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Authors

Cicerone, RJ
Shetter, JD

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Sources Of Atmospheric Methane: Measurements in Rice Paddies and a Discussion

RALPH J. CICERONE AND JAMES D. SHETTER

National Center for Atmospheric Research, Boulder, Colorado 80307
Scripps Institution of Oceanography, La Jolla, California 92093

We have made field measurements of methane fluxes from rice paddies, fresh water lakes, and saltwater marshes to infer estimates of the size of these sources of atmospheric methane. The rice-paddy measurements, the first of their kind, show that the principal means of methane escape is through the plants themselves as opposed to transport across the water-air interface via bubbles or molecular diffusion. Nitrogen-fertilized plants release much more methane than unfertilized plants but even these measured rates are only one fourth as large as those inferred earlier by Koyama and on which all global extrapolations have been based to date. We also compare our measured methane fluxes from lakes and marshes to similar earlier data and find that extant data and flux-measurement methods are insufficient for reliable global extrapolations.

In 1978 the tropospheric concentration of methane was about 1.72 ppm by volume in dry air in northern mid-latitudes and 1.62 ppm in southern mid-latitudes [Heidt *et al.*, 1980]. While the first unambiguous detection of methane in the atmosphere appears to be that of Migeotte [1948], who observed its infrared absorption bands in the solar spectrum there has been very little sustained effort to observe its temporal and spatial variations. In the 1960's and 1970's a number of workers have conducted a sizable number of methane measurements mostly by flame-ionization gas chromatographic analysis of air sampled directly or stored in flasks. Absolute calibrations for CH₄ mole fraction in clean air differ slightly; Bush *et al.* [1978] reported 1.63 ± 0.12 for a 1978 worldwide average while Rasmussen and Khalil [1981] were closer to 1.60 in clean northern hemisphere air in 1978. At these concentrations methane is important in atmospheric chemistry and radiation: The oxidation of methane initiates key tropospheric reaction chains [Levy, 1971; McConnell *et al.*, 1971; Wofsy, 1972; Crutzen, 1973; Chameides and Walker, 1973] that produce CO and H₂ and strongly influence tropospheric chemistry. Also, the stratospheric oxidation of methane leads to approximately 50% of the water vapor and H₂ found there and CH₄ itself serves as the dominant terminator of chlorine-atom chains that destroy stratospheric ozone [Stolarski and Cicerone, 1974]. Further, the 7.7 μ band of CH₄ traps a significant amount of outgoing planetary radiation so that increases in atmospheric CH₄ levels would lead not only to chemical perturbations such as those mentioned by Chameides *et al.* [1977] and Sze [1977] but also to surface temperature increases [Wang *et al.* 1976].

From the ¹⁴C content of atmospheric methane, Ehhalt [1974] and Ehhalt and Schmidt [1978] have estimated that about 80% of it is produced biogenically and have tabulated various CH₄ sources, source strengths, and annual sinks. This annual methane cycle shows sources of 5 to 11×10^{14} g/yr and atmospheric residence times of 4 to 7 years. An acute lack of field data forced Ehhalt to base his methane source estimates on a few laboratory simulations (with rice paddy soils) and on isolated other data. While abiogenic sources are clearly possible (e.g., from natural gas releases and from geologic faults [Gold, 1979]) the view that most of atmospheric

methane is biogenic is strongly supported by arguments such as those of Lovelock and Margulis [1974] who showed that a purely abiogenic thermodynamic equilibrium would predict 29 orders of magnitude less CH₄ in the air than is observed.

From Ehhalt's methane source surveys one can see that a large fraction of the biogenic sources are wholly or partly under man's control through his agricultural practices (mostly rice cultivation) and domestication of cattle, as are several other methane sources: natural gas handling, coal mining, etc. Coupled with possible anthropogenic influence on methane sinks [Chameides *et al.*, 1977] these factors could lead to man-induced changes in atmospheric methane levels. Rasmussen and Khalil [1981] are measuring a methane increase in clean background air.

To provide a better data base on methane sources and to develop techniques for measuring fluxes of other largely biogenic gases we decided to devise field experiments to measure methane fluxes from several areas in California. These areas included several key environments of the type that influenced Ehhalt's surveys: rice paddies, freshwater lakes, and saltwater marshes.

METHODOLOGY

Several problems arise in measuring fluxes of gases into the air from water bodies and soils. Though not completely documented, many problems associated with gas collectors are notorious, including those of perturbing the turbulence fields in air or water, perturbing the thermal environment, or gaseous composition and introducing artificial gradients [see e.g., Hitchcock, 1979]. Flux-measurement techniques based on meteorological gradient or correlation techniques offer advantages in many cases but we decided to use gas-collection methods (described below) largely because methane transport across water-air interfaces can proceed through bubble breaking [see e.g., Martens and Klump, 1980]. Still more considerations arise when one attempts to measure fluxes of biogenic gases: living systems, be they microbes or plants, exhibit spatial patchiness, and they are susceptible to many perturbations such as physical manipulations and thermal changes. Accordingly, we experimented with several different gas-collecting systems.

In open water situations we used a glass carboy collector, a closed chamber of volume ≈ 11 l with 50 ml stainless steel

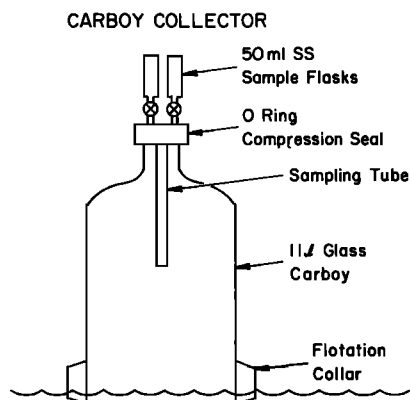


Fig. 1a. Schematic illustration of glass-carboy collector used for methane flux measurements (see text). The aluminum flotation collar is connected to polystyrene floats through three horizontal aluminum arms 40 cm long.

sample bottles attached via Swagelok fittings and an O-ring compression seal illustrated in Figure 1a. A flotation collar held the collector stable with the rim of the carboy opening 5 cm below the water surface. The evacuated sample bottles were opened at prescribed intervals to draw samples from a central location beneath the collector. Numerous problems can be associated with this approach: (1) one establishes an artificial environment of CH_4 , CO_2 , H_2O vapor and, possibly, elevated temperature; (2) one blocks any effect the wind might have on the flux; (3) one interferes with eddy transport in the water column (although our work was done in places where this was minimal), depending somewhat on how deeply the rim of the collector protrudes into the water and how the collector rim affects the liquid turbulence that renews the gas concentration near the water surface [see, e.g., Danckwerts, 1970]. Further, one must realize that methane transport by bubbles will be much less problematical in these regards than diffusive transport.

To measure fluxes that involved plant material we used two kinds of collectors besides the glass carboy described above. To minimize damage to the plants, we employed a flexible saran bag attached to a 17.5-cm diameter aluminum collar illustrated in Figure 1b. The volume was ~ 6 l and the sampling intervals were < 30 min. Evacuated 1 l spheres were connected to sampling tubes by feedthrough connectors on the aluminum collar and served also to hold samples and keep the apparatus afloat. The inertness of these bags toward methane in air samples was tested by filling the bags with a higher than ambient secondary standard of methane in zero air and testing for methane loss. Less than 2% loss was observed after storage of 5 ppm methane for periods up to 24 hours. Similar tests with zero-air storage were successful. The procedure was

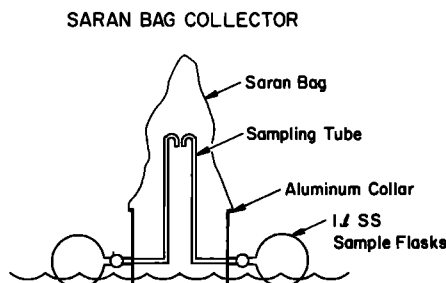


Fig. 1b. Schematic illustration of closed saran bag collector (see text) used for methane flux measurements.

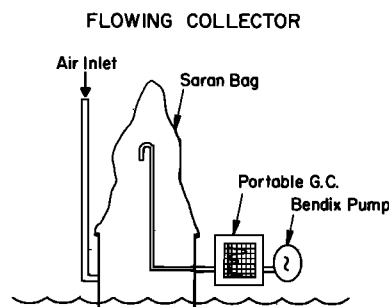


Fig. 1c. Schematic illustration of flowthrough saran bag collection system used for methane flux measurements (see text).

to set the collector down, let it sit for 10 min, and take a sample, then lift it and let it flush well with ambient air, and then start the procedure over by letting it sit for a longer period of time. One problem here, owing to the nonrigid construction, was ensuring a reproducible volume beneath the collector, but the shorter sampling interval reduced the artificial gradient.

In rice paddies we also used a third type of collector, a flowthrough bag shown schematically in Figure 1c. This is a modified saran bag collector that had ~ 1 l/min of ambient air drawn through it by a portable Bendix pump. The air passed from the collector directly to a portable gas chromatograph for immediate analysis. The procedure was to analyze a standard, analyze an ambient air sample, then a sample from the collector and repeat this several times. The flowing collector was used to maintain a near ambient environment around the rice plants beneath the collector. When the bag collectors were employed in rice paddies, no attempt was made to shade the bags from direct sun because in the collection interval (10–20 min), no appreciable heating occurred. Indeed, no significant day-night differences were evident, as reported below. With the glass-carboy collector we shaded (usually but not assiduously) the sunward side of the collector with an aluminum foil wrap.

In the field, sample analysis was accomplished on an A.I.D. portable gas chromatograph equipped with a flame-ionization detector and gas-sampling valve. Three ml air samples were separated on a $5' \times 1/8''$ Spherocarb column held at 100°C with 25 ml/min N_2 carrier flow. The methane retention time was about 3 min. Signals were fed to a 1mV recorder, and concentrations were calculated by using peak heights. The system minimum detectable methane concentration was 50 ppb and precision for repeated analysis was about 1%. Samples were compared to a standard prepared by Matheson of methane in zero air and calibrated in our laboratory by using a feedback flow system [Stedman et al., 1978]. When samples were returned to our laboratory at Scripps from saltwater marshes and lakes, analysis was performed on a Perkin Elmer Sigma 4 flame-ionization detector gas chromatograph configured as described above. System precision on this chromatograph was very good; standard deviations were 0.2–0.4% of the mean for repeated analyses. Careful tests in which air samples were dried with a Drierite desiccant showed that the principal effect of water vapor was to degrade column performance (after many moist-air injections). Samples were dehumidified through Drierite in most cases but not in the rice paddy studies where bag collectors were used. Sample moisture was, in fact, of no concern.

To enable us to run repeated analyses the atmospheric pressure samples were pressurized with 10 psig (68.9 kPa) of pre-

purified N_2 that had been previously checked for methane content. This dilution factor was applied to calculate the final methane concentrations. Once these concentrations were determined, the flux could be calculated by using the collector volume, the area covered by the collector, and the elapsed time. Dissolved oxygen was measured with an Orion Research model 399 A/F meter equipped with a model 97-08 oxygen electrode. The range was nominally 0–14 ppm (438 μM) with accuracy of ± 0.05 ppm.

RESULTS

Rice paddy flux measurements were made in an experimental rice field located on the grounds of the University of California at Davis, (40.2°N, 122.1°W). The work was done in late summer with daytime temperatures ranging from 26°–32°C dropping to 17°–20°C at night. Several parameters were measured with each collection. The water, which was 10–18 cm deep over the 350 m² area of the test paddy, was being replaced at a rate of ~ 3 l/min. It had a pH range of 6.9–8.1, while its temperature ranged from 18°–26°C. The dissolved oxygen exhibited a cyclic diurnal behavior as was expected with daylight values supersaturated (off scale, over 440 μM) and nighttime values as low as 95 μM . Soil temperature was relatively stable at 28°–29°C.

By placing a collector over a test area and sampling the gas inside the collector after measured time intervals, we deduced the methane flux across the plane defined by the collector orifice. Figure 2a displays the rates of increase of methane concentration under two glass-carboy collectors, one placed over rice plants and one placed over nearby, adjacent open paddy water with no rice plants in it. Note the nearly linear rates of increase under both collectors. After 4 hours the collector over rice plants contained 290 ppm methane and the collector over open water contained 3.80 ppm methane. Figure 2b displays similar data but with both collectors over rice plants, one group unfertilized and one group fertilized with $(NH_4)_2SO_4$ at a rate of 120 kg nitrogen per hectare per year. Fertilized rice plants consistently released more methane as discussed below.

In an unfertilized area of the paddy we compared data obtained with the three collectors by deploying the glass-carboy collector, the saran-bag collector, and the flowthrough bag collector near each other, each over rice plants. Table 1 shows the results of nine individual collections designed to compare

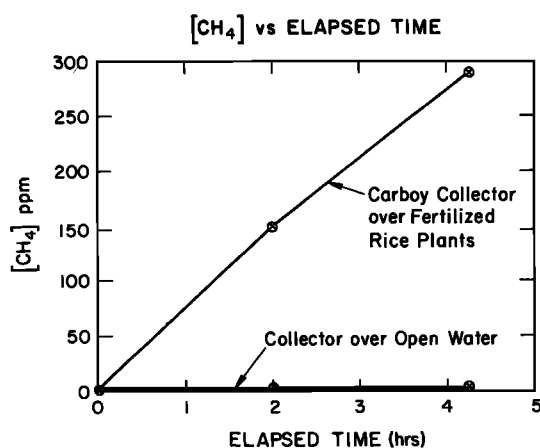


Fig. 2a. Measured rates of increase of methane mixing ratio inside two glass-carboy collectors, one deployed over open water in a rice paddy, one over rice plants. Initially, the glass carboy was filled with ambient air (mixing ratio = 1.65 ppm CH_4).

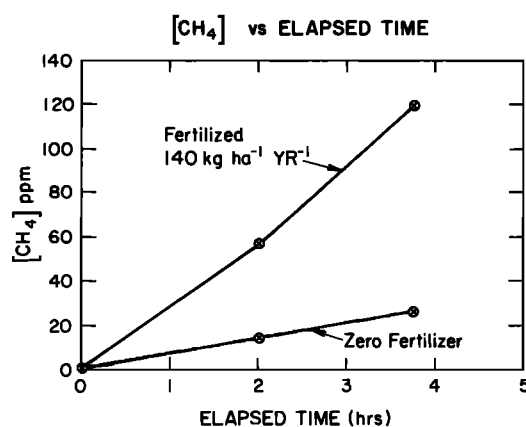


Fig. 2b. Measured rates of increase of methane mixing ratio inside two glass-carboy collectors, one deployed over fertilized rice plants and one over nearby control group unfertilized rice plants. Initial conditions as for Figure 2a.

collection methods. The individual collectors were deployed near each other over unfertilized rice, and fluxes were determined from measured rates of changes of methane versus time such as those exemplified in Figures 2a–2c. As Table 1 shows, the three methods compared rather well considering the different perturbations introduced by each collector, the spatial patchiness of the rice paddy, and other sources of error, (e.g., inaccuracies in bag volumes owing to variable deformations in the bags between deployments). In any case, the differences in fluxes measured by these different collectors are much smaller than (1) the interesting differences between fluxes from open paddy water (no plants) and from rice plants, and (2) the differences between fluxes from fertilized and unfertilized rice plants.

Table 2 summarizes our quantitative data on methane fluxes from rice paddies. These data strongly suggest that the major mechanism for CH_4 release is not upward transport from the sediments by rising bubbles or by gaseous molecular diffusion, but, instead, by direct passage from the sediment/soil through the rice plants. Further, nitrogen-fertilized plants release more methane. Adjacent collectors over open water and over rice plants gave fluxes of 0.0035 and 0.18 g $CH_4/m_2/$

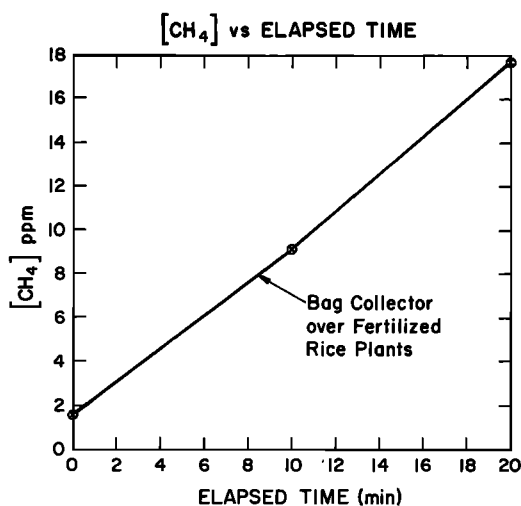


Fig. 2c. Measured rates of methane mixing ratio inside a closed saran bag over fertilized rice plants. Note that with this brief collection the rate of increase is almost linear with time as with the longer glass-carboy collections.

TABLE 1. Comparison of Methane Fluxes ($\text{g CH}_4 \text{ m}^{-2} \text{ d}^{-1}$) Measured With Different Collectors Near Each Other Over Unfertilized Rice Near Davis, California, in September 1980

Glass Carboys	Saran Bags	Flowthrough Bags
2.36×10^{-2}	6.82×10^{-2}	4.13×10^{-2}
3.05×10^{-2}	3.83×10^{-2}	2.30×10^{-2}
3.49×10^{-2}	5.10×10^{-2}	
	1.32×10^{-2}	
1.72×10^{-2}	1.91×10^{-2}	
$2.66 \times 10^{-2*}$	$3.80 \times 10^{-2*}$	$3.22 \times 10^{-2*}$

The average over all nine of these data points is $3.28 \times 10^{-2} \text{ g CH}_4 \text{ m}^{-2} \text{ d}^{-1}$.

*Average.

d, respectively, on average with no overlap at all in the range of observed fluxes (see Table 2). Proceeding down Table 2, rice fertilized with 140 kg N/ha/yr (as $(\text{NH}_4)_2\text{SO}_4$) released $0.15 \text{ g CH}_4/\text{m}^2/\text{d}$ while unfertilized rice released $0.032 \text{ g CH}_4/\text{m}^2/\text{d}$. A further indication that methane passes from the sediment/soil through the rice (as opposed to being produced in the rice plants) came from our observations with side-by-side unfertilized rice plants, some intact and others cut down slightly above the water line. Table 2 shows nearly equal fluxes, 0.053 and $0.044 \text{ g CH}_4/\text{m}^2/\text{d}$. Finally, we observed no significant day-night differences in methane release rates from fertilized rice plants.

We have also measured methane fluxes from several saltwater marshes and lagoons in southern California. These measurements were made with the glass-carboy collectors in standing water and are summarized in Table 3. Collections were often over 24-hour periods but always over one hour long. The increase in methane concentration versus time was determined by sampling at intervals of 30 min to 1 hour in the initial stages of each collection, then usually at 4, 8, and 16 hours later. Graphs similar to Figures 2a and 2b were thus generated. Straight-line segments were drawn through the individual data points and an overall best fit line through all data points. The slopes and thus the fluxes for each time interval were almost always within $\pm 25\%$ of the slope of the overall line. The observation of nearly linear increase in methane concentration in the collector over 24-hour periods rules out back diffusion as a serious concern in these measurements. Nonetheless, this technique is still susceptible to problems such as those mentioned earlier. The Batiquitos location is a shallow, several km^2 saltwater lagoon with a thick organic

muck base. It is covered by surface waters except in the end of the dry season, typically August and September. The Penasquitos location is similar but with much more swamp-grass vegetation. At Batiquitos the average flux was $2.16 \times 10^{-3} \text{ g CH}_4/\text{m}^2/\text{d}$ for the five dates shown, while at Penasquitos the average flux was $3.65 \times 10^{-4} \text{ g CH}_4/\text{m}^2/\text{d}$ for the 17 dates shown in Table 3.

With similar methods we made 10 flux measurements at three southern California freshwater lakes, as summarized in Table 4. Excluding the largest flux ($7.86 \text{ g CH}_4/\text{m}^2/\text{d}$ on August 31, 1979, at Lake Hodges) the remaining nine points averaged $0.13 \text{ g CH}_4/\text{m}^2/\text{d}$. The influence of bubbles on these experiments was evident; rising bubbles were often apparent. Methane concentrations inside bubbles from freshwater and coastal sediments are typically 35–85% [Martens and Klump, 1980; Dacey and Klug, 1979; Baker-Blocker et al., 1977] as we found. In an attempt to determine how much of our measured fluxes arose from bubble ebullition we did side by side collections where bubbles were excluded from one collector by placing a fine stainless steel mesh (100 micron holes) over the opening. The data appear in Table 5. In each case the collector without the screen showed a bigger flux, suggesting that bubble ebullition is often the dominant means of escape for methane from the water column into the air. It can be suggested that the screen is impeding eddy transport in the water column, but in the stagnant areas where this work was done eddy transport would be weak anyhow. Further, in the course of similar studies we have done on N_2O release from Michigan rivers and lakes we found that varying the depth to which the collector rim penetrates the water leads to only $\sim 10\%$ decreases in measured fluxes when the rim penetrates twice as far into the water. This suggests that our bubble-deflecting screen did not interfere materially with those eddies that deliver gases from below.

DISCUSSION AND CONCLUSIONS

Our rice paddy measurements are the first such field studies of methane release to the atmosphere. An earlier study by Koyama [1963, 1964] was performed by incubating rice paddy soils in the laboratory. On the basis of Koyama's estimate of an annual global average methane flux of $206 \text{ g/m}^2/\text{yr}$, Ehballt and Schmidt [1978] concluded that rice paddies account for $2.8 \times 10^{14} \text{ g CH}_4/\text{yr}$ globally or 33–49% of all biogenic atmospheric methane and 26–47% of all atmospheric methane from

TABLE 2. Summary of Measured Methane Fluxes ($\text{g CH}_4 \text{ m}^{-2} \text{ d}^{-1}$) From Rice Paddy Waters With and Without Rice Plants, Fertilized and Unfertilized Rice, Day-Night Differences, and From Cut and Intact Rice Plants

Flux From:	Number of Trials	Range ($\text{g CH}_4 \text{ m}^{-2} \text{ d}^{-1}$)	Average ($\text{g CH}_4 \text{ m}^{-2} \text{ d}^{-1}$)
Open water (no rice plants)	3	1.26×10^{-3} to 7.42×10^{-3}	3.5×10^{-3}
Rice plants (adjacent to open paddy water, see above)	6	7.5×10^{-2} to 3.0×10^{-1}	0.18
Unfertilized rice plants	9	1.32×10^{-2} to 6.82×10^{-2}	3.2×10^{-2}
Fertilized* rice plants	11	5.3×10^{-2} to 3.0×10^{-1}	0.15
Cut off rice plants (unfertilized)	2	$(4.78, 5.85) \times 10^{-2}$	5.3×10^{-2}
Intact rice plants (unfertilized)	2	$(3.85, 5.07) \times 10^{-2}$	4.4×10^{-2}
Day, fertilized rice plants	3	7.5×10^{-2} to 0.30	0.173
Night, fertilized rice plants	3	0.13 to 0.24	0.186

* With $140 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ as $(\text{NH}_4)_2\text{SO}_4$.

TABLE 3. Methane Flux Measurements From a Southern California Saltwater Marsh (Penasquitos) and From a Shallow Southern California Lagoon (Batiquitos)

Date	Depth, cm	Water Temperature, °C	Flux (g CH ₄ m ⁻² d ⁻¹)
<i>Penasquitos</i>			
May 24, 1979	40	26	8.44 × 10 ⁻⁴
May 30, 1979	29	23	5.11 × 10 ⁻⁴
June 4, 1979	18	21	9.82 × 10 ⁻⁵
June 6, 1979	38	20	1.35 × 10 ⁻⁴
June 14, 1979	25	30	5.20 × 10 ⁻⁴
June 19, 1979	16.5	27	8.67 × 10 ⁻⁵
June 20, 1979	16.5	23	9.25 × 10 ⁻⁵
June 27, 1979	21.5	23	2.36 × 10 ⁻⁴
July 12, 1979	10	27	6.27 × 10 ⁻⁵
July 18, 1979	5	31	1.98 × 10 ⁻⁴
July 18, 1979	114	26	9.33 × 10 ⁻⁴
July 30, 1979	9	28.5	5.46 × 10 ⁻⁵
Aug. 2, 1979	13	25	5.92 × 10 ⁻⁵
<i>Batiquitos</i>			
Aug. 13, 1979	5	30.5	2.46 × 10 ⁻³
<i>Penasquitos</i>			
Aug. 14, 1979	23	27.5	6.22 × 10 ⁻⁴
Aug. 22, 1979	25	27	1.07 × 10 ⁻³
Nov. 29, 1979	41	15	3.30 × 10 ⁻⁴
Jan. 25, 1980	46	16.5	3.51 × 10 ⁻⁴
<i>Batiquitos</i>			
March 14, 1980	7	25	6.38 × 10 ⁻⁴
April 28, 1980	13	23	7.88 × 10 ⁻⁴
May 30, 1980	25	24.5	2.32 × 10 ⁻³
June 29, 1980	32	26	4.59 × 10 ⁻³

At these locations, water pH ranged from 7.0 to 9.9 with highest pH values in daytime, lowest at night typically. Dissolved oxygen was near or supersaturated (>284 μM at 20°C) on bright days and went as low as 95 μM at night.

all sources. Our measurements, if extrapolated in the same way Koyama extrapolated his laboratory data, lead to 42 g CH₄/m²/yr and 5.9 × 10¹³ g CH₄/yr globally. Our figure of 42 g CH₄/m²/yr arises from our measured methane flux of 0.18 g CH₄/m²/d (see Table 2 and text) that applies to generously fertilized rice. Our global annual methane release (5.9 × 10¹³ g CH₄) arose from assuming the same temperature dependence for methane generation, the same United Nations rice-cultivation data, and 4-month growing season assumption that Koyama employed.

Clearly, our measurements of methane release from rice were more direct than Koyama's, and we found much less methane release, but our data are far from definitive. For example, if the methane release depends as strongly on nitrogen fertilization as our data indicate (Table 2), then one must take into account the lesser usage of N fertilizer in less developed

nations; even lower methane fluxes might be found elsewhere. Fertilizer type could also be an important variable. For example, because sulfate-reducing bacteria compete with methanogenic bacteria for available H₂ and acetate [Claypool and Kaplan, 1974; Martens and Berner, 1974] one might suspect that sulfate-containing fertilizer could suppress methane generation initially. It is not clear why nitrogen-fertilized rice plants deliver more methane to the atmosphere. If it is because they are larger, more mature, and with more developed roots, then one can guess that plant maturity affects methane release: Variations during the growing season need investigation. The increasing usage of symbionts like *Azolla* to provide fixed nitrogen in rice paddies in India and China should also be examined. Another likely factor is the organic content of rice paddy soils; Koyama's larger fluxes could have arisen if his research soils were more rich in metabolizable organic material than the University of California at Davis paddy soils. It is also likely that Koyama's sealed system, extremely low in oxygen, might have led to overestimates of methane release to the atmosphere. Even though his measured rates of methanogenesis could be correct, any oxidation of methane in the overlying water column of a natural rice paddy would have limited the methane release rate. For similar environments, Ehhalt and Schmidt [1978] and Martens and Klump [1980] have discussed the likelihood of methane oxidation in the water column above anoxic sediments; one might expect more oxidation in oxygen-supersaturated daytime waters. Our data (Table 2) show (1) that direct transport through rice plants strongly dominates the net methane release to the atmosphere, (2) no day-night differences, and (3) fluxes 20% as large as Koyama's. Finally, Koyama's [1963, 1964] global flux estimate (and ours) was based on a soil-temperature dependence he observed, a dependence that does not hold for all methanogenic microorganisms [Zeikus and Winfrey, 1976].

Our finding that methane transport through the rice plants dominates other forms of release was surprising but not totally. Kozuchowski and Johnson [1978] observed that gaseous mercury compounds escape through the stomata of plants (common reeds) growing in mercury-contaminated lake sediments. Further, Dacey and Klug [1979] found that 50% or more of the methane escaping from a eutrophic lake in Michigan rose through water lily plants. The apparent lack of a diurnal variation in our data for methane fluxes through rice plants needs to be confirmed with more data because we have few data points and because Dacey and Klug [1979] and Kozuchowski and Johnson [1978] found more gaseous release in daytime hours. Further, Dacey [1980] has reported tracer studies that suggest a pressurized flowthrough system that

TABLE 4. Methane Flux Measurements From Three Freshwater Lakes in Southern California

Location	Date, 1979	Depth, cm	Water Temperature, °C	Flux, g CH ₄ m ⁻² d ⁻¹
Lake Miramar	Aug. 7	91	27.5	2.39 × 10 ⁻³
Lake Guajome	Aug. 23	122	22.5	3.81 × 10 ⁻²
Lake Hodges	Aug. 31	>150	26	2.32 × 10 ⁻¹
Lake Hodges	Aug. 29	46	28	2.55 × 10 ⁻¹
Lake Hodges	Aug. 31	12.7	30	7.86
Lake Hodges	Sept. 26	91	31	4.43 × 10 ⁻¹
Lake Hodges	Oct. 18	122	24	8.40 × 10 ⁻²
Lake Guajome	Oct. 24	46	27	3.65 × 10 ⁻³
Lake Hodges	Nov. 8	25	21	5.03 × 10 ⁻²
Lake Hodges	Nov. 15	46	16	2.71 × 10 ⁻²

Water pH ranged from 7.2 to 9.0. In the shallower water nighttime dissolved oxygen values decreased to 60–90 μM while daytime values were near or supersaturated (284 μM at 20°C).

TABLE 5. Results of Six Carboy Collections to Estimate the Contribution of Bubbles to Methane Fluxes Across the Water-Air Interface

Location	Date, 1980	Flux Without Screen	Flux With Screen	Depth, cm
Lake Hodges	Sept. 25	4.43×10^{-1}	6.29×10^{-3}	90
Batiquitos Lagoon	July 24	4.43×10^{-4}	6.11×10^{-5}	15
Batiquitos Lagoon	July 18	4.32×10^{-4}	1.77×10^{-4}	15
Batiquitos Lagoon	July 31	5.79×10^{-4}	1.91×10^{-4}	15
Batiquitos Lagoon	Aug. 7	1.65×10^{-1}	2.18×10^{-4}	10
Batiquitos Lagoon	June 20	5.30×10^{-3}	2.48×10^{-3}	36

Fluxes are $\text{g CH}_4/\text{m}^2/\text{d}$. In all cases the collector with a bubble-excluding screen (see text) recorded a lower methane flux.

forces atmospheric oxygen to water lily roots and delivers CO_2 to the plant leaves and methane to the atmosphere through the leaves. Contrary to earlier ideas, Dacey [1980] found significant mass flows through plant lacunae.

Our freshwater lake data (Table 4) gave typical methane fluxes of $0.13 \text{ g CH}_4/\text{m}^2/\text{d}$, although a much higher flux was observed on 1 day. Including all the data points in Table 4 raises the average flux to $0.89 \text{ g CH}_4/\text{m}^2/\text{d}$. Clearly, extrapolating from these data is perilous. Previously, four swamp-gas samples analyzed by Conger [1943], as interpreted by Ehhalt and Schmidt [1978], implied a flux of $0.32 \text{ g CH}_4/\text{m}^2/\text{d}$ from a location in Maryland. Baker-Blocker et al. [1977] trapped rising bubbles below the water surfaces of two farm ponds in Michigan and deduced fluxes between 0.09 and $1.1 \text{ g CH}_4/\text{m}^2/\text{d}$. As Baker-Blocker et al. and Ehhalt and Schmidt [1978] have discussed, it is desirable to deduce a temperature dependence for the methane evolution (and escape). It is questionable whether there are enough data at present to permit an accurate temperature dependence to be inferred. Further, because bubbles dissolve rapidly under some conditions [Martens and Klump, 1980], the methane escape rate to the atmosphere is likely to be less than the rate of methane release from the sediments. Additional complexities arise from the recent recognition [Dacey and Klug, 1979] that substantial amounts of methane escaping from lakes rises through plants like water lilies. Dacey and Klug [1979] measured escaping methane fluxes of $0.35 \text{ g CH}_4/\text{m}^2/\text{d}$ (2.2×10^{-2} moles $/\text{m}^2/\text{d}$) from a small, eutrophic Michigan lake in August. Half or more of this flux came directly through plants; Dacey and Klug measured open-water contributions to the methane flux by static closed chamber trapping. The fact that methane can be oxidized as it rises [see discussion of Ehhalt and Schmidt, 1978; Martens and Klump, 1980], whether in bubbles or in dissolved form, especially in waters deeper than 2 m, combined with the transport-through-plants mechanism makes it difficult to know if the present data base is adequate for reasonable extrapolations. Our average flux, $0.13 \text{ g CH}_4/\text{m}^2/\text{d}$ (Table 4), although it arises from fairly warm water samples, is lower than the above-quoted figures. Over 365 days our figure would yield $47 \text{ g CH}_4/\text{m}^2/\text{yr}$, slightly below Ehhalt and Schmidt's [1978] lowest estimate. Further, the higher fluxes reported by Baker-Blocker et al. [1977] might be overestimates because they trapped bubbles below the water surface; subsequent oxidation might have led to a lower actual escape flux of methane. On the other hand, the role of plants as escape conduits for methane from lakes could lead to higher actual methane release than we have measured or Ehhalt and Schmidt [1978] have estimated. For purposes of global extrapolation, one must know the fraction of lake surfaces participating in methane release. This fraction, taken to be 0.01 to

0.1 by Ehhalt [1974], is very uncertain owing to lack of data and also owing to the great potential of plants to control the release. As a last note on freshwater lakes, we saw no evidence of diurnal variability in the methane release rate from open waters in several day and night measurements. Dacey and Klug [1979] and Dacey [1980] have reported a daytime maximum in the methane flux from plants in a small Michigan lake.

There are few data on fluxes from salt water marshes probably because it was established early on [Koyama, 1963] that the presence of salts inhibits methanogenesis. King and Wiebe [1978] show a wide range of 0.44 – $51 \text{ g CH}_4 \text{ m}^{-2} \text{ yr}^{-1}$ in Georgia salt marshes. Their measurements were made over soil with plant material and showed a seasonal dependence. The measurements we made in southern California yielded a $0.28 \text{ g CH}_4/\text{m}^2/\text{yr}$ average flux but were made in areas of standing water of 15 cm, which probably allowed a considerable amount of oxidation before the methane was released to the atmosphere. We saw no seasonal changes, but it should be noted that seasonal temperature changes are small in southern California (see Table 3). The possibility that methane and other gases escape from salt marshes directly through reed-like grasses remains to be investigated. Indeed, it seems clear that all future investigations of gas evolution from marshes, lakes, and rice paddies must recognize that areas covered with plants can be as important as open-water areas.

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