–1529

Utsumi M, Nojiri Y, Nakamura T, Nozawa T, Otsuki A & Seki H (1998) Oxidation of dissolved methane in a eutrophic, shallow lake: Lake Kasumigaura, Japan. Limnol. Oceanogr. 43: 471–480

Wannikhof R (1992) Relationship between wind speed and gas exchange over the ocean. J. Geophys. Res. 97: 7373–7382

Wassman R, Thein UG, Whiticar MJ, Rennenberg H, Seiler W & Junk WJ (1992) Methane emissions from the Amazon floodplain: characterization of production and transport. Global Biogeochem. Cycles 6: 3–13

Wassman R & Martius C (1997) Methane emissions from the Amazon floodplain. Chapter 7. In: Junk W (Ed) The Central Amazon Floodplain, Ecology of a Pulsing System. Ecological Studies, Vol. 126 (pp 137–143). Springer-Verlag, Berlin

Wiesenburg DA & Guinasso NL Jr (1979) Equilibrium solubilities of methane, carbon monoxide, and hydrogen in water and sea water. J. Chem. Engin. Data 24: 356–360