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FACTORS AFFECTING METHANE PRODUCTION UNDER RICE

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    To understand why atmospheric methane is increasing worldwide, accurate estimates are needed of the global input from rice fields. We report greenhouse and laboratory studies over three growing seasons to isolate and control factors that might affect methane emission from rice paddies, including soil texture, added exogenous organic matter (OM), nitrogen and sulfate ion, and water management. Without added OM, methane production was relatively low, increasing during the growing season, and continuing after harvest, provided the soil remained water-logged. If ground rice straw was added to the soil prior to planting, methane production began shortly after flooding, with an initial burst of the gas after 3 to 5 weeks, and then a gradual increase to a second peak later in the season (and after harvest), with rates considerably higher than in treatments without added OM. The initial methane burst was largest when the rice straw was added near the surface. We conclude that exogenous OM is the major contributor to methane production, with at least two distinct reaction patterns involved. Emitted methane accounted for 5% or more of the added organic carbon. Methane emissions were from 3 to 12 times higher with added OM than from identical soils without such additions with largest emissions when OM is added deeper in the soil. Methane release as bubbles was common (the main source in the absence of vegetation), but the plant normally was the main conduit for gas transfer to the atmosphere. Addition of sulfate ion (gypsum) to the soil resulted in a slight competitive suppression of methane production.

INTRODUCTION

    To understand why atmospheric methane is increasing worldwide, accurate estimates are needed of the global input from rice fields. Methane production in water-logged soils and other anoxic environments has long been recognized [Yamane and Sato, 1963; Koyama, 1963; Ehhalt, 1974; Zehnder, 1978]. In recent years it has become the subject of extensive studies, prompted by the realization of a steady rise in the level of atmospheric methane [Blake and Rowland, 1988] and concern over the significance of this increase to global heat exchange processes [Lacis et al., 1981; Dickinson and Cicerone, 1986].

    Earlier studies by us and others of methane production under field conditions verified the production of this gas as generally characteristic of rice fields, but exceedingly variable, both during the season, and from one field to another [Cicerone et al., 1983; Neue and Scharpenseel, 1984; Khalil et al., 1991; Cicerone et al., 1992]. Early studies also showed the rice plant itself as a

major conduit of methane from the soil to the atmosphere [Cicerone and Shetter, 1981; Seiler et al., 1984; Nouchi et al., 1990], and established a weak diurnal periodicity of methane release, particularly early in the season [Seiler et al., 1984]. They gave evidence for a correlation of methane production with exogenous sources of organic matter and suggested that under some field conditions, in the absence of added organic matter methane production was low.

In the past decade while large variability has been observed in actual methane emissions from rice fields, the need for better information has intensified, partly due to the realization that methane is a more effective greenhouse gas than carbon dioxide [Ramanathan et al., 1985; Lashof and Ahuja, 1990; Rodhe, 1990] and partly because strategies to limit methane emissions are beginning to be discussed. Reliable global estimates are not yet available; field observations that have recorded total methane emissions over whole growing seasons have revealed values from less than 1.0 to more than 100 g CH_4/m^2 and the temporal patterns within the growing season have also varied greatly [Cicerone et al., 1992; Yagi and Minami, 1990]. Until we can identify the factors that cause large differences in methane emission rates and their temporal patterns within a growing season we will not be able to derive accurate global estimates.

The inconsistencies revealed by these experiments and the differences between our observations and the reports of similar studies elsewhere led us to perform several greenhouse experiments where growth conditions could be manipulated more effectively than was possible in the field, and where specific growth conditions could be provided to assess their influence on methane emission.

INTERSPECIES HYDROGEN TRANSFER
AND THE PRODUCTION OF METHANE

The interpretation of the observed variability and the structuring of our greenhouse studies was guided by present-day concepts of the underlying microbial processes responsible for methane production. We provide here a brief review of these processes and their driving thermodynamic and kinetic principles.

Although microbial methanogenesis has been known at least since 1876, [Hoppe-Seyler, 1876], elucidation of the biochemistry of the process dates from the

1930s [Barker, 1936, 1956; Kluyver et al., 1947]. Most methane-yielding environments are oxygen-depleted and made up of a varied mixture of organic compounds and a mixed microbial flora, with methane resulting from a number of reactions. A number of heterotrophic species produce methane in the degradation of various organic compounds, but these are not all members of the family methanobacteriaceae or others of the methanogenic Archaebacteria. The latter are a diverse group of organisms capable of the autotrophic oxidation of hydrogen with carbon dioxide as electron acceptor, yielding methane, and using the energy of the reaction for the production of cell material [Zeikus, 1977]. Nomenclature of these organisms is in a state of change and probably will continue to be so pending extensive taxonomic work.

The fact that methane in natural systems comes from a variety of heterotrophic and autotrophic sources may explain in part some of the seasonal variability observed under different field conditions [Holzapfel-Pschorn et al., 1985; Holzapfel-Pschorn and Seiler, 1986; Mathews et al., 1991], differing organic substrates, and differing oxidation-reduction potentials [Takai, 1970; Ponnamperuma, 1972; Turner and Patrick, 1968]. Mixed fermentative reactions producing methane and hydrogen are the source of part of the methane, but reactions producing hydrogen generally become limited by the accumulation of hydrogen. Thus the autotrophic removal of hydrogen by the true methane bacteria furthers the heterotrophic reactions and a synergism between the two characterizes the overall process [Wolin, 1982], with the autotrophic reduction of carbon dioxide requiring generally lower oxidation-reduction potentials. This can be illustrated by the examination of the energetics of a few reactions. Although many of these reactions have been studied in detail, revealing the participation of nicotine-adenine dinucleotides, corrinoid compounds and other energy or electron mediating agents, only the overall reactions are given here.

Fermentation of ethanol with the production of acetic acid:

$$C_2H_5OH + H_2O \longrightarrow CH_3COO^- + H^+ + 2 H_2 \quad (1)$$

Delta G^o = 34.47 kilojoules (kJ)
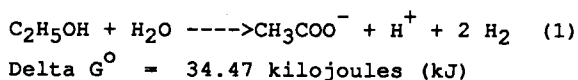
At pH 7 and with other reactants standard, the energy change is -5.31 kJ, still not sufficient to sustain growth. But if the partial pressure of hydrogen is reduced to 10^{-3} atmospheres, the calculated energy yield becomes -39.4 kJ, sufficient to

provide for growth, depending upon the frugality of the electron transfer system and the concentration of acetate ion.

The acetate produced in reaction (1) can then be further broken down to yield methane and carbon dioxide:

$$CH_3COO^- + H^+ \longrightarrow CH_4 + CO_2 \qquad (2)$$

$$Delta\ G^o = -64.1\ kJ$$
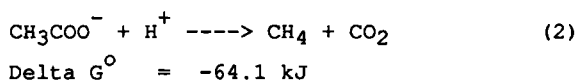
At pH 7 and atmospheric concentration of carbon dioxide (.00034 atmosphere) the energy yield is from -43.9 to -90 kJ depending upon the concentrations of acetate ion and methane. This reaction also will sustain growth for those organisms carrying it out.

The hydrogen from reaction (1) and carbon dioxide from reaction (2), as well as these gases from other sources, can then be utilized by methanogens carrying on the following reaction:

$$CO_2 + 4\ H_2 \longrightarrow CH_4 + 2\ H_2O \qquad (3)$$

$$Delta\ G^o = -126.6\ kJ$$
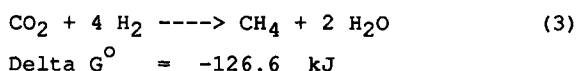
Here again the actual energy yield will vary depending upon concentrations of reactants and products, but the yield is sufficient to support active microbial growth at most commonly expected concentrations (activities). It is of interest but probably not of profound significance that at atmospheric concentrations of hydrogen, methane, and carbon dioxide ($5x10^{-7}$, $1.7x10^6$, and $3.4x10^{-4}$ respectively), the reaction is just about at equilibrium (Delta G = -0.06 kJ).

An examination of these reactions and others involved in microbial methane production provides a mechanistic explanation for some of the puzzling features of the process when it was first given attention by such pioneers as Barker [Barker, 1936, 1956], Kluyver and Schnellen [Kluyver and Schnellen, 1947] and others. In the process that has become known as interspecies hydrogen transfer, hydrogen produced by various fermentative processes such as those of reactions (1) or (2) is then utilized autotrophically by methanogens as in reaction (3), serving to keep the activity of hydrogen gas low enough to permit the reactions producing it to proceed. This synergistic arrangement can result in the processing of large quantities of organic matter and its conversion to methane (and other by-products). Because the energy yield in the individual reactions is low compared with that when oxygen is the electron acceptor, the yield of methane is high for a given quantity of cell material produced.

From these considerations, greenhouse studies were designed to examine the effects of soil texture (as it influenced water and therefore oxygen movement), the addition of organic matter, the presence or absence of sulfate ion as an alternate electron acceptor, and other variables. The time course of methane emission was followed through the growing season and after harvest.

MATERIALS AND METHODS

For greenhouse applications, a standard soil container approximately 36 cm high and 28 cm diameter was used, giving an effective area of approximately 0.06 m^2 (6 x 10^{-6} ha). Containers were painted black to provide opacity and then covered with white paint to limit heating by the absorption of sunlight. Some containers were provided with a drain connected (through a sediment filter) to a peristaltic pump to permit soil solution movement as desired. In some studies an underlayer of expanded silica ("pearlite") was provided to aid in drainage, and in one series of treatments, a completely artificial soil system was used consisting of expanded silica covered with a thin (8 cm) layer of coarse sand to prevent flotation. In these treatments, necessary mineral elements were provided using shelf reagents according to standard water culture procedures [Johnson et al., 1957]. Organic matter when included, was added usually as ground rice straw, but in some treatments other organic sources were used.

As the plants grew, the containers were extended upward, first with polycarbonate cylinders to assure light penetration, and beneath these as the plant height increased, polyvinyl chloride cylinders in the lower sections which gave some shading to simulate as closely as possible the natural field environment. These cylinders made possible a more natural environment of humidity and air movement, at the same time providing opportunity when covered for short periods, for the collection of gas samples.

Rates of addition of nitrogen, organic matter, sulfate ion and other treatments when used, were designed to simulate typical field practice except as noted below, and certain other treatments were clearly artificial, and deliberately so, for the purpose of control. Yields obtained were good, however, and in some cases remarkably high, so that growth conditions could be considered reasonably representative of field conditions. These will be discussed in greater detail in connection with the individual experiments.

For determination of methane production, the cylinders surrounding the plants were covered for from 10 to 30 min. at the selected sampling time, and gas samples were then collected by means of syringes through a septum in the cover of the individual container. Methane was determined with a gas chromatograph using a 3-mm-diameter stainless steel column approximately 1-m-long packed with porous polymer beads at a temperature of 100 C and with N_2 as the carrier gas and a hydrogen flame ionization detector. Samples were compared with standard samples prepared by conventional dilution techniques. Reproducibility of the analyses of standard samples was usually within 2%, and the variability observed in successive samples, as well as that seen on successive days, was usually attributable to emission of bubbles and variability of temperature which was not controlled under the conditions of the study.

RESULTS

1986 (Year 1) Experiment

For this study, four of the eight containers were provided with filters and outlets at the bottom so as to permit different rates of water movement through the soil. Containers were filled with about 18 kg soil (Yolo silty clay). Ground rice straw (30 g) was incorporated throughout the soil layer in half of the containers (see Table 1) giving a rate of approximately 5000 kg ha^{-1} added organic matter. The soil came from a well-drained field that had been fallow the previous year and so had little residual, readily decomposable organic matter. Drainage rates of 0, 300, and 600 ml per day were adjusted initially (representing 0, 0.5, and 1 cm per day respectively), but these were difficult to control and slowly deteriorated as the filters became plugged so that after 80 days all except treatment four had ceased infiltration. Two of the treatments had added gypsum ($CaSO_4.2H_2O$) at the rate of 10 g per container (1670 kg ha^{-1} or 320 kg ha^{-1} S) to observe the influence of added SO_4^{-2} ion as electron acceptor.

On July 9 a top dressing of 10 g urea was applied to each container, soils were flooded and planted with 12 10-day-old rice seedlings per container. This was a rather heavy application rate (about 780 kg N per ha) but there were no further applications through the season. Drainage rates were established for appropriate containers and drainage waters were measured and returned to the containers

daily with water added as required to accommodate evaporated and transpired losses. Methane determinations were then made periodically with the procedures outlined above.

By the twelfth day after planting there was evidence of sulfur deficiency in those treatments to which gypsum had not been added and so top dressing of 10 g $CaSO_4 \cdot 2H_2O$ was made to all containers. Although deficiency symptoms were corrected by this application, the role of sulfate as an electron acceptor was clouded. For treatments 7 and 8, however, the gypsum was mixed into the soil where it could compete with carbon dioxide as electron acceptor, whereas the surface applications were directly available to the plants but not as available to microbial action in deeper zones except as transported by infiltrating water. Yields of total (above ground) dry weight in the late-treated containers were somewhat lower than those receiving sulfur from the beginning, but were good nevertheless.

Plant tops were harvested 124 days after planting by which time seeds had matured and senescence was advanced. Dry weight yields (total aboveground crop) ranged from 5.4 to 6.7 kg per square meter with the best yields in those treatments that had added gypsum at the beginning of the study.

Treatments and observations are summarized in Table 1 giving total methane emission for the period over which measurements were made. Although the containers were kept flooded and measurements of methane emission were made for 20 days after harvest, under normal field conditions the field would be drained a week or more before harvest and would be dried sufficiently for aeration. Under these conditions a burst of methane release from deeper in the soil would have been expected as observed in our earlier field studies, and aerobic decomposition of residual organic matter with carbon dioxide release would be expected. Thus the total methane release probably is higher than might have been expected had the containers been allowed to drain and dry.

The excess of methane production where organic matter was added to the soil over those treatments where no exogenous organic matter was applied gives a measure of methane yield attributable to the organic matter, from which conversion efficiency is calculated. The seasonal methane emission totals from the four containers that received added organic matter (numbers 1, 3, 5, and 7: see Table 1) averaged 21.0 gC/m^2 (± 2.8 gC/m^2, one standard deviation), while the four containers without added organic matter

TABLE 1. Treatments and Observations of 1986 Experiment

Container Number	Organic Matter Added, gC/M²	Total H$_2$O Drained, l	Total H$_2$O Drained, cm	Seasonal CH$_4$ Emission, gC/m²	Net Recovery of Carbon, gC/m²	Percent Recovery	Dry Weight Yield (Tops), g/m²
1	200			24.1	17.8	8.9	5416
2				6.3			5633
3	200	18.4	29.9	20.0	13.7	6.9	5400
4		8.3	12.5	6.3			5450
5	200	37.3	60.5	22.4	14	7.0	5516
6		25.5	41.3	8.4			5466
7	200			17.6	16.2	8.1	6683
8				5.5			6333

All containers received a top dressing of 10 g (167 g per m²) urea at the beginning of the study and 10 g gypsum on the twelfth day after transplanting. Treatments 7 and 8 received 10 g (167 g per m²) gypsum incorporated into the soil at the start of the experiment (see text). Organic matter when added was 30 g ground rice straw per container or the equivalent of 200 g carbon per m² calculated as (HCHO). The percent recovery column gives the percent of exogenously applied organic carbon recovered in methane when compared with the corresponding treatment with no added organic matter. Maximum theoretical recovery would be 50%.

(numbers 2, 4, 6, and 8) averaged 6.6 gC/m^2 (±1.2 gC/m^2). Note that here we use units of carbon and not methane.

Methane emission as a function of time for the added organic matter treatments and those treatments to which no organic additions were made are compared in Figure 1. Although methane production and emission began shortly after flooding where organic matter was added to the soil, it did not show the sharp rise we had observed in earlier field studies [Cicerone et al., 1992] but reached a preharvest peak at about 90 days after planting. This probably is attributable to the manner in which added rice straw was dispersed throughout the soil layer. (See discussion below.)

Rate of drainage did not influence methane emission greatly, but the presence or absence of added organic matter did. Even though much of the methane recovered later in the season and particularly after harvest, undoubtedly came from decomposing root material, those treatments with added organic matter produced about 3.2 times more methane over the period of measurement than comparable treatments with no added organic matter, including treatments 7 and 8 where gypsum had been mixed into the soil and methane production was somewhat reduced.

For this study although plants were harvested on day 124, the containers were kept flooded and methane collections continued until day 145. By this time, the principal source of methane probably was decomposing root material from the harvested crop and measured methane was increasingly sporadic as the vascular

system of the plant degenerated and the mode of release became dominated by bubbles. With the living plant the primary mechanism for methane movement to the atmosphere is through the plant or at the leaf surface [Nouchi et al., 1990]. At the time of harvest a syringe could be connected to the plant stubble by means of a short latex tube and gases collected directly from the stump. Quantities of gas containing several percent methane were readily obtained by this means.

1987 (Year 2) Experiment

This series was generally of the same pattern as the 1986 study with several changes intended to build on the previous findings. Two soils were compared, both of them lighter textured than those of the 1986 study to permit water drainage. The soils are described further in Table 2; both soils were taken from previously fallow fields. A 10-cm-deep layer of expanded silica ("pearlite") was placed in the bottom of the containers as an infiltration aid before adding the soil. Treatments summarized in Table 2 included a comparison of the presence or absence of added organic matter, depth of placement of organic matter, water penetration rates and the presence or absence of vegetation.

As with previous experiments, added exogenous organic matter was the single most important determinant in methane production. Where organic matter was added there was a rapid rise in methane production within 30 days after flooding and then a decline with a gradual increase as the season progressed, as shown in
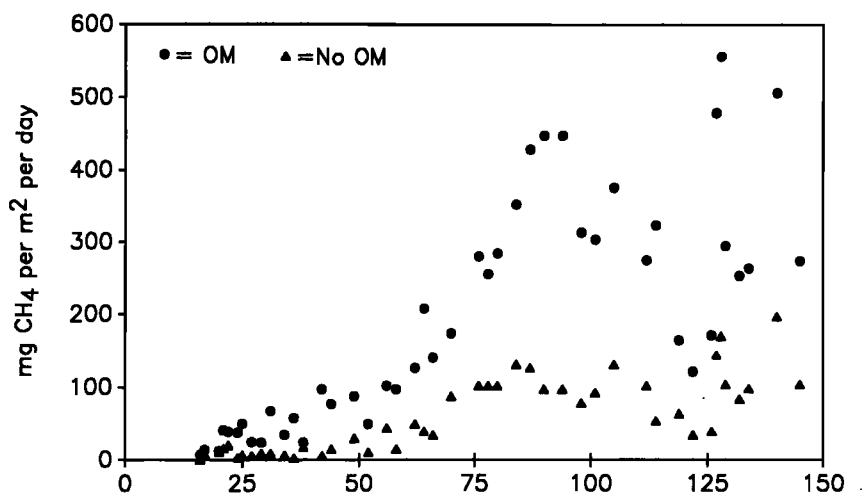

Fig. 1. Time course of methane emission in the presence and absence of added organic matter (1986 experiment). Solid circles: average of data from containers 1, 3, 5, and 7. Solid triangles: average of data from containers 2, 4, 6, and 8. See Table 1 for description of treatments for each container.

TABLE 2. Treatments and Observations of 1987 Experiment

Container Number	Soil Used	Depth of OM	Total H_2O Drained l	Total H_2O Drained cm	Seasonal CH_4 Emission, gC/m^2	Net Recovery of Carbon, gC/m^2	Percent Recovery	Dry Weight Yield (Tops), g/m^2
1	Ri	no OM			4.55			6483
2	"	no OM			2.45			6350
3	"	10-20 cm			20.36	16.86	5.05	6233
4	"	"			25.02	21.52	6.45	5416
5	"	"			30.95	27.45	8.23	6216
6	"	"			6.23		1.86	
7	"	0-10 cm			19.95	16.45	4.93	5983
8	"	"			6.17	2.67	0.80	5866
9	"	"			7.10	3.60	1.13	6050
10	"	"			11.52	8.02	2.51	5833
11	"	"			7.94		2.39	
12	"	"			13.70	10.20	3.05	5700
13	Re	"	38.0	61.8	12.84	11.83	3.71	5650
14	"	"	49.0	79.6	20.12	18.92	5.67	5766
15	"	no OM	29.1	47.1	1.01			5316
16	"	no OM	50.1	81.4	1.20			5833
17	"	no OM			0.64			6216

All containers received 10 g urea and 10 g $CaSO_4.2\ H_2O$ (167 g/m^2) except treatments 7 and 8 in which the gypsum added was 50 g (833 g/m^2) incorporated in the top 30 cm. Organic matter when added was ground rice straw at the rate of 50 g (or an estimated 33 gC/m^2) incorporated into the soil at either the 0-10 cm or 10-20 cm depth as shown. Both soils were relatively light textured. ri, Rincon Silty Clay Loam; Re, Reiff Very Fine Sandy Loam. The percent recovery column gives the percent of exogeneously supplied organic carbon recovered as methane when compared with the corresponding treatment with no added organic matter. Maximum theoretical recovery would be 50% assuming the stoichiometry given in the opening discussion. Containers 6 and 11 were controls with no vegetation.

Figure 2. This performance, in contrast with the 1986 study, was more consistent with our earlier field observations and probably is made more evident by the local placement of organic material rather than its dispersion throughout the profile as in the 1986 experiment. Where no exogenous organic matter was present, the production of methane increased as the season progressed, but never to the level of the organic matter treatments. This is shown in Figure 2a. We attribute the first pulse of methane release early in the season to the fermentation of the added rice straw with direct release of methane. Later in the season, as oxidation-reduction potentials become lower, methane production involving the autotrophic reduction of CO_2 by methanogens and utilizing electrons from other fermentative processes appears to assume a larger role. Degradation of added organic matter probably continues, but organics from the plants themselves and decaying abandoned rootlets contribute further to the total fermentation. Direct

measurement of Eh was made with buried electrodes and supported such an hypothesis, but because the variation of Eh through the mosaic of the rhizosphere is on a much smaller scale than the dimensions of the electrodes used (Pt wire circa 0.5 mm diameter, 10 mm length), such correlations may be misleading [Soedarsono, 1976] and are not reported here.

Overall recovery of added carbon as methane through the season, although not as large as that observed with the finer textured soils of the 1986 study, still ranged from about two to ten percent in those treatments where vegetation was present. Methane emission was greater throughout the season in those treatments with added organic matter than where no exogenous organic matter was supplied. This demonstrates that the pulse of methane early in the season does not represent the complete destruction of that organic matter. Continued fermentation of less readily decomposed material as well as that of released organics from the vegetation and decomposing root residues
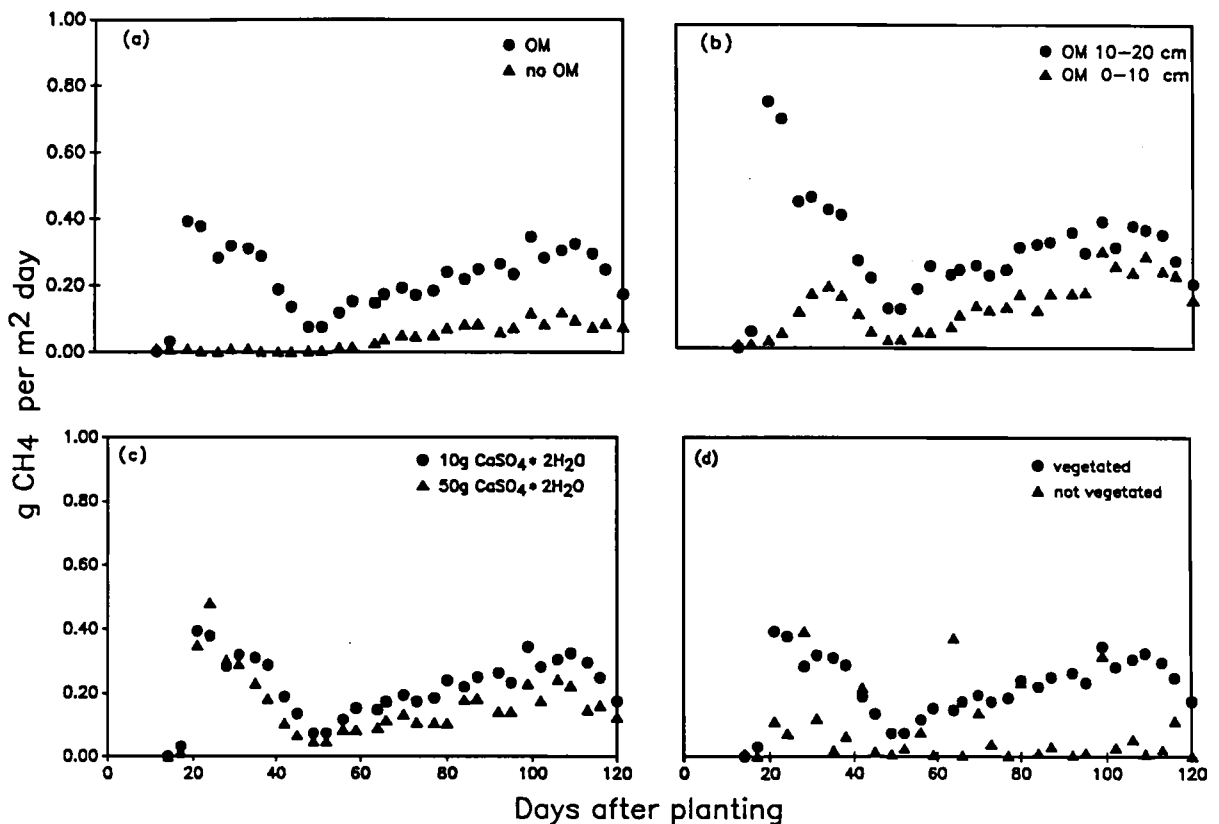

Fig. 2. Methane emission (1987 experiment) showing (a) influence of added organic matter, (b) depth of organic matter placement, (c) influence of added sulfate ion, and (d) the presence or absence of vegetation. The solid circles and triangles represent average emissions for containers with the same treatment; see Table 2.

contributes to the total methane production.

The average values (and standard deviations) of total methane emitted over the season were 16.8 ±7.9 gC/m^2 for the 12 containers with added organic matter (excepting containers without plants, i.e., numbers 6 and 11), and 2.0 ± 1.6 gC/m^2 for containers without added organic matter (containers 1, 2, 15, 16, and 17). Depth of placement of added organic matter seemed to have some influence on methane emission, both in terms of total methane recovered and peak values observed. The average values (with standard deviations following) of the total methane emitted over the growing season were 11.9 ± 5.0 gC/m^2 for the six containers with organic matter added between zero and 10 cm depth (container numbers 8 thru 14, excepting container number 11), and 24.1 ± 5.1 gC/m^2 for the four containers with organic matter added between 10- and 20-cm depth (container numbers 3, 4, 5, and 7). There was a greater variability from one treatment to another and in time with the treatments having organic matter in the 10- to 20-cm depth compared with those where it was in the top 10 cm. The variability may have been attributable to problems of diffusion or the accident of root location. Root density was greatest in the top 10 to 15 cm. In both of these treatments, the burst of methane early in the season with a subsequent decline and gradual increase later in the season are evident.

Sulfate ion was provided initially for all treatments to assure that sulfur deficiency did not restrict plant growth but treatments 7 and 8 to which additional gypsum had been applied showed a lessened production of methane as would have been expected [Sansone and Martens, 1981; Oremland, 1988] and in agreement with the observations of the 1986 experiment. It is not possible from the data to arrive at any stoichiometric comparison, but the qualitative result agrees with the assumption that sulfate ion served as an alternative to carbon dioxide as electron acceptor for the oxidation of organic matter. The rate of application of gypsum, 50 grams per container or the equivalent of 833 grams per square meter (or 8.3 metric tons per hectare) was sufficiently high that toxicity to plants and microorganisms from H_2S might have been possible, but no reduction in dry weight yield was encountered and so it seems reasonable to assume that there was no inhibition of microbial activity other than the expected competitive substitution of sulfate ion for carbon dioxide as electron acceptor.

The presence or absence of vegetation as depicted in Figure 2d, confirms the observation that although there is an initial burst of methane from the added organic matter, the production of methane continued throughout the season regardless of whether plants were there. The variability in methane emission in the unplanted treatments reflects the mechanism of release including bubbles. In none of the treatments was it possible to make any estimate of the re-oxidation of methane by heterotrophic methane oxidizing organisms although this undoubtedly took place to some extent [Holzapfel-Pschorn and Seiler, 1986; Sass et al., 1990]. Thus the recoveries of added organic carbon as methane calculated in Tables 1 and 2, besides being influenced by any residual organic material in the starting soils, probably also are affected by any reoxidation that may have taken place.

1988 (Year 3) Experiment

The 1988 experiment was conducted using a completely artificial growing medium in which expanded silica ("pearlite") was the mineral base covered with a 8-cm layer of washed sand to prevent flotation and using reagent grade chemicals as mineral element source based upon the formulation of Johnson et al. [1957]. The treatments given in Table 3 were designed to compare different sources of organic matter and test the hypothesis that where no exogenous organic matter was supplied, methane production in the later portion of the growing season originated from organic materials released from the plants or decaying abandoned root material or a combination of these sources. It was also anticipated that the more coarse-textured supporting medium would permit more effective diffusion of oxygen (or other electron acceptors), making for a more homogeneous oxidation-reduction potential in the vicinity of plant roots, and thereby suppressing methane formation to some extent. The work of Soedarsono [1976] demonstrated that the immediate vicinity of individual roots of the rice plant is sufficiently oxidizing to permit the existence of ferric iron and support the respiration of the root itself which is clearly "aerobic"; see also Raskin and Kende [1985].

Treatments, in addition to the presence or absence of the organic additions used previously (ground rice straw), included one in which cellulose was used as organic source and another using vanillin as surrogate for lignin. Vanillin is one of several derivatives of lignin (which is not extractable from plants in undenatured

TABLE 3. Treatments and Observations of 1988 Experiment

Container Number	Organic* Matter Added, gC/m²	Total H₂O Drained, l	Total H₂O Drained, cm	Seasonal CH₄ Emission Production, gC/m²	Net Recovery of Carton, g/m²	Percent Recovery	Dry Weight Yield (Tops), g/m²
1				1.2			3368
2				1.13			2858
3				2.57			3093
4	333 (RS)			19.0	17.4	5.2	2493
5	333 (RS)	42.4	68.9	14.1	12.6	3.8	2508
6	333 (RS)	41.6	67.6	19.5	18.0	5.4	2485
7	370 (Cel)	44.5	72.3	25.7	24.2	6.5	2485
8	370 (Van)	44.1	71.7	1.13	1.12	.2	1765

* RS, Rice Straw; Cel, Cellulose; Van, Vanillin.
All containers received the same artificial mineral base and artificial nutrient supply (see text). Organic matter added at the rate of 50 g per container (833 g/m²) as shown. RS, ground rice straw; Cel, cellulose; Va, vanillin. Percent recovery column gives the percent of added organic carbon recovered as CH₄ compared with the corresponding treatment with no added organic matter.

form), and was intended as a substitute source of the methoxy groups of lignin and hence a potential methane precursor. The vanillin turned out to be toxic to the plants, even with careful adjustment of pH and so the vanillin treatment was also without plants (although a slight surface growth of algae was observed).

Results are presented in Table 3 and Figure 3. As in other experiments [Neue and Scharpenseel, 1984; Cicerone et al., 1992; Yagi and Minami, 1990; Sass et al., 1991a, b; Schutz et al., 1989; Sass et al., 1990], added organic matter was the single greatest contributor to methane production. When the added organic matter was rice straw, methane yield showed an early peak at about 30 days after planting with some decrease thereafter followed by a gradual increase later in the season. Where cellulose was the organic source, by contrast, this early peak production was not observed but a maximum was reached at about 80 days with a gradual decline thereafter. This performance is consistent with the hypothesis that with ground rice straw as added organic matter, fermentable protoplasmic residues are the main contributors to methane production early in the season with further fermentation and autotrophic methanogenesis coming later in the season. The lignin moiety of the cell wall is essentially unavailable for degradation under the anoxic conditions of methanogenesis, shielding at least some of the cellulose from further degradation. By contrast, cellulose itself (treatment number 7) appears to have been less immediately available, possibly because of its limited solubility, but more completely converted to methane.

Approximately 5% of the added carbon was recovered as methane in treatments receiving rice straw, and slightly more, 6.5% in the single treatment where cellulose was the organic source. These figures for carbon recovery must be taken as minimum values since there was methane production after harvest and some of this probably represented residual organic matter from the initial application. Under typical field conditions where the field is permitted to dry before harvest the burst of methane release observed upon drying in our field studies [Cicerone et al., 1992] would be expected.

Vanillin suppressed plant growth completely, and so the observed methane production in treatment number 8, although slight, must have come from vanillin degradation. The limited surface algal growth and the small quantity of decaying material from the initial transplant of rice seedlings appear to be insufficient organic source to explain this methane
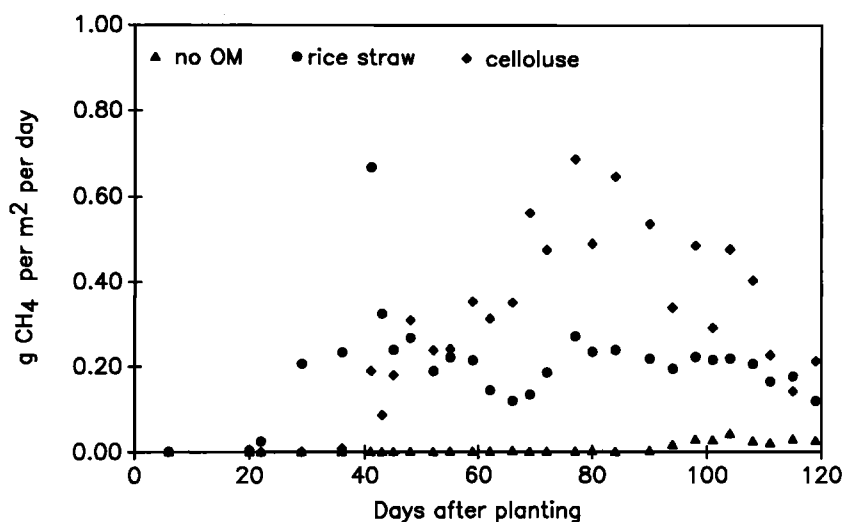
Fig. 3.   Methane emission in an artificial system with culture solution as nutrient source comparing rice straw and cellulose as the organic matter source (1988 experiment). Solid circles, diamonds, and triangles represent average emissions for containers with the same treatment; see Table 3.

yield and there was no dowry of "soil" organic matter.

The three containers that received no added organic matter (numbers 1, 2, and 3) averaged 1.6 ± 0.8 gC/m² as methane emitted over the growing season while the four containers with added organic matter (numbers 4 thru 7) and excluding the vanillin treatment emitted 19.6 ± 4.8 gC/m² as methane.

The drainage of water through four of the treatments did not greatly influence methane production; see Table 3. Drainage rates were greater than those likely under typical field conditions and served to verify earlier observations that water movement plays little significant role in methane emission. The transport of soluble organics to lower levels in the profile would be slow compared with other process rates and the delivery of oxygen dissolved in the water likewise limited.

The expanded silica proved to be less readily penetrated by roots than is the typical soil, and the root mass was mainly in the top layer of sand and along the sides of the container. The organic matter when added was placed in the lower 2.5 cm of the sand layer. This localization of organic matter in the lower part of the root zone may have contributed to a greater efficiency in converting added organic matter to methane.

The somewhat larger recovery of carbon as methane in the single treatment where cellulose was the carbon source and the

seasonal trend of its production deserve further investigation. For example, the stability of wood in anoxic waters, particularly at low pH levels, probably is due in a large part to the protective nature of the lignin matrix. The contrast between cellulose and rice straw observed here places the question in sharper focus.

SUMMARY AND CONCLUSIONS

The series of experiments reported here serve to isolate some of the variables contributing to methane production under rice and help explain some of the apparent inconsistencies in earlier observations. Methods and practices of rice culture differ greatly from one location to another depending upon soil, climate, and economic factors particularly, but also as a matter of cultural heritage and technological change. The delivery of methane to the atmosphere from whatever source is of concern as it applies to heat exchange processes and therefore climate change, and so it is of interest to examine this role of the rice field as a methane source.

1. Consistent with earlier observations by us [Cicerone et al., 1992] and others [Yagi and Minami, 1990; Schutz et al., 1989; Sass et al., 1991a, b], the exogenous supply of organic material to the soil, whether it be for the disposal of crop residues or as a source of fertilizer, appears to be the single most important contributor to methane production.

2. The depth at which applied organic matter is placed affects the quantity of methane emitted. More methane is released and the emission is more sporadic when organic matter is placed at a greater depth.

3. Methane emission was not directly influenced by soil texture in the soils that we used. The very light textured soils used in the 1987 study and the artificial system used in 1988, although they provided for more rapid diffusion and did tend to yield less methane, would not be acceptable for rice culture for other reasons (primarily water management). Other soils that support rice production should be studied.

4. Water infiltration was not an important determinant in methane production, particularly under those conditions most likely to be manipulated in field practice. This result differs somewhat from those of others [Yagi and Minami, 1990; Yagi et al., 1990].

5. Other electron acceptors such as sulfate ion are unlikely means of manipulating methane yield, primarily for stoichiometric reasons, although the potential toxicity of hydrogen sulfide also limits the applicability of gypsum.

6. The pattern of methane yield indicates that early in the season methane comes from fermentative sources, and as conditions in the soil become more reducing, autotrophic reduction of carbon dioxide assumes greater importance.

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