GLOBAL BIOGEOCHEMICAL CYCLES, VOL. 8, NO. 2, PAGES 127-134, JUNE 1994

Impact of gypsum application on the methane emission from a wetland rice field

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Abstract. Methane emission from Philippine rice paddies was monitored with a closed chamber technique during the 1991 and 1992 wet season. The methane emission from plots amended with 6.66 tons.ha^{-1} gypsum was reduced by 55-70% compared to non-amended plots. Although CH_4 emission from fields with a high input of fresh organic matter was strongly enhanced, the experiments showed that the relative reduction in CH_4 emission upon gypsum application was independent of organic matter addition. The reduced CH_4 emission upon gypsum application was most likely due to inhibition of methanogenesis by sulfate-reducing bacteria. Observed SO_4^{2-} concentrations in the soil solution of gypsum-amended plots were well above minimum concentrations reported in the literature for successful competition of sulfate-reducing bacteria with methanogens. The data provide a base for reducing the estimates of CH_4 emissions from rice grown on high-sulfate containing soils or gypsum-amended soils.

Introduction

Methane (CH_4) is an important greenhouse gas, accounting for about 17% of the enhanced greenhouse effect during the 1980s [*IPCC*, 1990; *Lelieveld et al.*, 1993]. Measurements at various locations of the world show that the average annual increase of atmospheric methane is ~0.8% per year over the last decades [*Lelieveld et al.*, 1993]. Like other greenhouse gases, methane traps part of the thermal radiation from Earth's surface [*Wang et al.*, 1976]. Furthermore, CH_4 plays an important role in the atmospheric chemistry [*Logan et al.*, 1981]. Studies on the atmospheric CH_4 cycle have stressed the need for identification of individual CH_4 sources and their source strength. A next step is to look for possibilities to stabilize or even reduce atmospheric CH_4 mixing ratios.

Methane is produced by strict anaerobic bacteria that are common in anoxic soils such as natural wetlands and wetland rice fields [*Cicerone and Oremland*, 1988]. Wetland rice fields are an important source of methane and may account for ~20% of the global anthropogenic methane annually produced [*IPCC*, 1992]. Moreover, emission of CH_4 from rice fields is estimated to increase at an average rate of 1.1% per year over the next 30 years [*Anastasi et al.*, 1992]. The residence time of CH_4 in the atmosphere is relatively short compared to that of other greenhouse gases, such as CO_2 and N_2O [*Bouwman*, 1990]. Therefore reduction of the global -methane source strength offers possibilities for curtailing the trend of increasing warming potential of the atmosphere on a relatively short timescale. A frequently suggested mitigation option is the use of sulfate-containing fertilizers such as ammonium sulfate ($(NH_4)_2SO_4$). The distribution of CH_4 and dissolved SO_4 in the interstitial waters of recent organic-rich marine sediments indicated that SO_4 reduction and CH_4 production are mutually exclusive metabolic processes [*Martens and Berner*, 1974]. In anoxic incubations with these sediments the CH_4 concentration did not increase until the dissolved SO_4^{2-} concentration approached zero [*Martens and Berner*, 1974] Inhibition studies demonstrated that sulfate reducers (in the presence of sulfate) can outcompete methanogens for substrates [*Lovley and Klug*, 1983; *Oremland*, 1988].

Nevertheless, in rice fields fertilized with $(NH_4)_2SO_4$ or other sulfate-containing fertilizers, CH_4 emission either increased [*Cicerone and Shetter*, 1981], stayed constant [*Wassmann et al.*, 1993] or decreased [*Schütz et al.*, 1989a]. In theory, these contradicting results may be due to differences in substrate availability at the various field sites. If sufficient substrate is available, methanogenesis is not inhibited by sulfate reduction [*Wiebe et al.*, 1981]. However, in rice fields, CH_4 emissions increase after incorporation of straw or other organic compounds [*Schütz et al.*, 1989a; *Yagi and Minami*, 1990], suggesting substrate limitation for CH_4 production. Acetate and H_2/CO_2 are the most important precursors for methane in a flooded rice field [*Schütz et al.*, 1989b] and can also be utilized by sulfate reducers. So simultaneous occurrence of SO_4^{2-} reduction and CH_4 production in a flooded rice field because of utilization of different substrate is unlikely. However, while competition for substrate is more common, synergistic relationships between methanogens and sulfate reducers have been reported (for a review on the subject of methanogenesis, sulfate reduction and their interaction we refer to *Wiebe et al.* [1981] and *Oremland* [1988]. Another explanation for contradicting results from $(NH_4)_2SO_4$ fertilization is that the sulfate concentration in the soil solution of some field experiments did not reach the threshold limit necessary for a successful

Paper number 94GB00386.
0886-6236/94/94GB-00386$10.00

competition of sulfate reducers with methanogens. Model calculations for freshwater sediments revealed that at sulfate concentrations greater than 30 µM a sulfate-reducing zone develops, and sulfate reducers maintain acetate concentrations too low for methanogenesis, while at lower sulfate levels a methanogenic zone develops [*Lovley and Klug*, 1986]. This indicates that also in flooded rice fields, which resemble freshwater sediments, a minimum sulfate concentration is required for sulfate reducers to outcompete methanogens.

Competition between methanogens and sulfate reducers in flooded rice soils is not restricted to fields fertilized with $(NH_4)_2SO_4$. Competition may be important also in soil types, such as (coastal) saline soils with high-sulfate content and acid sulfate soils. Several million hectares of these soils are used for rice [*Bhumbla and Abrol*, 1978; *Van Breemen and Pons*, 1978]. Furthermore, gypsum ($CaSO_4.2H_2O$) is the most common soil amendment on sodic and/or alkaline soils for rice agriculture [*Bhumbla and Abrol*, 1978]. For example, in India alone, several million hectares of the Indo-Gangetic plains are alkaline soils on which rice is the major crop in the wet season [*Abrol et al.*, 1985]. So a small but significant part of the total rice soil acreage consists of soils that may be low methane producing soils due to competition between sulfate reducers and methanogens. On the other hand, methane emission is the result of CH_4 production, CH_4 oxidation and gas transport in the complex soil-water-plant-atmosphere system [*Conrad*, 1989]. Lower production may be (partly) counterbalanced by other changes (e.g., in CH_4 oxidation rate) or may be relatively unimportant for the transport rate of CH_4 to the atmosphere. Therefore a reduction in total CH_4 production does not necessarily result in lower emissions. To elucidate the impact of sulfate availability on methane emission, field experiments with gypsum application were carried out in a Philippine rice paddy. The importance of different substrate levels was studied by performing experiments with and without organic manure.

Materials and Methods

Field Preparations

Field measurements of CH_4 emission were performed during the 1991 and 1992 wet season (July-November) in wetland rice fields of the International Rice Research Institute, Los Baños, Philippines. The soil at the field site is an Andaqueptic Haplaquoll consisting of 66% clay, 28% silt, and 6% sand with 1.97% organic C, 0.166% total N and a pH-H_2O of 5.9. Two plots, adjacent to each other, were planted with rice variety IR72 at a spacing of 25x25 cm (1991). Both plots received 55.2 kg N ha^{-1} as urea in the 1991 wet season. In addition to this, one plot received a gift of 6.66 tons ha^{-1} $CaSO_4$. In the 1992 wet season, two plots were selected in the same block of the research farm as the 1991 plots but without previous gypsum or organic manure application. Rice variety IR72 was planted at a plant spacing of 20x20 cm. The plots received 20 tons ha^{-1} fresh weight of green manure (*Sesbania Rostrata*) and 30 kg ha^{-1} urea at panicle initiation and flowering. The green manure was chopped and ploughed in one week before transplanting. Total nitrogen fertilization (organic and inorganic) amounted to 165 kg N ha^{-1} (one plot was amended with 6.66 tons ha^{-1} $CaSO_4$). Urea and gypsum were broadcast and incorporated at final harrowing, except for the urea gifts at panicle initiation and flowering in 1992, which were broadcast.

Experimental Setup

Methane emission rates were monitored with an automatic measurement system based on the closed chamber technique as developed and described by *Schütz et al.* [1989a] with small modifications. The system allowed 24-hour semicontinuous determination of CH_4 emission rates from different gas collector chambers. Measurements were performed in 2-hour cycles, allowing 12 flux measurements per day of each chamber. Such an intensive monitoring is essential on account of the high diurnal variations of CH_4 fluxes from rice fields [*Schütz et al.*, 1989a, 1990]. Two chambers were placed in each experimental plot. The chambers (0.6x0.6x1.2 m) were made of smooth colorless Plexiglas and equipped with a Plexiglass cover which could be opened and closed by a time-controlled pneumatic cylinder. Inside the boxes two electrical fans (12 V DC) were mounted to ensure rapid mixing of the air inside the closed chamber during sampling and with the ambient air when the cover was open. Air samples from the individual closed chambers are analyzed for CH_4 on a gas chromatograph equipped with a six-port valve, sample loop, and flame ionization detector. For a schematic overview and technical details of the measurement system we refer to *Schütz et al.* [1989a] and *IAEA* [1992]. Modifications of the system used in this study included (1) closing time of the chambers during sampling was 48 min in 1991 but was reduced to 24 min in 1992 and (2) injection of calibration gas was not directly from a gas cylinder but from a separate container, simulating the chambers in the field, ensuring equal pressure in the gas flow system during sampling and calibration of the system.

The methane emission rate from a chamber was calculated with linear regression from the temporal increase of the CH_4 concentration in the chamber. Each emission rate r is based on four samples, and r squared of the linear regression is typically > 0.95.

In 1991, microporous (< 0.2 µm) polyetheneimide soil solution samplers (length, 10 cm; inner diameter, 1 mm) were placed horizontally in stainless steel wire frames. The frame was pushed into the puddled soil, fixing the samplers at 7.5 cm depth below the soil surface. Four samplers were installed in each experimental plot. Each sampler was connected to tygon tubing (length, 20 cm; inner diameter, 1 mm) fitted with a luer-lock and a needle. Soil solution was sampled by suction into 100-ml vacuum bottles at 43, 49, 62, 71, and 103 days after transplanting. The first sample (20 ml) was used to rinse the tubing, needle, and vacuum bottle. In the subsequent sample (10 ml), electrical conductivity (EC) was measured. At 43, 49, and 103 days after transplanting a second sample (10 ml) was collected for determination of chloride and sulfate concentrations. Cl^- and SO_4^{2-} were measured on a dionex ionchromatograph. Technical problems with the instrument prohibited continuous monitoring of dissolved Cl^- and SO_4^{2-} concentrations.

Statistical Complications of the Field Design

Financial means and logistic restrictions of the field experiment and monitoring setup prevented a fully satisfactory field design from a statistical point of view. Different plots were selected in the 1991 and 1992 season to avoid memory effects. Although measurements were duplicated (two gas-collector chambers per field), there were no duplicate fields available. However, monitoring of CH_4

Table 1. Total Seasonal CH_4 Emission and Standard Deviation From Philippine Rice Fields on the Same Soil Type for Various Fertilizer Treatments During the 1992 Wet Season

Fertilizer	Seasonal CH_4 Emission, g m^{-2}	s.d. in CH_4 Emission, %
Urea	7.8	18
$(NH_4)_2SO_4$	7.3	25
Green manure	19.2	30
Straw and urea	17.0	25

Recalculated from data of *IRRI* [1993].
Each variety of fertilizer used in four plots.

emissions from 16 different adjacent plots (randomized block design, one gas-collector chamber per plot) in the 1992 wet season [*IRRI*, 1993], showed that variation in CH_4 emissions among fields with the same treatment was 25% ± 4% (Table 1).

Results and Discussion

The duplicate measurements of CH_4 emission from individual plots were in good agreement, but the CH_4 emission from plots amended with gypsum was significantly lower. This is illustrated by Figures 1a and 1b for the 1992 wet season. CH_4 emission peaked at noon or early afternoon. The diurnal variation was high early in the season and became less important later in the season. The diurnal variation and the variance in the diurnal emission pattern

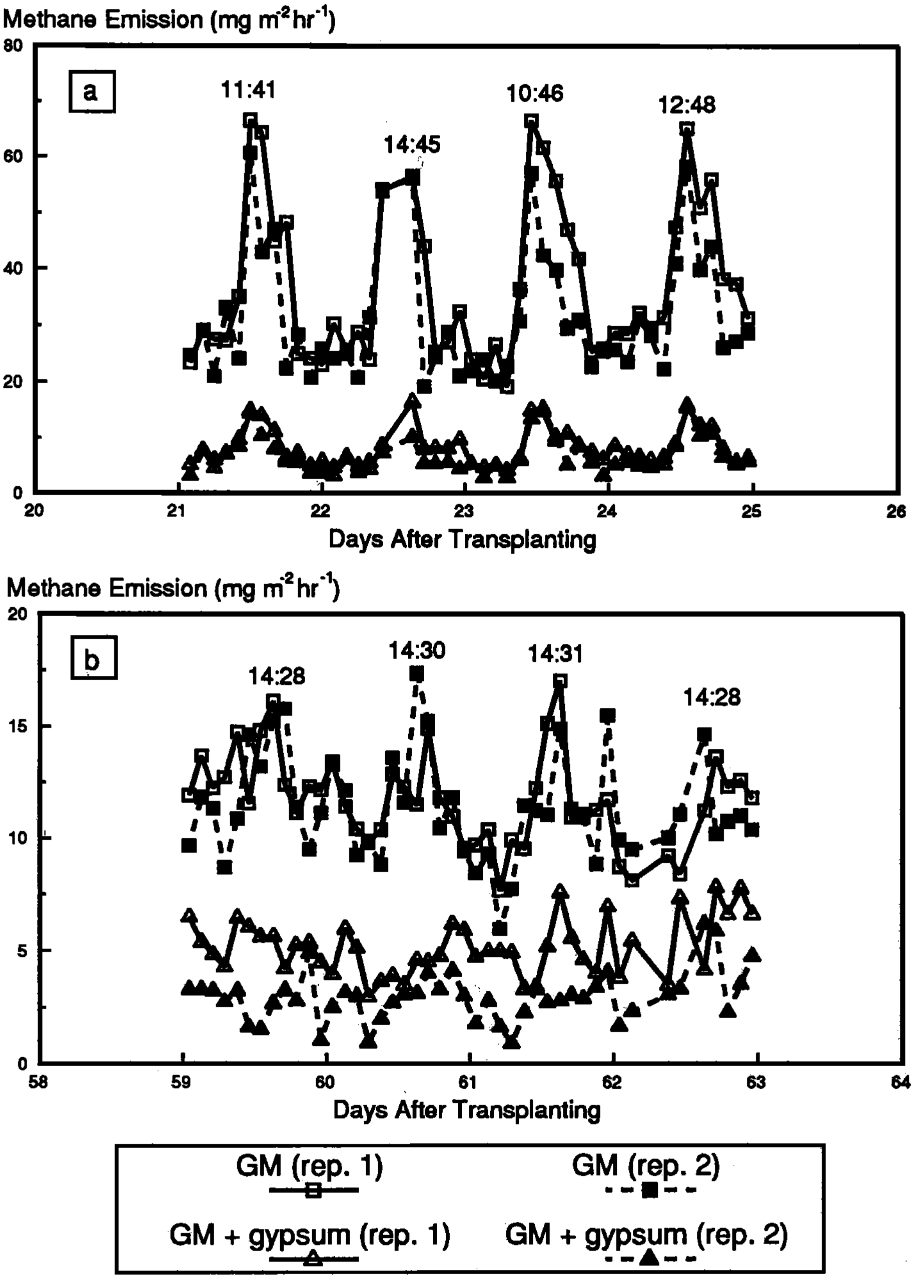

Figure 1. Diurnal variation in methane emission from green manure fertilized rice fields, with and without gypsum amendment, approximately (a) three weeks after transplanting and (b) nine weeks after transplanting.

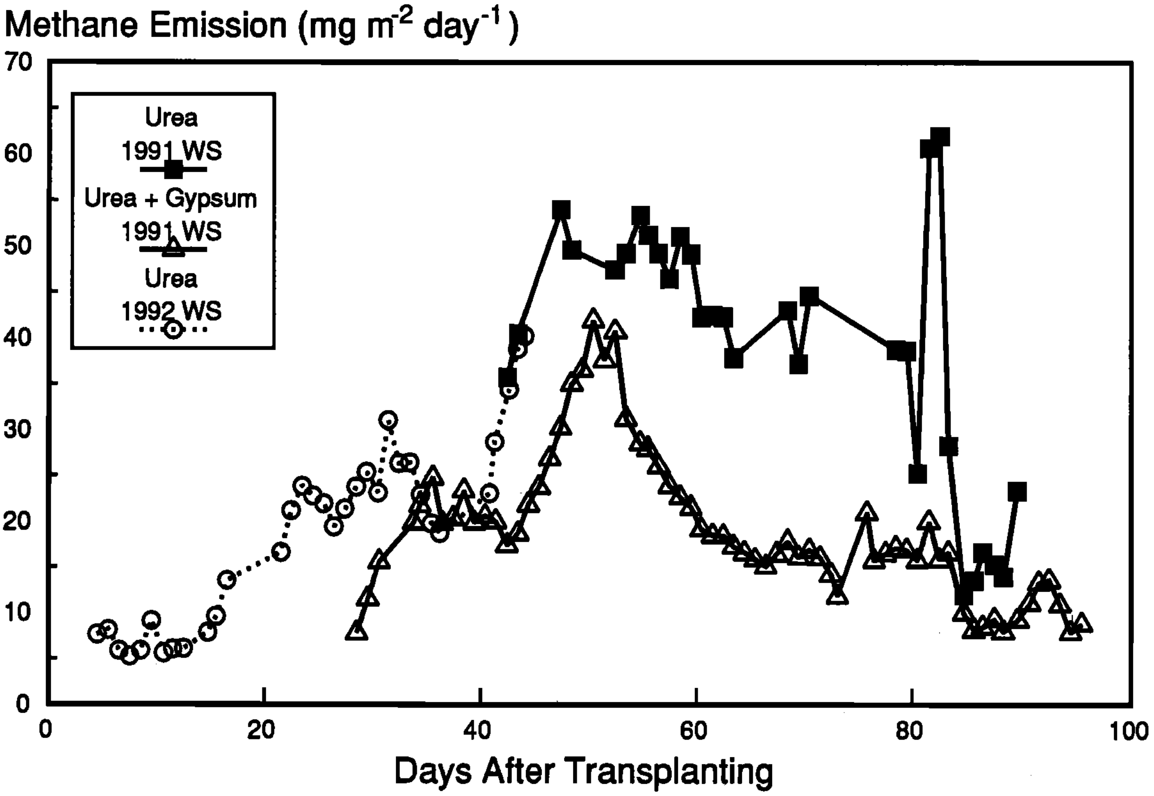

Figure 2. Methane emission from urea fertilized rice fields, with and without gypsum amendment, in the 1991 wet season.

clearly indicate that several measurements distributed over 24 hours are a prerequisite for a good estimate of the daily CH_4 flux. The average CH_4 flux was calculated from the two per hour flux measurements for the different plots (Figures 2, 3a, and 3b). On account of technical problems, a limited set of data was available for the nongypsum-treated plot in the 1991 wet season, and data for the first 40 days after transplanting, especially, are lacking (Figure 2). Therefore emission data during the first 40 days after transplanting in the 1992 wet season from a urea-fertilized plot with the same soil type and rice variety were included in Figure 2 for a better comparison between the gypsum and nongypsum-treated plot. The data from the urea-fertilized plot in 1992 show that the CH_4 emission rate gradually increased during the first 40 days after transplanting. Although the absolute values may have been slightly different in the 1991 wet season, the trend most likely was similar. The CH_4 flux from the plot amended with gypsum was consistently lower; the total CH_4 emission for the 1991 wet season was reduced by ~55% compared to that from the nongypsum-treated plot (Table 2).

CH_4 emission rates from plots treated with green manure in 1992 were ~10 times higher than CH_4 emissions from the urea-fertilized plots in 1991. An increase in CH_4 emission upon application of organic manure or incorporation of straw was previously observed in several field studies [e.g, *Schütz,* 1989a; *Yagi and Minami,* 1990]. However, the difference between CH_4 emission in the 1991 and 1992 wet season cannot be attributed to green manure application alone because plant spacing and amount of N fertilizer applied were also different, resulting in higher biomass and yield in 1992. A more extensive discussion on the impact of green manure incorporation on CH_4 emission will be given in a separate paper [H.A.C. Denier van der Gon and H.U. Neue, unpublished data 1994]. In the first week after transplanting, the CH_4 emission from the green manure-treated plot reached a peak value of 4.5 g m^{-2} day^{-1}. The high emission in the first week after transplanting was probably caused by the quick turnover of easily decomposable organic carbon from the chopped green manure which was incorporated one week before transplanting. A temporary very strong reduction just after flooding, characterized by very low Eh peak values and formation of H_2, is a well-known phenomenon in wetland rice soils with large quantities of fresh, easy decomposable organic matter [*Yamane and Sato,* 1968; *Motomura,* 1969]. No peak of CH_4 emission was observed in the plot amended with gypsum. After the first week the emission from both plots followed the same pattern, but emission levels differed significantly. Application of gypsum, averaged over the season, reduced the CH_4 emission by ~70% (Table 2). The 55-70% reduction in CH_4 emission upon gypsum amendment was well above the variation that can be expected between various fields due to spatial variation (Table 1; 25% ± 4%). Grain yields from plots with or without gypsum application were not significantly different (data not shown) but straw yields from plots with gypsum application were 10-30% lower. It is unlikely that the lower straw yields were caused by sulfide toxicity because grain yields were not different. Furthermore, in normal nondegraded rice soils, such as those used in this study, Fe^{2+} will always be present in the soil solution by the time H_2S is produced, so that H_2S will be converted to insoluble FeS [*Patrick and Reddy,* 1978]. Although lower biomass may cause lower CH_4 emissions [*Sass et al.,* 1990], this cannot explain our observations since

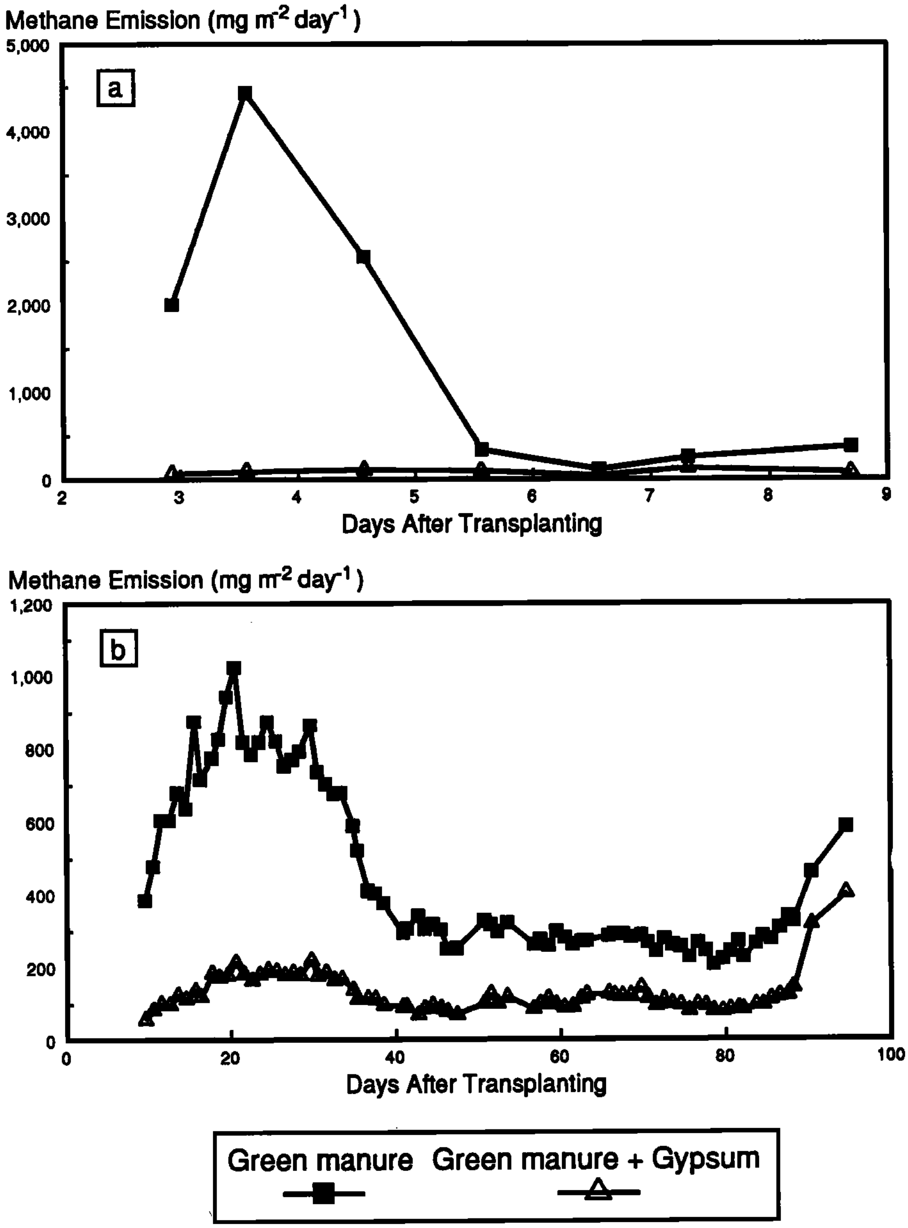

Figure 3. Methane emission from green manure fertilized rice fields, with and without gypsum amendment, in the 1992 wet season (a) during the first week after transplanting and (b) from the second week after transplanting onward.

Table 2. Average Daily Methane Flux From Wetland Rice Fields in the Philippines With Gypsum and Without Gypsum Application

Year	Fertilizer	Average CH_4 Flux, mg m^{-2} d^{-1}	
		Without Gypsum	With Gypsum
1991	Urea	40.2	18.6
1992	Green manure	443	128

Average flux calculated without extreme CH_4 emission rates shown in Figure 3a.

CH_4 emission from in the gypsum-amended plot was already strongly reduced early in the season, when plant-mediated CH_4 transport was still of minor importance (Figure 3a).

The lower CH_4 emission due to gypsum application can be explained by competition for substrate between sulfate reducers and methanogens. The thermodynamical sequence of soil reduction indicates that sulfate reduction occurs before CH_4 formation [*Patrick and Reddy,* 1978], which is in line with the results of *Martens and Berner* [1974]. So the observation that substantial amounts of CH_4 evolve from our experimental plots indicates that the soil redox potential was low enough to promote sulfate reduction. However, in situ-dissolved SO_4^{2-} concentrations may limit sulfate reduction. In most inland, humid rice-growing areas, the amount of total inorganic sulfur in the soil is relatively low (usually less than 0.52 mmol kg^{-1}) [*Patrick and Reddy,* 1978]. Within six

Table 3. Sulfate Concentration in the Soil Solution of a Wetland Rice Field in the First 45 Days of Flooding for the Dry Fallow Rice System on the IRRI Research Farm

Days of Flooding[a]	SO_4^{2-}, mmol L^{-1}
0	1.44
3	1.34
10	0.56
17	0.44
24	0.38
31	0.22
38	0.16
45	0.05

Data from *Robles* [1989].

[a] In the dry fallow rice system fields are flooded about 2-4 weeks before transplanting.

weeks of submergence, the concentration of water soluble sulfate in these soils becomes practically zero, as is illustrated for the soil used in this study by Table 3. In gypsum-treated soils, sulfur oxidation and numbers of anaerobic thiobacilli were found to be significantly higher than in control soils [*Freney et al.*, 1982]. Assuming a puddled layer of 0.15 m, a pore volume of 60% [*Sharma and De Datta*, 1985], and a floodwater layer of 5 cm, application of 6.66 tons ha^{-1} of gypsum ($CaSO_4$ $2H_2O$) would cause gypsum to dissolve to saturation with SO_4^{2-} concentrations of ~10 mM [*Novozamsky et al.*, 1978], well above concentrations necessary to suppress methanogenesis by sulfate reducers. Successful outcompetition of methanogens by sulfate reducers occurred in freshwater sediments at in situ SO_4^{2-} concentrations as low as 60 μM [*Lovley and Klug*, 1983]. Initially, high SO_4^{2-} concentrations will decrease with time by percolation of dissolved SO_4^{2-} and reduction by sulfate reducers. The loss due to percolation can be estimated. Percolation in a puddled clay soil is ~1.8 mm d^{-1} [*Sharma and De Datta*, 1985]. Percolation during a growing season of 100 days, including dissolution of remaining solid gypsum, would reduce the SO_4^{2-} concentration in the gypsum-amended plot to ~4.4 mM, indicating that percolation alone will not hinder sulfate reduction. Sulfate reduction itself may be a more important sulfate sink than percolation. Unfortunately, the sink strength cannot be calculated or even estimated because (1) the SO_4^{2-} reduction rate is unknown and (2) reoxidation of sulfide to sulfate in the rhizosphere [*Freney et al.*, 1982] and floodwater-soil interface may occur. Cycling of sulfur through oxidized zones could maintain the inhibition of CH_4 production over a long time period. Information on sulfate dynamics can be obtained from the soil solution data (Table 4). In control plots at 43 days after transplanting, dissolved SO_4^{2-} was below concentrations where sulfate reducers can outcompete methanogens. Although no data are available before 43 days after transplanting measured SO_4^{2-} concentrations are in line with measurements of a rice field on the same soil type and location (Table 3). The data in Table 3 indicate that in control fields sulfate reduction may play a role in the first 2-3 weeks before transplanting, but that the soluble sulfate pool is depleted soon after transplanting. By contrast, after gypsum application, dissolved SO_4^{2-} was still well above concentrations necessary for sulfate reducers to compete with methanogens until the end of the growing season. In the absence of SO_4^{2-} analyses at 62 and 71 days after transplanting, the EC data indicate no major changes in SO_4^{2-} concentration in the soil solution of the gypsum-amended plot. At the end of the growing season (103 days after transplanting) the EC and dissolved SO_4^{2-} concentration in the gypsum-amended plot decreased. That sulfate reduction is maintained in part by cycling of sulfur through oxidized zones and may continue to inhibit methanogenesis is supported by the observation that CH_4 emission levels from the gypsum-amended plots never reached the level of the plots without gypsum addition, even after addition of green manure.

In spite of clear evidence for sulfate inhibiting methanogenesis, appreciable CH_4 emission still occurred in the gypsum-amended plots. Coexistence of methanogens with sulfate reducers may be caused by a rate of supply of sulfate to sulfate reducers that is too low to deplete all acetate and H_2 that is produced [*Lovley et al.*, 1982]. In that case, methanogenesis should be inhibited more strongly at low substrate availability, that is without green manure addition. Suppression of CH_4 emission by gypsum, however, was not affected by adding green manure. Furthermore, the SO_4^{2-}

Table 4. Average Chloride Concentration, Sulfate Concentration, and Electrical Conductivity in Soil Solutions From Wetland Rice Fields Without Gypsum and With Gypsum Application in the 1991 Wet Season

Days After Transplanting	Cl^- mmol L^{-1} [a]	SO_4^{2-} mmol L^{-1} [a]	EC dS m^{-1} [a]
	Without Gypsum		
43	0.54 (0.05)	0.038 (0.004)	0.94 (0.03)
49	0.64 (0.09)	< 0.01	1.18 (0.08)
62	nd	nd	1.28 (0.08)
71	nd	nd	1.33 (0.03)
103	1.29 (0.11)	< 0.01	1.33 (0.04)
	With Gypsum		
43	0.65 (0.03)	6.88 (1.16)	2.03 (0.22)
49	0.81 (0.15)	7.01 (1.75)	2.22 (0.37)
62	nd	nd	2.07 (0.35)
71	nd	nd	2.01 (0.33)
103	1.31 (0.10)	3.36 (3.03)	1.69 (0.43)

nd, not determined.

[a] Average of four samples; standard deviation in parentheses.

concentration in the soil solution remained high throughout the growing season (Table 4). Methanogens may coexist with sulfate reducers also when there are zones or spots with low-sulfate contents *[Martens and Berner*, 1974], as was observed in sediments where both sulfate reduction and methane production occur [*Cappenberg*, 1974; *Hines and Buck*, 1982]. This hypothesis is supported by a similar relative depression of CH_4 emission upon gypsum addition in plots with and without green manure addition. The existance of zones or spots with low-sulfate contents where methanogenesis occurs implies that (1) removal of sulfate by SO_4^{2-} reducers is quicker than its supply by dissolution of gypsum (or that the solid gypsum source was quickly depleted), and (2) cycling of sulfur occurred in special zones (e.g., the oxidized rhizosphere), and the regenerated SO_4^{2-} is consumed before it is evenly distributed in the bulk soil.

Recently, *Delwiche and Cicerone* [1993] reported a greenhouse experiment on the impact of added gypsum on CH_4 emission from irrigated rice. Addition of $CaSO_4$ to the soil resulted in a slight competitive suppression of CH_4 production only. However, *Delwiche and Cicerone* [1993] compared two gypsum additions (1.67 and 8.33 tons ha^{-1}) and did not include a (nongypsum) control because the rice plants appeared to be sulfur deficient. The discrepancy between the strong reduction of CH_4 emission upon gypsum addition in our experiments, and the slight suppression observed by *Delwiche and Cicerone* [1993] can be explained by efficient cycling of SO_4^{2-}, resulting in reduced CH_4 emissions from both the low and high gypsum treatment of Delwiche and Cicerone. Therefore in the study of Delwiche and Cicerone, a comparison to a non-SO_4^{2-} situation cannot be made. Assuming that the CH_4 emissions in the low gypsum treatment of Delwiche and Cicerone were depressed by the presence of SO_4^{2-}, addition of 2-3 tons gypsum ha^{-1} to a rice field would be sufficient for a significant reduction in CH_4 emission.

The amount of gypsum used in our study is within the normal range of gypsum amendments used to reclaim alkaline or sodic soils [*Abrol et al.*, 1985]. In global budgets for methane emission from rice agriculture these soils should be treated accordingly. *Bachelet and Neue* [1993] introduced a correction factor for methane emission from rice grown on soil types that were expected to be low CH_4-emitting soils based on so-called "expert judgment." The results presented in our study provide a legitimate base for the use of a correction factor for the CH_4 emission from flooded rice fields on soils naturally high in sulfate or soils amended with large amounts of sulfate-containing substances.

The contradicting impact of $(NH_4)_2SO_4$ fertilization on CH_4 emission may be due to variations in in situ SO_4^{2-} concentrations in the different field experiments. Fertilization with for example 100 kg ha^{-1} $(NH_4)_2SO_4$ results in an ~50 times lower SO_4^{2-} input compared to 6.66 tons ha^{-1} gypsum. Although the initial SO_4^{2-} concentration in $(NH_4)_2SO_4$-fertilized soil is probably above the lower limit necessary for sulfate reducers to grow, percolation and sulfate reduction itself would quickly deplete this SO_4^{2-} pool. We suggest that fertilization with 50-200 kg $(NH_4)_2SO_4$ ha^{-1}, as used in most field experiments, result in in situ SO_4^{2-} concentrations just above or just below the concentration where sulfate reducers can successfully compete with methanogens. Therefore dependent on the fate of SO_4^{2-}, one should expect either no reduced emission from plots fertilized with $(NH_4)_2SO_4$ or a reduced emission early in the growing season and a return to normal emission rates toward the end of the growing season. Stimulation of CH_4 emission upon fertilization with $(NH_4)_2SO_4$ as reported by *Cicerone and Shetter* [1981] is a special case, previously observed by *DeLaune et al.* [1983]. CH_4 release from soil cores taken from brackish marshes was enhanced by small additions of SO_4^{2-} (1 mM), but higher additions of SO_4^{2-} (10 mM) reduced CH_4 release [*DeLaune et al.*, 1983]. We speculate that in the study of *Cicerone and Shetter* [1981], higher additions of SO_4^{2-} also would have reduced CH_4 emission.

Addition of organic matter (e.g., green manure, straw, etc.) could neutralize the inhibiting effect of $(NH_4)_2SO_4$ fertilization on CH_4 emission by enhancing depletion of the sulfate pool. Indeed, this was observed in field experiments [*Schütz et al.*, 1989a].

Conclusions

Adding gypsum to a flooded rice field reduced methane emissions by 55-70%. Most likely, the reduced emission was due to suppression of methanogens by sulfate-reducing bacteria. However, inhibition of methanogenesis was incomplete, and appreciable CH_4 emission still occurred. The amount of gypsum used in this study is within the normal range of gypsum amendments used to reclaim alkaline or sodic soils. The results support the use of a correction factor for the CH_4 emission from flooded rice fields on soils naturally high in sulfate or soils amended with large amounts of sulfate containing substances, when estimating global CH_4 emission from wetland rice fields. Further research on other (problem) soil types that cover a relevant part of the total rice crop acreage is necessary to adjust and improve estimates of the global CH_4 source strength of rice paddies. Future research will not only require good quality emission data but also more emphasis on soil (solution) dynamics to elucidate the complex biogeochemical interactions in rice fields that control the CH_4 emissions.

Acknowledgments. We thank R. Wassmann, R.S. Lantin, J.B. Aduna and R. Eugenio for help and support with the field experiments, N. van Breemen for discussion and critically reading the manuscript and three reviewers for valuable comments. This research received financial support from the Dutch National Research Programme on Climate Change and Global Air Pollution and was done in collaboration with the IRRI-EPA project on methane emissions from wetland rice fields.

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(Received November 5, 1993; revised January 27, 1994; accepted February 8, 1994.)