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METHANE EMISSIONS FROM CALIFORNIA
RICE PADDIES WITH VARIED TREATMENTS

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Abstract. Two field experiments in California rice paddies are reported, one with a single treatment of a research plot and the other with varied treatments in a typical commercial rice field. Small total methane emissions, only 11 g CH_4/m^2, were measured for the entire growing season in the first experiment. In the second experiment, the addition of exogenous organic matter (rice straw), the presence or absence of vegetation, and the nitrogen fertilizer amounts were examined for their influence on methane emissions. The total methane emission over the growing season varied from 1.2 g CH_4/m^2 (with no added organic matter) to 58.2 g CH_4/m^2 (with largest organic matter treatments). Added organic matter was the major factor affecting methane emissions. Vegetation did not greatly affect total methane fluxes, but it did influence the mode and timing of release. Nitrogen fertilizer did not greatly affect the amount of methane emitted, but it influenced slightly the time course of the process. A diurnal effect in methane emission was observed during the early ontogeny of the crop. The variation of methane emission with time during the course of the growing season was very unusual in this experiment; only one peak was observed, and it was early in the season. During the period of largest emissions, $\delta^{13}C$ values of the methane were measured to be -55.7 ± 1.8 ‰ in plots with added organic matter.

1. INTRODUCTION

Methane has become one of the most interesting gases in the atmosphere partly because its concentration has increased worldwide at a rate of about 1% per year over the last 100-150 years [Rasmussen and Khalil, 1981; Fraser et al., 1984; Steele et al., 1987; Blake and Rowland, 1988]. Continued increases of methane can have global effects because methane interacts strongly with planetary infrared radiation (greenhouse effect) [see Wang et al., 1976; Lacis et al., 1981; Ramanathan et al., 1985] and because of its roles in atmospheric chemistry. Atmospheric methane oxidation produces water vapor; this H_2O source is most significant in the upper stratosphere and insignificant in the troposphere. Stratospheric methane also interacts with chlorine chemistry through its reaction with Cl atoms to produce HCl. Tropospheric reactions destroy perhaps 90% of the methane that enters the atmosphere; OH radicals initiate this attack. Atmospheric chemical species and processes involved in methane oxidation are also central to the control of the oxidation state of the atmosphere. These points are discussed more fully by Crutzen [1987] and Cicerone and Oremland [1988].

Thus it is important to discover the causes of the increasing trend of methane concentrations and to identify the sources and sinks of atmospheric methane and the processes that control them. Ehhalt [1974] presented the first quantitative analysis of the sources of atmospheric methane. On the basis of several indicators and Koyama's [1963] laboratory studies, Ehhalt postulated that the world's rice paddies would be a major methane source. Flooded soils are certainly

good candidates to be methane producers: flooding results in a rapid lowering of oxidation-reduction potential with the consumption of all available electron acceptors including inorganic ions such as ferric and manganic ions, nitrate, and sulfate. This sequence terminates with the reduction of carbon dioxide and with the formation of methane. Methane is also produced in the direct heterotrophic demethylation of lignin and other organics such as acetate. Soil chemists and microbiologists have shown clearly how methane is formed in such environments [e.g., Yamane and Sato, 1963; Takai, 1970; Ponnamperuma, 1972; Neue and Scharpenseel, 1984; Oremland, 1988]. In soils that can remain flooded, and hence favor rice agriculture, rice is relatively shallow-rooted and diffusion of oxygen into the soil is slow, particularly when the soil is flooded. Thus any readily decomposed organic matter remaining in the soil at the time of flooding results in a rapid lowering of oxidation-reduction potential with the reduction of all available electron acceptors and soil transformations that produce methane, as outlined above.

Early field investigations of methane emissions from rice paddies were reported by Cicerone and Shetter [1981], Cicerone et al. [1983], and Seiler et al. [1984]; the latter two studies covered almost complete growing seasons. Cicerone et al. [1983] reported large changes in the rate of methane emission with peak emissions observed in September; 90% of the total emission for the growing season occurred in September. Seiler et al. [1984] found a strong but different seasonal variation and a distinct time-of-day (largest emissions in the late afternoon) variation. Time-of-day variations correlated positively with soil temperatures. In addition, these studies showed that methane transport through the rice plants greatly exceeded the rate of methane escape carried by diffusion across the water-air interface and by bubbles. Evidence that methane is transported primarily through the plants has become more convincing with time [Cicerone and Shetter 1981; Seiler et al. 1984; Nouchi et al. 1990].

Given the growing importance of atmospheric methane and the clear evidence of methane emissions in the early field experiments it became clear that more observations were needed to determine how much variability would be observed between rice fields and how methane emissions would vary with factors such as soil organic matter and fertilizer types and amounts, factors that vary in actual agricultural practice around the world.

In this paper we report results of two further field experiments in California. The first was a relatively simple season-long observation of methane fluxes that we conducted in 1983. The second was a more comprehensive experiment in 1985 in which, through the cooperation of a local rice grower, we were able to monitor and manipulate a portion of one of the more

typical and more progressive large-scale rice producing activities in California.

In the next section, we describe the design of these experiments, along with the soils of the experimental sites and the analytical methods. Sections 3 and 4 of the paper report and discuss the results of the field experiments.

2. EXPERIMENTAL DESIGN AND METHODS

2.1. The 1983 Experiments

The 1983 experiments were designed to monitor the variation of methane emission over the course of a growing season and to see if the seasonal variation observed at the same site in 1982 [Cicerone et al., 1983] would be repeated. The site of this work was the Rice Research Facility of the University of California, Davis. The soil is classified as Capay Silty Clay, a vertisol with a silty clay surface grading into a silty clay loam at varying depths of from 30 to 50 cm. It is moderately well drained, somewhat atypical of rice fields where percolation rate usually is low. Its availability and proximity to research laboratories were the principal factors determining its application to rice.

Methane emissions were measured through the use of static chambers placed over the rice plants. The chambers were rigid cylindrical sections of transparent polycarbonate material; the bases of the collectors were grooved, circular aluminum sections placed permanently into the paddy soil and beneath water level. During a sampling period, the polycarbonate collector (22 cm diameter) was placed into the grooved base, thus preventing gaseous exchange with the atmosphere. Sampling ports of stainless steel tubing extended from the top of the polycarbonate collectors downward to the midpoint of the collector. An open capillary tube in the collector top allowed internal and external pressures to equalize without appreciable air flow. Early in the season we used a shorter collector (45 cm high) and as the rice grew, longer sections (70 cm high). Samples were withdrawn into evacuated stainless steel flasks from the collectors 10 or 20 min after emplacement as were air samples of ambient air (just below rice-top height). Equipment and method of analysis were the same as those described by Cicerone et al. [1983]. Soil treatments and dates of treatments and of other significant events are listed in Table 1. A wooden pier was placed into the field before flooding. From this pier we were able to reach the first five rows of rice plants in the field without disturbing the water-covered soil.

2.2. The 1985 Experiments

The 1985 experiment was more complex and intensive using twelve test plots in a commercial

TABLE 1. Dates of Field Treatments for 1983 Experiment at University of California, Davis,
Rice Research Facility Plots

Date	Day Number	Event	Notes
May 10	0	preplant fertilizer added	36 kg N/ha (200 lb/acre of 16-20-0)
May 21	11	field flushed with water	
June 7	28	rice planted	
June 7		topdress fertilizer added	78 kg N/ha (150 lbs/acre of urea)
June 7		field flooded permanently	
September 30	143	water supply stopped	
October 1 to 5	144-148	draining of water	October 1983 was unusually dry
October 14	157	soil surface dry, cracks appear in soil.	

Field was leveled in summer, 1982 and lay fallow until 1983. Rice was not cut or harvested during this experiment. Soil type was Capay silty clay; see text.

rice-growing field. During the previous year, rice was also grown commercially on this field; after harvest the remaining crop stubble was burned in place. This soil is less permeable to water than was the case for the sites of the 1983 experiment described in this paper or the 1982 experiment described by Cicerone et al. [1983]. It is classified as Sacramento Clay, a poorly drained montmorillonitic, noncalcareous thermic clay with a low water penetration rate. Although this heavy soil with limited drainage poses some management difficulties for wheat and maize, it is ideally suited to rice culture in many respects and is representative of many commercial rice-producing areas of the world where tillage characteristics and factors of water management tend to select for rice as the main agricultural cereal. One of the more notable differences between the management of this and similar California rice fields and many other rice growing regions lies in the use of mineral nitrogen fertilizers or urea as contrasted with higher carbon "organic" sources.

Table 2 lists the various events in the preparation and treatment of the 12 test plots and corresponding dates in 1985. Fertilizer types and amounts are listed there. Six plots (7-12) were given nitrogen fertilizer (urea) and the other six (1-6) were not. Four plots (1, 4, 7, 10) received no added organic matter. To four other plots (2, 5, 8, 11) were added 250 g/m^2 of dry organic matter (rice straw), and the remaining four plots (3, 6,

9, 12) received 500 g/m^2 of the same organic matter. The rice straw was reduced to particles of about 1 mm diameter (by grinding) before application. Rice was planted on the entire field, including all 12 test plots, by aerial broadcasting of seeds on May 10. Plants and roots were removed from plots 1, 2, and 3 on June 13 and from plots 7, 8 and 9 on June 19. Figure 1 illustrates the configuration of the 12 test plots. Although the individual test plots were only 1 m^2, there was no evidence of interactions between plots. For example, the lines of demarkation between plots with and without added nitrogen fertilizer were quite sharp, as can be seen in Plate 1a. Before the field was flooded we placed a wooden pier alongside the test plots (see Plate 1) to allow access to each of the 12 plots without causing excessive pressure or disturbance to the soil, water or plants.

We measured the methane fluxes from the 12 plots using cylindrical chambers, or enclosures as shown in Plate 1. Each enclosure was constructed of right-circular cylinder sections that were designed to allow the enclosure height to be altered. As rice plants grew taller, sections were added. The base of each enclosure was a cylindrical section about 15 cm high, cut from large-diameter (30 cm) polyvinyl chloride (PVC) pipe. This base section was planted into the paddy soil and it was supported by three external aluminum rods (see Plate 1) that were forced about 1 m into the soil on the outer perimeter of the enclosure

TABLE 2. Field Treatment dates for the 1985 Experiment in a Commercial Rice Paddy
Near Sacramento, California

Date	Day Number	Event	Notes
April 30	0	preplant fertilization	78 kg N/ha (150 lbs/acre of urea for plots 7-12, zero for plots 1-6)
April 30		organic matter added to 8 of 12 plots	
May 3	3	field flooded	
May 10	10	rice planted	seeds broadcast by airplane
June 13	44	plants removed from plots 1, 2, 3	
June 19	50	plants removed from plots 7, 8, 9	
September 9	132	field drained	
October 4	157	rice harvested	

During the previous summer (1984) the field was planted to rice and at the end of the season after harvest the residual straw and stubble were burned. Soil type was Sacramento Clay; see text.

base. Sampling ports were fed into these base sections; inside each section, copper sampling tubes (1/8 inch) rose to about 30 cm above water level. Gas samples were withdrawn by external teflon lines (1/8 inch joined to the internal tubes through a connector mounted on each base section. The inner edge of each PVC base section was machined so that a cylindrical section of polycarbonate (inner diameter about 29.5 cm, height about 35 cm) would fit tightly into the base. Successive sections were added to extend the enclosure
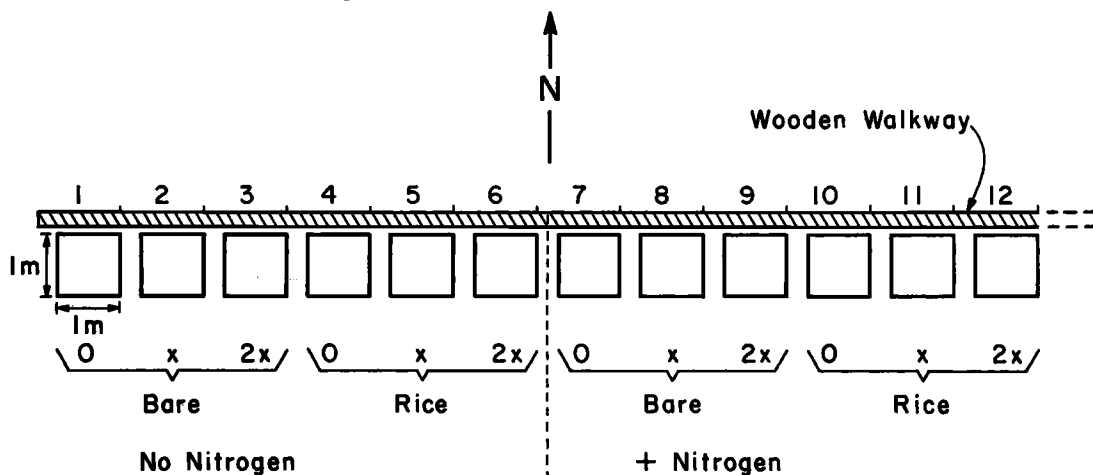

Fig. 1. Diagram of the 12 test plots used in the 1985 rice paddy experiment. The test area was within a commercial rice field near Sacramento, California. Each test plot was about 1 m^2. Treatments are shown in the diagram and are discussed further in the text. The labels 2x, x, and 0 indicate amounts of added organic matter 500 g/m^2, 250 g/m^2, and zero, respectively. Circles in the center of each plot represent cylindrical chambers. Designated plot numbers appear above the walkway near each plot.
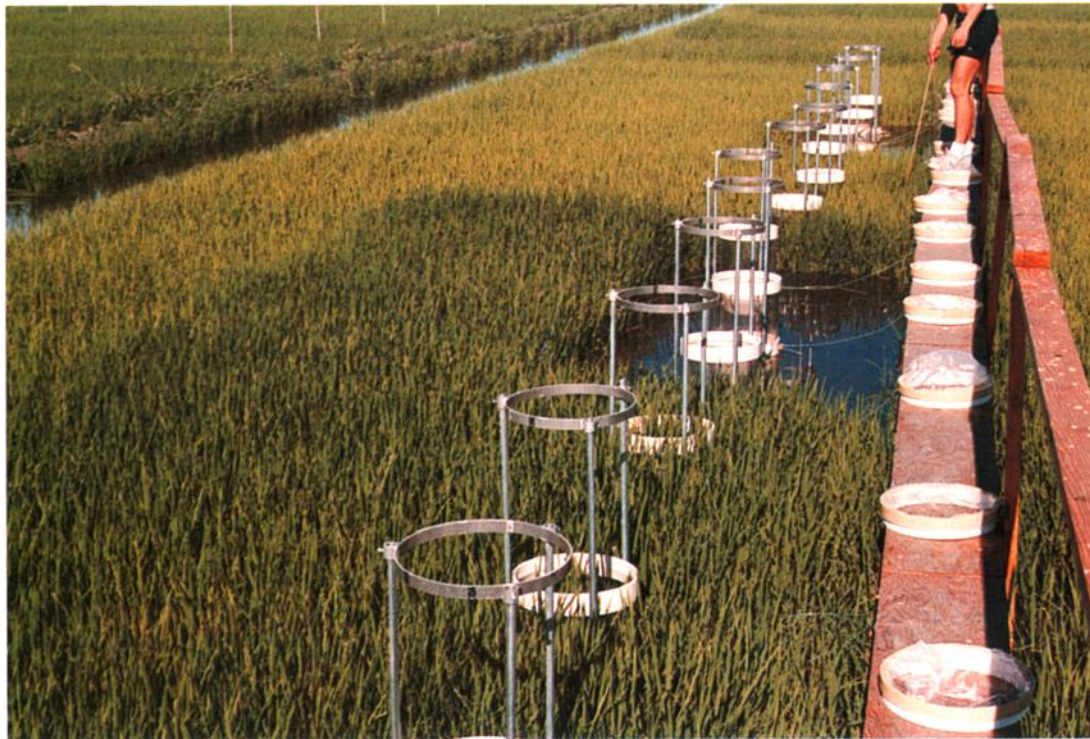
Plate 1. Photographs of the 12 test plots with differing treatments in the 1985 experiment in a commercial rice field at Knights Landing near Sacramento, California. (a) Treatments 7-12 appear greener due to added nitrogen (see Figure 1), (b) an individual chamber's framework in place.

height as needed, by placing PVC collars (about 10 cm high) on the top of each polycarbonate section, and then fitting the next polycarbonate section into the top of the connecting collar. In this way, most of the enclosure was transparent (to visible and ultraviolet light) and the enclosure height could be changed as needed with minimal disturbance to the plants and the underlying soil. At times of sampling the top of each enclosure was closed by fitting a final PVC circular rim down into the top PVC collar. The PVC rim was covered by a collapsible transparent Teflon membrane. In this way, gaseous samples could be withdrawn through the sampling ports without decreasing the total pressure inside the enclosure. Sample extraction (see below) simply caused the membrane top to collapse in proportion to the volume of gas extracted. The enclosure assembly and aluminum support rods were placed in the 12 test plots on June 12, 1985, and were first used one day later. On three separate dates in May 1985, before permanent enclosures were in place, we deployed floating enclosures.

Air samples were extracted from the collectors as a function of time elapsed after closing the collector by placing the top section. The rate of change of methane concentration was determined by subtracting ambient methane concentrations from the concentrations in these samples. Typically, the collection period was 10 or 15 min and samples were taken from the collectors only at the end of the period, although on occasion periods as long as 26 min were used and samples were taken at intervals to observe whether the methane buildup was linear with time. Samples were extracted using either 30 cm^3 plastic syringes or evacuated stainless steel flasks of approximately 500 cm^3 volume. In the case of syringe extraction, needles were fitted to the syringes, the needle points were inserted through a septum (encased in a fitting at the end of each teflon sampling line), the contents of the lines were pre-flushed by extracting one syringe full of air (30 cm^3), and then the actual sample was withdrawn for analysis. Flask samples were pulled through the sampling lines through quick-connect fittings. Background air outside the collectors was collected at rice-top height either by syringe, flask or both just before collector tops were emplaced. Methane concentrations in background air varied from 1.64 to 2.74 parts per million (ppm).

Two gas chromatographic (GC) analysis systems were used. One was operated portably in the field about 30 m from the test plots; syringe-gathered samples were analyzed immediately (within 1 hour) with the field GC. The second GC was in a laboratory at the University of California, Davis. Flask samples were analyzed with this GC which employed an evacuated inlet system. Both GC units were A.I.D. Inc. Model 511 with flame-ionization detectors. Separation was performed with a chromatographic column of carbosieve and length = five feet. Methane peaks were quite sharp and well-separated from other eluents; typical retention time for methane was 2.4 min and total run time was about 4 minutes per sample. Sample-loop sizes were 3 cm^3 for both GCs, and signals were displayed and processed by recording integrators (Hewlett-Packard Model 3390). Ultrapure nitrogen was used as a carrier gas; flame gases (hydrogen and oxygen) were prepurified by passing through molecular sieve traps.

Methane concentrations in whole-air samples (includes water vapor) were determined by peak areas ratioed to peak areas obtained from analysis of pressurized reference standards. Standards were prepared at four concentrations: 1.71, 3.9, 23 and 72 ppm by volume. These reference standards were stored at high pressures in stainless steel flasks. Methane concentrations in each flask were compared against reference standards supplied by the National Bureau of Standards and GC responses were essentially linear over the concentration range of the standards.

Methane emission fluxes F were calculated from the measured concentrations inside the collectors as follows:

$$F = M(T) \ [V/A] \ [\Delta f \ / \ \Delta t], \qquad (1)$$

where V is the above water volume of the collector, A is its cross-sectional area, Δf is the increase in molefraction of methane observed in Δt units of time, and

$$M(T) = 298 \ [M_o \ / \ (273 + T)] \qquad (2)$$

and T is temperature in degrees celsius. M_o is Lochschmidt's number, 2.69×10^{19} molecules/cm^3. As described above, initial methane concentrations were measured and were used to compute Δf values.

Supporting data were gathered during each sampling period on temperatures of air (inside and outside the enclosures), of water, and of soil. In addition, the heights of the rice plants were recorded along with surface wind direction and estimated speed and indicators of cloudiness or lack of. Visual scans were made for presence of bubbles rising from the soil surface upward through the water column. Water depth was also measured, and the lowest rim of each collector system was adjusted (if necessary) to remain below water.

On two dates, enclosure samples were collected for stable carbon isotope analysis of the methane. On June 27, 1985, samples were collected from each of the organic matter plots which had been treated with 500 g/m^2 of rice straw (plot numbers 3, 6, 9, and 12). The samples were obtained by withdrawing headspace air

from the chambers into the evacuated cylinders after an enclosure time of 13 min. One additional sample was collected from plot 6 on September 6, 1985. This sample was collected from the enclosure using a 7.61-L stainless steel cylinder and metal bellows pump. Three 30-min enclosures of the rice plot were combined to obtain enough methane for sample analysis. Each time, about 7.61 L atm of headspace air were collected, the latter two collections being made using the pumping system. Between each enclosure time period, the rice was uncovered for a period of 40 min.

Samples for stable carbon isotope analysis were measured using gas chromatography techniques described in this paper. They were then prepared for mass spectrometer analysis. The procedure for methane combustion and subsequent measurement on a Nuclide 6-60 isotope ratio mass spectrometer are described in detail by Tyler [1986].

3. RESULTS AND DISCUSSION

3.1. The 1983 Experiment

Figure 2 displays methane fluxes measured during the 1983 experiment; daily averages are shown for the period July 9 through October 27, 1983. Vertical error bars extend above and below most of the data points from early September through early October to illustrate how much variation was observed in the measurements. Measurements were made once per week during July and August, 1983 (although on each day two distinct measurements were made with paired chambers) and more frequently in September and early October. Altogether there were 86 observations in the

111-day period from July 9 - October 27. Most measurements were made between 1100 and 1300 LT, but during September other times were sampled, including various times of night from dusk to dawn.

Between September 5 and 9, 1983, a period of relatively large methane emissions, we performed 13 daytime measurements and 10 measurements in darkness. The means (and standard deviations) of the 13 daytime and 10 nighttime fluxes were 0.152 (0.14) and 0.108 (0.03) g CH_4/m^2d, respectively. Although these results could indicate larger daytime fluxes than at night, the large standard deviation of the daytime fluxes renders the difference statistically insignificant. Of the 13 daytime fluxes, there were two that were much larger than average, about two standard deviations above the mean; these values were 0.41 and 0.49 g CH_4/m^2d at 1020 and 1650 local time on September 7, 1983. Such fluxes that are abnormally large compared to the daily averages of the period have been observed previously and they probably are due to sporadic bubbles rising through the water into the air of the collection chamber [Cicerone and Shetter, 1981; Holzapfel-Pschorn and Seiler, 1986]. When present, bubbles also cause larger variability in the data. Although we did not sight bubbles visually in the period September 5-9, 1983, the fact that the standard deviation of the daytime fluxes was about 4 times as large as the nighttime value suggests that bubbles were present at times during sunlight even if they were not easily seen. If we remove the two largest daytime fluxes from this data group, then the means (and standard deviations) become 0.095 (0.03) and 0.108 (0.03) g CH_4/m^2d for day and night, respectively. These values indicate no significant differences from
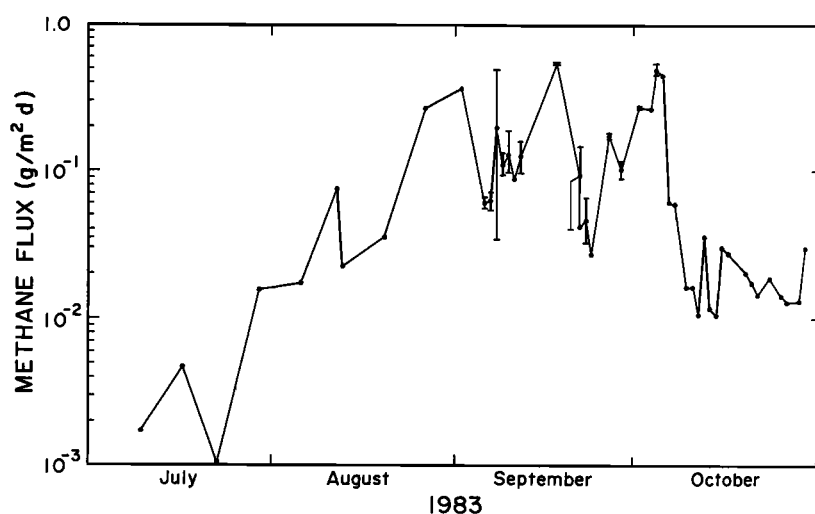
Fig. 2. Graph of daily average of measured methane emission during the 1983 growing season. See text and Table 1 for location and details of soil treatment. Most data points from early September through early October show range of daily measurements with vertical error bars.

day to night in either the mean fluxes or the variability of the fluxes during this period of about 4 days. During this period, rice-plant heights were between 58 and 72 cm so that the underlying soil was rather well shaded. Soil temperatures (at 5-to 10-cm depth) varied between lows of 17o C (late night and early morning) and highs of 22o to 24o C in late afternoon. In any case, the point of these tests was not to investigate the mechanism underlying any diurnal variations but instead to estimate how the computed total flux over the growing season might be affected by the times of day of the individual observations.

The total amount of methane emitted during the period from July 9 until October 27, 1983 computed from the daily averages shown in Figure 2 was 10.8 g CH_4/m^2; it is considerably less than the values of about 25 g CH_4/m^2 found in 1982 in an adjacent research plot [Cicerone et al., 1983]. As described above, we have not accounted for any unobserved day/night differences in our experiment. If fluxes were actually lower on average at night then our seasonal total value, 10.8 g CH_4/m^2, is an overestimate because most measurements were made in daylight hours.

Even with the relatively low time resolution of the measurements in the 1983 experiment, three distinct peaks of methane emission can be seen in Figure 2 in late August, mid-September, and early October. The rise of emissions in early August is real, but the apparent peak around August 10 is defined by only one day's data.

3.2. The 1985 Experiment

3.2.1. Summary data for the 12 plots.
In this study we made 1354 individual measurements of methane emissions. Summary curves giving the average values for emission (milligrams $CH_4 m^{-2} d^{-1}$) are given in Figure 3. These show the results of different treatments as indicated as well as the seasonal trends and variability noted. Some of the variability can be accounted for by bubbles of gas, particularly on sites where the vegetation had been removed. The presence and the effects of bubbles were apparent from both visual observations and by occasional changes of slopes in (1) that were determined by sequential collections. This kind of behavior, especially for unvegetated plots, has been reported by Holzapfel-Pschorn and Seiler [1986]. Where rice plants were present there was some release of bubbles, particularly before tillering was extensive, but the major transport and release was probably by the vascular system of the plants.

Methane production was not appreciable until oxygen became limited, about 30 days after planting depending upon the amount of organic matter present. Undoubtedly, a considerable fraction of added organic matter had been oxidized by this time. However, when methane production did become significant, it rose rapidly to a maximum value at about day 50 and then declined exponentially through the season, the timing of peak emission and the decay constant depending upon the treatment.

The influence of added organic matter, nitrogen fertilizer, and the presence or absence of vegetation can be discerned from Figure 3 and is discussed in greater detail below.

3.2.2. The influence of added organic matter.
Added organic matter was the single most important factor influencing methane production in this system. Most of the readily decomposed organic material from the previous year had been oxidized prior to planting. Figure 4 compares the mean values for treatments 1, 4, 7 and 10 (no added OM) with those for treatments 3, 6, 9, and 12 (500 g/m² or 5 metric tons/ha ground rice straw). Those plots to which 500 g/m² of organic matter had been added had about a 20-fold greater methane emission (presumably due to proportionately larger methane production rates) than did the control plots. Where there was this larger methane production, it showed a steep rise at about 30 days, reaching a maximum about 50 days after flooding and then a decline with the rate influenced by the amount of nitrogen fertilizer applied (see below).

For ease of comparison, the same scale was used for all 12 treatments in Figures 3 and 4. This leaves the impression that no methane was emitted from those plots to which no organic matter was added. When the data from plots with no added organic matter are shown on expanded ordinates (Figure 5), the same general pattern of methane emission as in the added organic matter treatments is revealed. Without vegetation to serve as a conduit for methane more variability is seen (Figure 5a, 5c), probably due to sporadic bubble release. The seasonal yield of the four plots without added organic matter was about 5% of the methane released from the four plots with 500 g/m² of added organic matter (see also Table 3).

By the end of 125 days, methane emission had dropped off to generally low values for all plots and draining of the field preparatory to harvest was begun. When the soil surface had begun to show dry spots and some cracking in the clay, there was an increased release of methane; on day number 136, some plots showed high values comparable with the peak production earlier in the season. This probably represented a physical release of trapped methane and contributed significantly to the season total. Because of the random nature of cracking and timing of the peak release, it also contributed to variability in the data. When linear interpolation is made between data points, including those of this pulse at the end of the crop season, it is possible to make an estimate of the total seasonal methane release.
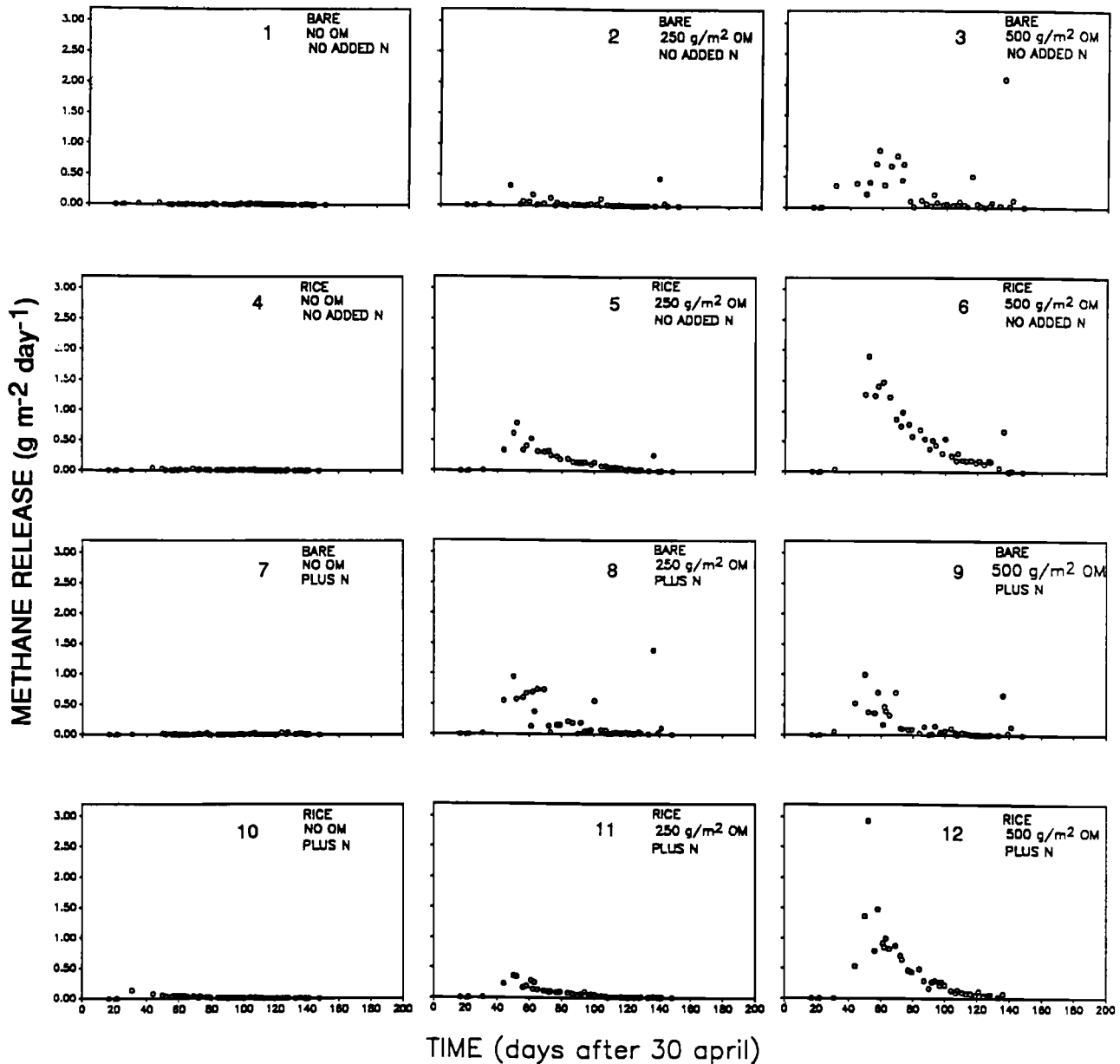
Fig. 3. Daily average of methane emissions measured versus time in 1985 growing season from each of the 12 treatments (see Table 2 and Figure 1). Only one peak period of methane emission was observed, near day 60, or 50 days after planting.

3.2.3. The influence of nitrogen fertilizer. The addition of nitrogen resulted in a visibly enhanced plant growth as is evident in Plate 1 and appeared to accelerate organic decomposition as would be expected. This is particularly evident from the data shown in Figures 6a and 6b. The near absence of methane emissions in the latter half of the 1985 growing season allowed us to examine the rate of decay of the early season peak. Figure 6a shows data from the eight of our 12 plots that received added organic material, plots number 2, 3, 5, 6, 8, 9, 11, and 12. The risetime of this peak was about ten days, both for the plots with added N and the plots without added N, but the decay rates of the methane emission were different, as shown in Figure 6b. Methane emissions from plots with added N, plot numbers 11 and 12, decreased faster between days 50 and 120 than did the emissions from plots without added N, plot numbers 5 and 6. (For Figure
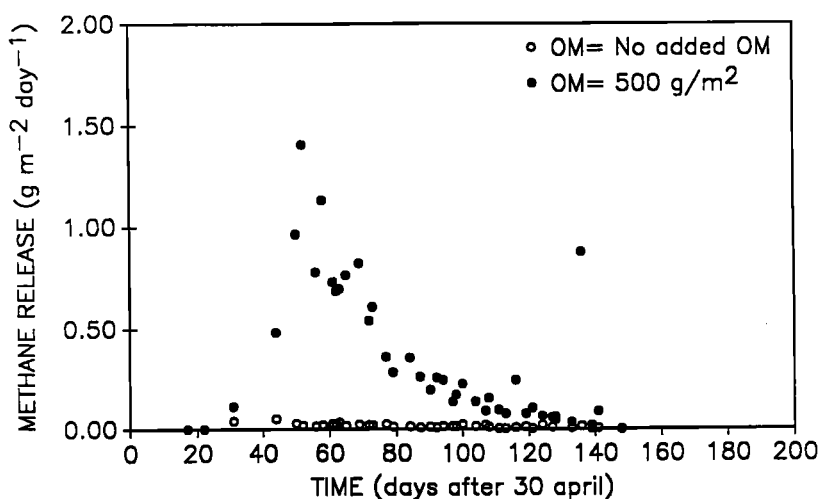
Fig. 4. Same as Figure 3 except that the data for all the eight plots with added organic matter (treatments 2, 3, 5, 6, 8, 9, 11, and 12; see Figure 1) have been grouped together and data for all the treatments with no added organic matter (treatments 1, 4, 7, 10) have been grouped together.

6b we used only data from vegetated plots because the added variability from unvegetated plots led to less good curve fits.) This may have been due to faster consumption of available organic matter by methanogenic bacteria when N was less limiting. Interpretation of these data is clouded by the probability that added nitrogen also accelerated organic decay in the first part of the season before plant growth and other oxygen demand had depleted oxygen supply. Under the highly reducing conditions of methane formation the fixation of nitrogen by autotrophic methanogens as well as other organisms can help provide a nitrogen source, but the energy requirement for splitting the dinitrogen bond still must be met and places limitations on the system. Because the study was conducted with the cooperation and support of a commercial grower and because other logistic and work force limitations prevented large enough treatment areas to get statistically significant data on yield, we were not able to make reliable comparisons of methane production or other variables relative to yield.

3.2.4. The role of vegetation. The vegetation factor did not appear to have any large effect on the timing and quantity of methane release which were determined mainly by the quantity of added organic matter. Vegetation did affect the manner of methane release, however. Where rice was present it probobably served as the main means by which methane produced in the soil was conveyed to the atmosphere, whereas on those plots from which vegetation had been removed, methane release was largely by bubbles with some direct diffusion into the water. Probably because of this release in bubbles, the variability observed from one sampling to another was

greater on the unvegetated areas than on those with rice. Plants provide a more continuous transport of methane through their vascular systems. When plants of vegetated areas were removed by cutting, methane could be collected directly from the stubble of individual plants.

It is almost certain that there was some destruction of methane by its autotrophic oxidation once it reached aerobic environments. We did not make any evaluation of how significant this factor was in the total system, and we report here only the net methane emissions to the atmosphere. It would not be surprising if 50% or more of all the methane produced in the soil were oxidized before escape to the atmosphere [Holzapfel-Pschorn et al., 1985; Sass et al., 1990].

3.2.5. Diurnal periodicity of methane emissions. Some periodicity in methane production has been reported by others including Seiler et al. [1984], Holzapfel-Pschorn and Seiler [1986], Schütz et al. [1989], Yagi and Minami [1990] and Khalil and Rasmussen [1991]. Generally, largest methane emissions have been seen in the late afternoon hours and smallest emissions in the last hours of darkness and the earliest hours of sunlight. Holzapfel-Pschorn and Seiler [1986] observed variations as large as a factor of 40 (highest in late afternoon) while Schütz et al. [1989] observed large variations, up to a factor of 5, early in the season, diminishing to 50% or less as vegetation matured, possibly due to more shading of soils by the plants and hence lower maximum daytime soil temperatures. Yagi and Minami [1990] and Khalil and Rasmussen [1991] found variations of about 15% to 20%. Most of these studies have demonstrated a strong correlation between methane release rate and the
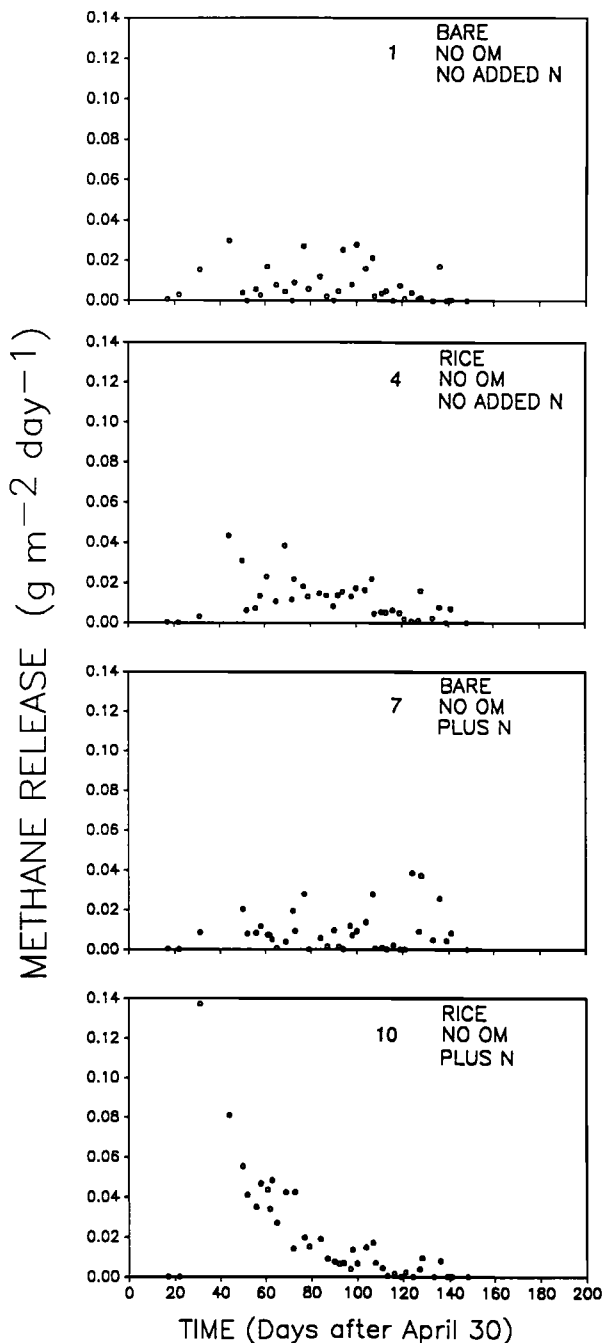
Fig. 5. Data from Figure 3 but regraphed on a different vertical scale to show small nonzero emissions from the plots that received no added organic matter, plots 1,4,7, and 10.
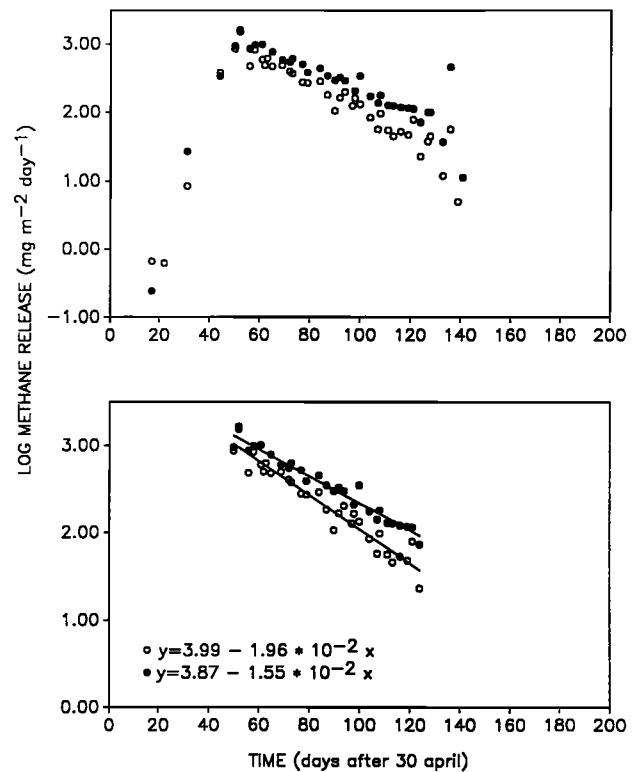

Fig. 6. Daily averaged methane emissions versus time after April 30, 1985. (a) The period from days 17-150; all plots with added organic matter; (open circles) treatments with extra N (solid circles) treatments without extra N. (b) Same as Figure 6a but for days No. 50-120 and for vegetated plots only.

diurnal temperature changes at soil depths of about 5 cm.

We examined this question within the logistic limitations of the study. During that part of the season when methane emissions were largest we found a periodicity with peak emission in early afternoon and minimum in the early morning. No strong pattern was observed once the crop canopy was closed, and temperature fluctuations in the soil were less. Figure 7 gives mean values for all samples from vegetated areas for days 50 through 65 using 3 hour bins. It is apparent that daylight hours show a stronger activity; the daytime peak is as much as 70% larger than the nighttime minimum, at least for this time period (no other time period showed such clear variations in this experiment). It is assumed that this is largely a positive temperature effect in methanogenesis. Because release is presumably largely through the vegetation, stomatal opening may be a factor. Diurnal variations could also be influenced by diurnal changes in methane oxidation rates.

3.2.6. Seasonal totals of methane emission. Because sample collection was at irregular times and intervals as dictated by logistic factors, it was necessary to normalize observed values for methane production according to collection time in order to estimate integrated production through the season. For
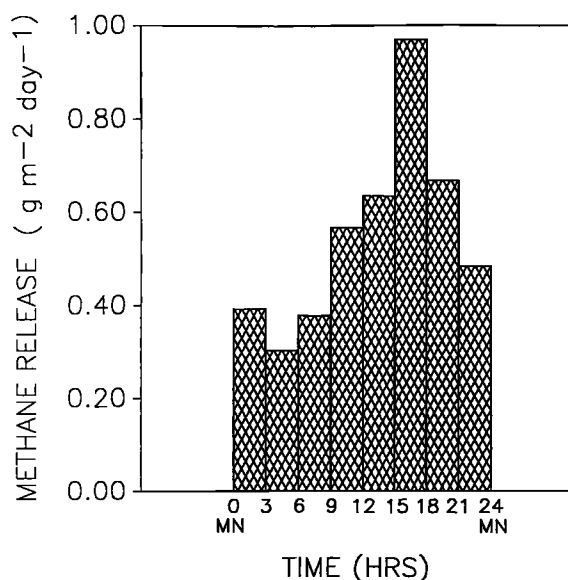
Fig. 7. Methane emissions in 3-hour time periods from days 50 through 65 after April 30, 1985. Daylight hours (local times) show largest emissions. No other period during the growing season showed such clear diurnal variations.

this purpose the data for days 50 through 65 given in Figure 7 were used to calculate normalization factors. Table 3 gives calculated season totals for methane for the various treatments. The variability in recovery of added organic matter as methane is evident and an expression of the difficulty inherent in measurements of this sort. The low recovery of carbon as methane in treatments 2, 9, and 11 when compared with the remaining treatments is not easily explained. Variability in soil and vegetation as well as the difficulty experienced in getting uniform distribution of

added organic matter and the random effect of bubbles all undoubtedly contribute to this inconsistency.

Mean recovery of carbon as methane amounted to 15.6% of that applied for plots receiving 500 g of rice straw per meter square at the beginning of the season. For those plots receiving 250 g straw per meter square the recovery was 12.0%. Variability was sufficiently large that no significance is attached to this difference, although it is consistent with the expected influence of added organic matter. When all treatments are considered, the overall recovery of added carbon in methane was 14.4%.

3.2.7. $\delta^{13}CH_4$ in the 1985 experiment. Data for the stable carbon isotope measurements of the rice paddy field methane emissions are shown in Table 4. The average $\delta^{13}CH_4$ value for the methane emitted on June 27 was -55.7 ± 1.7 ‰ (1σ). At this time of the season, 48 days after flooding, the eight plots with rice straw treatment were at or near the maximum flux observed during the entire experiment, with the 500 g/m2 treatment fluxes generally higher than the 250 g/m² treatment. The $\delta^{13}CH_4$ of one sampling on September 6, 1985, was -62.7 ‰. This sample was taken just 3 days before draining the field and 28 days before harvest.

Because relatively large quantities of sample are needed for isotopic measurements, the rapid drop off in methane flux soon after the end of June prevented us from obtaining systematic collections of methane for isotopic analysis throughout the growing season. However, the difference between the earlier June values and later September value is well outside the uncertainty of measurement. It might indicate a difference between the pathways of methane production and/or consumption during the growing season. This seems quite plausible, although with few exceptions the idea has not been tested in other published data sets.

TABLE 3. Estimated Carbon Recovery as Methane

Plot Number	Treatment	Rice Straw Added g/m2	Total Methane g/m²	Percent Carbon Recovered as CH₄
1	-N, bare	none	1.19	--
2	-N, bare	250	6.26	4.3
3	-N, bare	500	30.1	12.4
4	-N, rice	none	1.40	--
5	-N, rice	250	19.62	15.8
6	-N, rice	500	58.18	24.3
7	+N, bare	none	1.18	--
8	+N, bare	250	27.8	22.8
9	+N, bare	500	20.8	8.42
10	+N, rice	none	2.88	--
11	+N, rice	250	9.10	5.33
12	+N, rice	500	42.8	17.1

TABLE 4. $\delta^{13}CH_4$ Values for Rice Paddy Methane at Knight's Landing
Near Sacramento, California, 1985

Rice Plot Description	CH_4 in Sample	$\delta^{13}CH_4$
June 27, 1985, plot 3, 500 g/m² OM, no nitrogen	80.5 ppmv	-55.0‰
June 27, 1985, plot 6, 500 g/m² OM, no nitrogen	135.9 ppmv	-55.2‰
June 27, 1985, plot 9, 500 g/m² OM, with nitrogen	79.0 ppmv	-54.2‰
June 27, 1985, plot 12, 500 g/m² OM, with nitrogen	94.7 ppmv	-58.5‰
Sept. 6, 1985, plot 12, 500 g/m² OM, with nitrogen (three 30-min enclosures combined)	6.0 ppmv	-62.7‰

A few other measurements of $\delta^{13}CH_4$ from emitted methane in rice paddies have been reported. Stevens and Engelkemeir [1988] measured rice paddy emissions from the Sacramento, California region in August 1981 (3 weeks before harvest) and found $\delta^{13}CH_4 = -67.2 \pm 0.9$ ‰ for four samples. Wahlen et al. (1989) measured rice paddies in Louisiana in May and June 1987 and found $\delta^{13}CH_4 = -63.2 \pm 2.9$ ‰ for 8 samples.

Very little work has been done in the area of seasonal isotopic studies of CH_4 emitted by rice paddies. Tyler et al. [1988] studied paddy fields in Mwea, Kenya, in 1986 and found a value of $\delta^{13}CH_4 = -59.4 \pm 2.0$ ‰ for 10 samples. These samples were taken over a period of 2 days but were intended to systematically sample rice representing the entire growing season. Dates of sowing, flooding, and harvest of the rice are staggered in Mwea. That practice allowed Tyler and coworkers to sample from five fields representing time periods from 44 to 156 days between sowing and sampling. Little variation was seen in the above fields although flooded fields which were fallow at the time of collection had $\delta^{13}CH_4 = -51.2$ ‰ for two samples.

In another seasonal study, Nakamura et al. [1990] measured carbon isotopes of both CO_2 and CH_4 from soil gases in paddy fields in northeast and central Japan (Konosu, Japan, 1976 to 1980). They investigated four types of fields each of which have undergone a long-term (over 28 years) fertilization experiment (varying treatments) for total inorganic carbon and related organic carbons. However, they report only a single $\delta^{13}CH_4$ value of -55.1‰ for samples taken over the entire time period. This was for methane bubbles from submerged soil in the field receiving chemical fertilizer. They also report a value of -52.9 ± 5.1‰ for samples taken from incubation studies in the organic mature plot over a 6-week time period. This relatively large standard deviation could be due to changes in methane production and/or consumption, but the data as presented are not sufficient to draw conclusions about the seasonality of $\delta^{13}CH_4$ emissions from the paddy fields.

4. FURTHER DISCUSSION AND CONCLUSION

A major goal of this research and of many other investigators is to estimate the total annual emission of methane from the world's rice paddies. It has become apparent [e.g. Holzapfel-Pschorn and Seiler, 1986] that it is no easy task to accurately measure the total amount emitted even by a single field over a full growing season; this is because of variations with time of day, time of season, soil treatments, and several other factors. Before accurate estimates of total annual emissions can be derived we must observe how methane emissions vary and determine the factors that control these variations. Now we discuss the patterns that were observed in this study and how they depended on experimental variables.

The seasonal variations that we observed in 1985, Figures 3, 4, and 5, were unanticipated. In almost all of the 12 plots methane emissions displayed a single maximum on or before day 50 (measured from April 30), or 40 days after planting (see Table 2). The absence of middle and late season emissions (except for day 136 when the soils were dry with large cracks) was not a feature of our earlier seasonal studies in 1982 [Cicerone et al. 1983] or in 1983 (see Figure 2) nor was this kind of pattern observed by Seiler et al. [1984], Holzapfel-Pschorn and Seiler [1986], Schütz et al. [1989], Yagi and Minami [1990], Sass et al. [1990] or Khalil et al. [1991].

From measurements over 3 consecutive growing seasons in Italy, Schütz et al. discerned three times when large emissions were observed. The first maximum occurred in late May or early June in two of the three years; Schütz et al. proposed that this early methane flux is due to decomposition of soil organic matter that was in the soil prior to the flooding, such as crop stubble from the previous year. The second maximum discussed by Schütz et al. occurred in July; it was also seen by Seiler et al. [1984] in Spain and by Cicerone et al. [1983] in California. This maximum may be due to the action of methanogenic soil bacteria

on organic material released by rice roots as root exudates. The third seasonal peak discerned by Schütz et al. occurred in August in two of the three years in Italy but not in the third. An extremely large late-season peak was observed by Cicerone et al. [1983] in September in California in 1982 and major peaks were seen by Seiler et al. [1984] in late August in Spain and by Yagi and Minami in early September in Japan. Schütz et al. suggested that this late peak may be due to microbial decomposition of rice roots.

It is important to learn whether there are three or more distinct peaks to be seen at each site and the causes for them. In our 1985 studies, only the first peak appeared. Why were the second and third peaks suppressed? The answers could be both low methane production rates at those times and high methane oxidation rates. These processes were not studied in our experiments. In any case, the strong relationship between methane emissions and above ground biomass that was observed by Sass et al. [1990] in one of two Texas fields through most of a growing season did not obtain in our 1985 experiments. Other factors such as water management practices and fertilizer applications can also cause variations in methane emissions during the growing season [Yagi and Minami, 1990], as can cultivar sensitivity to soil anaerobiosis (and hence to added organic matter) [Sass et al., 1991].

The dominant variable that controlled methane emissions in our 1985 experiments was the amount of added organic matter, as can be seen from Figures 3 and 4 and Table 3. The total methane emitted over the entire growing season from the four plots that received no added organic matter was 1.7 g/m^2 (average over four plots); the range was 1.2 to 2.9 g/m^2. For the four plots that received 250 g/m^2 of organic matter the average total methane emission was 15.7 g/m^2, and the range was 6.3 to 27.8 g/m^2. The four plots that received the largest application of organic matter, 500 g/m^2, emitted 38.0 g CH_4/m^2 on average; values ranged from 20.8 to 58.2 g/m^2. These total methane emissions were calculated by integrating over the period of the observations, May 17 through October 3 (days 17 through 148) using the diurnal temporal dependence described in the previous section and Figure 7 to normalize observations from different times of day.

The strong influence of organic matter additions over methane emissions has also been observed by Schütz et al. [1989], Yagi and Minami [1990], and Sass et al. [1991]. Schütz et al. found that emission rates of methane increased with increasing quantities of incorporated rice straw and reached maximum values at an application rate of 12 tonnes/hectare (t/ha). At this maximum, methane emissions were about 2.4 times higher than from an untreated control plot. In our 1985 experiments the enhancement was almost 10-fold (1.7 g/m^2 to 15.7 g/m^2) between untreated control plots

and those treated with 250 g/m^2 (2.5 t/ha) organic matter. At 5 t/ha application rate our emissions were enhanced by about another factor of 2 over the 2.5 t/ha case, 38 g CH_4/m^2 compared to 15.7 g/m^2. Yagi and Minami [1990] used application rates of between 6 and 9 t/ha, and they found enhancements of methane emissions of 1.8 to 3.5 times. Sass et al. [1991] found that methane emissions were enhanced by 2 to 3 times and rice yields decreased when 8 to 12 t/ha of rice straw were applied to test plots.

The total amount of methane emitted over the entire growing season in our 1985 experiments was extremely small except for the plots to which organic matter was added. Values of only 2 g CH_4/m^2 are much smaller than most other published totals except for values of 0.6, 1.1, 3.6, and 4.1 g/m^2 from several plots studied by Yagi and Minami [1990] in Japan. Most other annual emission totals fall in the range 10-55 g CH_4/m^2 [Cicerone et al., 1983; Seiler et al., 1984; Holzapfel and Seiler, 1986; Schütz et al., 1989; Yagi and Minami, 1990; Sass et al., 1990]. Our 1983 experiment yielded a total emission of 10.7 g CH_4/m^2, at the extreme low end of the 10 to 55 g range. The largest total emission for entire growing seasons have been reported by Khalil et al. [1991]; they observed emissions of about 60 mg $CH_4/m^2/h$ or 1.4 g $CH_4/m^2/day$ averaged over two growing seasons, or annual totals of about 160 g CH_4/m^2. These extremely high values may have been due to treating the soils with fermented sludge.

The array of environmental, microbiological, and agricultural factors that control methane fluxes from rice paddies into the atmosphere is quite large and complex. First, future efforts to minimize these emissions must be firmly based on mechanistic understanding of the controlling factors. Second, they must recognize the goals and needs of rice growers. In our 1985 study [and those of Schütz et al. [1989], Yagi and Minami [1990], and Sass et al. [1990], added organic matter was the principal contributor to methane production and escape. The crop residue had been burned the previous year, and ample time had passed for the oxidation of remaining readily decomposable organic material to be oxidized in the disked field before the flooding and planting in 1985. The decline of methane fluxes that we observed through the growing season (except for the terminal burst when the field was drained) was very different from our observations of 1982 and 1983, and it has not appeared in other studies; generally, methane fluxes have been observed to increase through the season. Many factors could have combined to cause this seasonal behavior in 1985, including past history of the field, soil texture and water penetration rates. More complete studies of methane production, oxidation and escape rates will be needed along with manipulation of soil, plant, and

water variables to understand how seasonal patterns unfold. Stable isotopes of carbon and hydrogen should be measured in the methane in soil, water and air as functions of time throughout the growing season; these isotopes could provide evidence of shifting pathways of methanogenesis and of methane oxidation. In addition, such data are needed before isotope-weighted methane flux budgets can be constructed.

Given the clear methane-emission consequences of adding organic matter to rice-paddy soils, a final word about the practice of burning crop stubble is indicated. In California (and elsewhere) it is common practice to dispose of postharvest field residues of straw and stubble by burning, but this practice is coming under increasing criticism because of air pollution problems in surrounding regions. Rice growers express other concerns such as the control of fungal diseases and other problems of sequential cropping, concerns that would be amplified if burning were to be prohibited. Further, if the organic residues are disked into the soil instead of being burned, their decomposition represents a potential source of methane, subject to the uncertainties of rainfall and temperature. Each mole of methane emitted into the atmosphere exerts a greenhouse radiative forcing that is about 5 times that due to a mole of carbon dioxide [Dickinson and Cicerone, 1986; Lashof and Ahuja, 1990; Rodhe, 1990], so burning the residues could reduce the greenhouse radiative forcing due to rice agriculture. Before deciding on such a course, however, each of these factors deserves some attention along with the effects of NO_x and CO emitted by burning.

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