Biol Fertil Soils (1993) 15:174–178

Biology and Fertility of Soils

Methane mitigation in flooded Louisiana rice fields*

C.W. Lindau[1], P.K. Bollich[2], R.D. DeLaune[1], A.R. Mosier[3], and K.F. Bronson[3]

[1] Wetland Biogeochemistry Institute and Nuclear Science Center, Louisiana State University, Baton Rouge, LA 70803, USA
[2] Rice Research Station, Louisiana Experiment Station, Crowley, LA 70527, USA
[3] U.S. Department of Agriculture, Agriculture Research Service, Fort Collins, CO 80522, USA

Received July 31, 1992

Summary. A field experiment was conducted to determine whether selected nitrification inhibitors (encapsulated calcium carbide and dicyandiamide) and SO_4^{-2}-containing compounds [$(NH_4)_2SO_4$ and Na_2SO_4] had mitigating effects on CH_4 emissions from flooded rice. Microplots were established within a rice bay drill-seeded with the Texmont rice cultivar and CH_4 fluxes were measured over the main rice cropping season. Methane emissions over the 77-day sampling period were approximately 230, 240, 260, 290, 310, and 360 kg CH_4 ha^{-1} from the calcium carbide, Na_2SO_4-rate II, Na_2SO_4-rate I, $(NH_4)_2SO_4$, dicyandiamide, and urea (control) treatments, respectively. Reductions in CH_4 evolution, compared to the control, ranged from 14 to 35%, depending on treatment. The selected inhibitors and SO_4^{-2}-containing compounds appear to be effective in reducing the CH_4 emitted from flooded rice fields.

Key words: Methane emissions – Flooded soil – Greenhouse gas – Wetland rice – Mitigation

Methane is an important "greenhouse gas" because of its strong infrared absorption characteristics and recent worldwide atmospheric increases. A gram of CH_4 emitted to the atmosphere will absorb approximately 70 times more infrared radiation than a gram of CO_2 (United States Environmental Protection Agency 1990). Methane is currently increasing in the atmosphere by about 1% per year and by the year 2100 concentrations in the troposphere may be about 4 ppmV, or more than double the current level of 1.7 ppmV (Blake and Rowland 1988; Bouwman 1991).

Wetland rice cultivation is the major anthropogenic source of CH_4 to the atmosphere and current emissions are estimated at 60–170 Tg $year^{-1}$. Annually this represents approximately 25% of the CH_4 released on a worldwide scale (United States Environmental Protection Agency 1991). Over the next 30 years projections of global population indicate an increase the rice demand by as much as 50%, and about 700 million tonnes will have to be produced (International Rice Research Institute 1988). Methane emissions over the next 10 years may increase by as much as 20%, due to the increase in the area of flooded rice. This increase in CH_4 may directly affect global warming (United States Environmental Protection Agency 1990). Methane has a relatively short atmospheric residence time (10 years) and future CH_4 reductions from flooded rice systems could reduce the atmospheric warming potential relatively quickly (United States Environmental Protection Agency 1990).

In order to reduce the CH_4 emission from flooded rice, soil CH_4 production and evolution processes must be investigated. Field management practices must be developed that will reduce CH_4 emissions without decreasing rice quality and yield.

Methanogenesis is strictly an anaerobic microbial decomposition process of organic material. The methanogens cease to function if O_2 and/or other oxidized inorganic compounds are present (Van Breeman and Feijtel 1990). Within 8 h of flooding, depending on soil temperatures and the organic matter content, a rice soil is virtually O_2-free, which forces the anaerobic microorganisms to use, in sequential order, NO_3^-, Mn^{+4}, Fe^{+3}, SO_4^{-2}, and CO_2 as electron acceptors for respiration and organic matter decomposition (Reddy and Patrick 1984; Van Breeman and Feijtel 1990). The sequential reduction of these inorganic compounds must take place before CH_4 is generated. After the disappearance of SO_4^{-2}, methane will be produced by methanogens at soil redox potential values of less than −200 mV if a sufficient energy source is available (Bouwman 1991). High concentrations of the oxidized inorganic compounds may delay or inhibit CH_4 generation. Recent reports have indicated that specific nitrification inhibitors added with urea fertilizers can decrease CH_4 emissions from flooded rice soil (Bronson and Mosier 1991). In a greenhouse study, Bronson and Mosier (1991) demonstrated that the

Correspondence to: C.W. Lindau

nitrification inhibitor encapsulated calcium carbide, in combination with urea, significantly reduced CH_4 emissions from flooded rice pots. The inhibition of CH_4 emission was thought to be due to the slow release of C_2H_2 by the calcium carbide. Knowles (1979) also showed that C_2H_2 reduced CH_4 production from lake sediment. In a 1978 study, De Bont et al. (1978) demonstrated that CH_4 oxidation was also supressed by C_2H_2.

The objective of the present study was to determine the effects of encapsulated calcium carbide, dicyandiamide, and selected SO_4^{-2} compounds on CH_4 emissions from a flooded Louisiana rice field.

Materials and methods

Field plot procedures

The experimental field study was conducted at the Rice Research Station, Crowley, Louisiana. The rice soil was a Crowley silt loam (Typic Albaqualf) with 7.0 g total C kg^{-1} and 0.8 g total N kg^{-1} soil. The cation exchange capacity was 9.4 $cmol_c$ kg^{-1} soil and the pH was 5.8 (1:1, soil/water). The silt loam contained 12% clay and 71% silt.

The rice bay (0.75 ha) was drill-seeded (April 9, 1991) with Texmont, a semidwarf very early long-grain cultivar, and emergence occurred about 14 days later with a plant density of 190 plants m^{-2}. P and K were applied at the time of seeding at a rate of 67 kg ha^{-1} and permanent flooding was established 34 days later. Urea-N and $(NH_4)_2SO_4$-N were applied to the microplots 2 h before the permanent flooding at 100 kg ha^{-1}. Irrigation maintained a 5–10 cm floodwater depth throughout the Texmont growing season. The field plots were drained 108 days after seeding and the harvest occurred 10 days later.

The field treatments included (1) urea; (2) $(NH_4)_2SO_4$; (3) urea plus encapsulated calcium carbide (30 kg ha^{-1}); (4) urea plus dicyandiamide (10 kg ha^{-1}); (5) urea plus Na_2SO_4-rate I (510 kg ha^{-1}); and (6) urea plus Na_2SO_4-rate II (1020 kg ha^{-1}) applied 2 h before permanent flooding to the Texmont experimental chambers. The SO_4^{-2} rates of the Na_2SO_4 treatments approximated the SO_4^{-2} concentrations in 100 and 200 kg $(NH_4)_2SO_4$-N. The treatments were replicated three times.

Eighteen plexiglass base chambers (microplots) were placed in a rice bay and driven 10 cm into the soil down to the hardpan before the permanent flooding. Each gas collection chamber consisted of a permanently installed base unit (30.0×30.0×30.0 cm) with an open bottom and a removable clear plexiglass top (30.0×30.0×30.0 cm). Floodwater was used to seal the top to the base during CH_4 collection periods. As the height of the rice increased, the base units were stacked to prevent leaf damage. Chamber headspace heights averaged about 80–85 cm during the middle and late growing season. A rubber-septum sampling port, glass thermometer, battery-operated fan, and a pressure equilibrator were installed in the top of each chamber (Lindau et al. 1991). The equilibrator was constructed of 7.6 m of plastic tubing (1.5 mm inside diameter) and helped maintain an equilibrium gas pressure between the inside and outside of the chambers during gas sampling.

Headspace gas samples were collected 21 times, on days 0, 4, 8, 17, 21, 24, 28, 31, 35, 38, 42, 45, 49, 52, 56, 59, 63, 66, 70, 73, and 77 after treatment and permanent flooding. Chamber tops were sealed to the base units to determine the linear rate of CH_4 buildup and collection times ranged from 1 h (early growing season) to 0.25 h (remainder of growing season). Methane gas samples were withdrawn from the headspace volume through the sampling port with a gas-tight syringe and immediately transferred into evacuated glass Vacutainers and sealed (Lindau et al. 1991). Chamber headspace heights and temperatures were measured and recorded on each sampling date. All collected gas samples were analyzed for CH_4 within 2 h of field sampling.

Laboratory procedures

A Perkin-Elmer 900 flame ionization gas chromatograph equipped with a peak integrator was used to measure CH_4 concentrations in the collected headspace gas samples. A 1.5-cm^{-3} gas aliquot was injected into a stainless steel column (0.003×2.4 m) packed with HayeSep D polymer (100–200 mesh). The column temperature was set at 40 °C and the injector and manifold at 110 °C.

Methane fluxes (F) were estimated using the following closed-chamber equation (Ryden and Rolston 1983):

$$F = (V/A)(273/T)(\Delta c/\Delta t),$$

where V is the volume of the chamber headspace, A is the chamber-base soil-surface area, $\Delta c/\Delta t$ is the change in CH_4 concentration per unit time, and T is the absolute temperature of the headspace air. The CH_4 emission data were subjected to analysis of variance using the General Linear Models and Duncan's multiple range test ($P = 0.05$) procedures of the Statistical Analysis System (SAS Institute 1988).

Results and discussion

Methane emissions from the Texmont experimental microplots were measured over the 1991 Louisiana main rice-cropping season. Gas sampling was initiated 2 h before the permanent flooding and was continued for 77 days or up to 3 days before the harvest.

Fluxes of CH_4 from the experimental plots receiving the two major sources of rice fertilizer N over the Texmont cropping season are graphed on Fig. 1. The lowest CH_4 emissions were measured for about 2–3 weeks after the flooding and were attributed to soil redox potentials above the critical CH_4 production Eh value of about −200 mV (Patrick and DeLaune 1977). After the initial 3 weeks, CH_4 emissions from the urea- and $(NH_4)_2SO_4$-treated plots steadily increased over the next 28 days to the first peak emission period, and then declined over the next 10 days (Fig. 1). Methane emissions rose sharply over the next 4 days and reached the highest recorded seasonal flux values on day 63. During the remaining 14 days CH_4 emissions declined, due to bay drainage and drying soil conditions. Measured CH_4 fluxes from the urea-treated plots were consistently higher than the CH_4 fluxes from the $(NH_4)_2SO_4$ plots except on days 49 and 77. Methane evolution from the urea-treated plots ranged from <30 g ha^{-1} day^{-1} (early growing season) to 12.04 kg ha^{-1} day^{-1} (day 63) and the daily rate over the

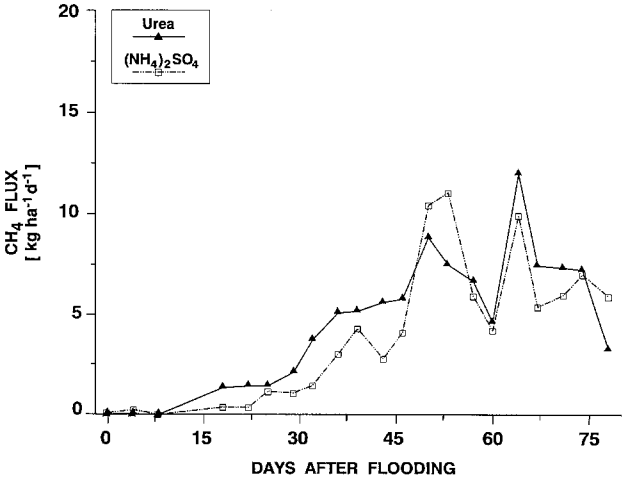

Fig. 1. Effect of urea and $(NH_4)_2SO_4$ fertilizers on CH_4 emissions from flooded Louisiana Texmont rice field plots

77-day sampling period was 4.6 kg CH_4 emitted ha^{-1} day^{-1}. Emissions of CH_4 from the $(NH_4)_2SO_4$-treated microplots varied from a low of <30 g ha^{-1} day^{-1} to a peak of 10.48 kg ha^{-1} day^{-1} (day 49), followed by a second peak of 9.98 kg ha^{-1} measured on day 63 (Fig. 1). The daily flux from the $(NH_4)_2SO_4$ plots averaged about 3.8 kg ha^{-1} day^{-1} over the Texmont season. Statistical data showed that the CH_4 emissions from the urea-N plots were significantly higher than the measured fluxes from the $(NH_4)_2SO_4$-treated plots for 48% of the 21 sets sampled. An additional 10 sampling sets showed no significant differences. Only on the final sampling date were CH_4 fluxes from the $(NH_4)_2SO_4$ treatment plots significantly higher (Fig. 1). The decrease in CH_4 emissions from the $(NH_4)_2SO_4$ plots was attributed in part to the presence of the SO_4^{-2} ions and to sulfate-reducing bacteria outcompeting the methanogens for substrates (Patrick and DeLaune 1977; Kristjansson et al. 1982). Freney et al. (1982) has also suggested that the reoxidation of S^{-2} to SO_4^{-2} in the rice plant rhizosphere may maintain CH_4 inhibition in flooded rice paddies over longer periods of time, as measured in the $(NH_4)_2SO_4$ Texmont plots.

The effects of the nitrification inhibitors encapsulated calcium carbide and dicyandiamide on CH_4 emissions from the treated urea plots are shown in Fig. 2. An overview shows the same general seasonal CH_4 flux pattern that was observed for the urea- and $(NH_4)_2SO_4$-treated plots. Methane evolution from the calcium carbide- and dicyandiamide-treated plots steadily increased over the first half of the growing season, followed by two peak periods around the heading and grain-ripening stages. After plot drainage CH_4 fluxes declined. Methane from the calcium carbide- plus urea-treated plots ranged from a low of <30 g ha^{-1} day^{-1} (day 8) to 7.73 kg ha^{-1} day^{-1} on day 49. Between days 49 and 66, CH_4 emissions dropped to 2.77, followed by an increase to 5.72 kg ha^{-1} day^{-1} (days 63–66). Emissions of CH_4 on the final sampling date still averaged 4.8 kg ha^{-1} day^{-1}, which was 7 days after bay drainage. Over the rice season, CH_4 fluxes from the calcium carbide- plus urea-treated plots averaged 3.0 kg ha^{-1} day^{-1}, which showed a significant decrease compared to the urea treatment (4.6 kg ha^{-1} day^{-1}). Methane fluxes from the dicyandiamide plus urea plots were higher compared to the calcium carbide treatment but lower than those from the urea treatment (Fig. 2). Emissions from the dicyandiamide treatment varied from <30 g ha^{-1} day^{-1} (days 4 and 8) to 9.53 kg ha^{-1} day^{-1} measured on day 73. Additional peak emissions were recorded on days 38 (6.20), 49 (6.47) and 63 (9.05 kg ha^{-1} day^{-1}). Over the first 60 days, dicyandiamide reduced CH_4 evolution but for the remaining growing season appears to have lost its inhibition affect on CH_4 production. This indicates that the applied dicyandiamide had been consumed or degraded late in the growing season (Bronson et al. 1989). Analysis of variance for 40% of the sampling sets showed no significant differences between urea, encapsulated calcium carbide plus urea and dicyandiamide plus urea in CH_4 emission rates. For the remaining sets, significant differences were computed. On four sampling days the urea treatment CH_4 emissions were significantly higher (0.05 level) than the calcium carbide and dicyandiamide treatment CH_4 fluxes but the calcium carbide and decyandiamide treatments were not significantly different. For an additional four collection sets, the CH_4 urea treatment fluxes were significantly higher than the calcium carbide fluxes but no differences were computed between urea and dicyandiamide and calcium carbide and dicyandiamide. For the remaining sets, either the urea or the dicyandiamide treatment fluxes or both were significantly higher than the measured CH_4 fluxes from the encapsulated calcium carbide plots.

The effect of two application rates of Na_2SO_4 on CH_4 evolution from the urea plots is displayed in Fig. 3. Methane concentrations from the Na_2SO_4 treatments steadily increased over the first 56 days but decreased on day 59. The peak CH_4 periods occurred from days 63 to 70, followed by a decrease in emissions (Fig. 3). Methane emissions from the Na_2SO_4-rate I-treated plots ranged from non-detectable to 9.21 kg ha^{-1} day^{-1} (day 63) and rate II fluxes varied from <30 g ha^{-1} day^{-1} to

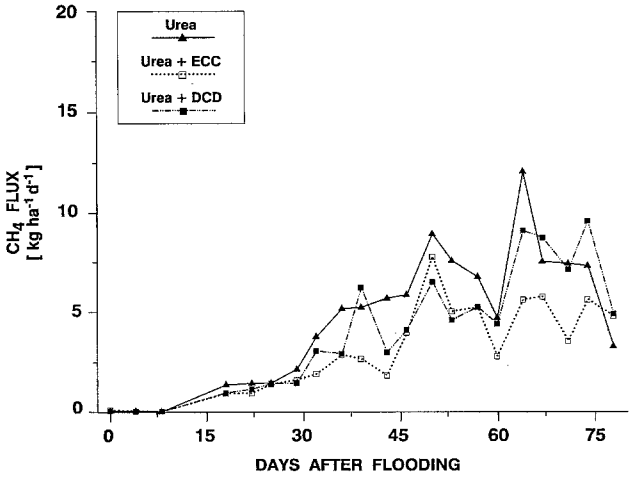

Fig. 2. Effect of ECC and DCD nitrification inhibitors on CH_4 emissions from flooded Louisiana Texmont rice field plots

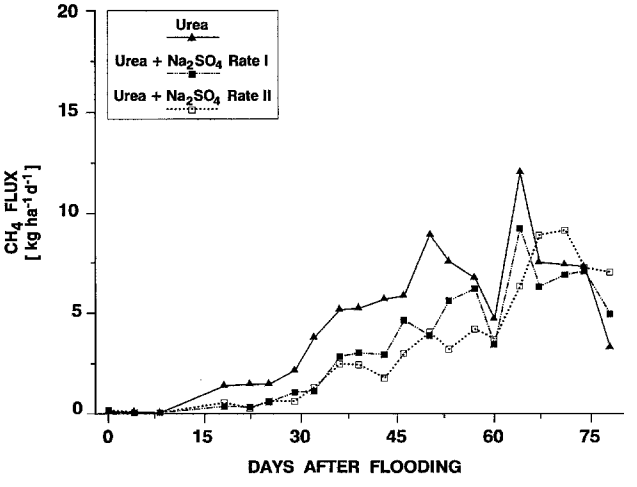

Fig. 3. Effect of 2 application rates of Na_2SO_4 on CH_4 emissions from flooded Louisiana Texmont rice field plots

9.11 kg ha^{-1} day^{-1} measured on day 70. For the first 63 days, emissions of CH_4 from the Na_2SO_4 treatments were reduced compared to the urea plots (Fig. 3). Average daily CH_4 emissions from the Na_2SO_4-rate I and Na_2SO_4-rate II (over the rice season) were approximately 3.4 and 3.2 kg ha^{-1} day^{-1}, respectively. On seven sampling dates (early and late season) no significant difference in CH_4 emissions was recorded between the urea, urea plus Na_2SO_4-I, and urea plus Na_2SO_4-II treatments. Fourteen sampling sets showed significant differences and for 71% (10 sets) the CH_4 fluxes from the urea-treated plots were significantly higher than Na_2SO_4-I and Na_2SO_4-II but no differences were observed between Na_2SO_4 treatments. For three of the remaining significant sets, CH_4 emissions from the urea-treated plots were significantly higher compared to one of the Na_2SO_4 treatments. The reduction in CH_4 emissions from the Na_2SO_4 treatments was due in part to the SO_4^{-2} and Na^+ (165 and 330 kg ha^{-1}) ion effects on methanogenic bacteria (Freney et al. 1982; Holzapfel-Pschorn et al. 1985).

Over the rice-growing season, estimates of total CH_4 evolution were calculated from the areas under the treatment emission curves (Figs. 1, 2, 3). Approximately 230, 240, 260, 290, 310, and 360 kg CH_4 ha^{-1} were released to the atmosphere from the calcium carbide plus urea-, Na_2SO_4-rate II plus urea-, Na_2SO_4-rate I plus urea-, $(NH_4)_2SO_4$, DCD plus urea-, and urea-treated microplots, respectively. Of the compounds investigated, encapsulated calcium carbide was the most effective in reducing CH_4 emissions. Reductions in CH_4 emissions ranged from 14 (dicyandiamide) to 35% (calcium carbide).

Methane emissions from the Texmont rice plots as affected by N source, nitrification inhibitor, and SO_4^{2-} source are comparable to those in published research. In a California study, Cicerone et al. (1983) measured CH_4 emissions from flooded rice paddies, and daily emissions ranged from <10 g to 49.4 kg ha^{-1} with the highest fluxes measured 2–3 weeks before the harvest. Methane fluxes from the Texmont treatment plots displayed a strong seasonal dependence, which has also been shown in Californian and Italian field studies (Cicerone et al. 1983; Holzapfel-Pschorn and Seiler 1986; Schutz et al. 1989). Rice paddies in Spain evolved CH_4 at 0.5–3.4 kg ha^{-1} day^{-1} with maximum emissions during the heading and flowering stages (Seiler et al. 1984). These peak CH_4 emission periods have also been measured in the Texmont field experiment and by other rice researchers (Holzapfel-Pschorn et al. 1986; Schutz et al. 1989). The two CH_4 flux maxima measured from the Louisiana Texmont plots may have been caused by rice root exudates, decaying roots, and development of the rice-plant gas-transport system (Schutz et al. 1989; Sass et al. 1990). The observed drop in CH_4 emissions between the two maxima may have been due to reduced organic matter availability and/or the plant growth stage (Lindau et al. 1991). In an earlier study, Lindau et al. (1991) measured CH_4 emissions from flooded Lemont rice plants as affected by the rate of applied urea-N. Over the 86-day Lemont cropping season approximately 210, 300, 310, and 370 kg CH_4 ha^{-1} was evolved from the 0, 100, 200, and 300 kg urea-N ha^{-1} treatments, respectively. Bronson and Mosier (1991) assessed the effect of encapsulated calcium carbide on CH_4 emissions from flooded rice in a greenhouse study. After 30 days, total CH_4 emitted from the calcium carbide plus urea and urea treatments averaged 3.6 and 39.0 mg per pot. The application of encapsulated calcium carbide reduced CH_4 emissions by 90% compared to the urea control plots (Bronson and Mosier 1991). In a laboratory experiment, Holzapfel-Pschorn et al. (1985) investigated the influence of a 0.1% Na_2SO_4 solution on CH_4 emissions from a flooded rice culture. After an incubation period of 100 days, CH_4 emissions from the control and 0.1% Na_2SO_4 treatments averaged about 50 and <0.2 μg culture^{-1} h^{-1}.

Conclusion

The results of this field study showed that encapsulated calcium carbide, dicyandiamide, $(NH_4)_2SO_4$, and Na_2SO_4 had a mitigating effect on CH_4 emissions from flooded Texmont rice microplots compared to the urea treatment. Encapsulated calcium carbide and dicyandiamide reduced CH_4 emissions from urea-treated plots by 35% and 14% over the Louisiana cropping season. The $(NH_4)_2SO_4$, Na_2SO_4-rate I, and Na_2SO_4-rate II treatments reduced CH_4 by 20%, 28%, and 33%, respectively. Bay size (0.75 ha) field studies need to be conducted over several rice-growing seasons to verify the microplot results and determine the effects of nitrification inhibitors on CH_4 oxidation and grain yields. The results of these studies may help agriculturists to design local management practices that can use nitrification inhibitors to increase N uptake and reduce CH_4 emissions in flooded rice systems.

Acknowledgment. Funding for this research was provided in part by the Department of Energy (Award No. DE-FC03-90ER61010). This paper is a joint contribution from Louisiana State University and the US Department of Agriculture.

References

Blake DR, Rowland FS (1988) Continuing worldwide increase in tropospheric methane, 1978–1987. Science 239:1129–1131

Bouwman AF (1991) Agronomic aspects of wetland rice cultivation and associated methane emissions. Biogeochemistry 15:65–88

Bronson KF, Mosier AR (1991) Effect of encapsulated calcium carbide on dinitrogen, nitrous oxide, methane, and carbon dioxide emissions from flooded rice. Biol Fertil Soils 11.116–120

Bronson KF, Touchton JT, Hauck RD (1989) Decomposition rate of dicyandiamide and nitrification inhibition. Commun Soil Sci Plant Anal 20:2067–2078

Cicerone RJ, Shetter JD, Delwiche CC (1983) Seasonal variations of methane flux from a California rice paddy. J Geophy Res 88:11022–11024

De Bont JAM, Lee KK, Bouldin DF (1978) Bacterial oxidation of methane in a rice paddy. Ecol Bull 26:91–96

Freney JR, Jacq VA, Baldensperger JF (1982) The significance of the biological sulfur cycle in rice production. Dev Plant Soil Sci 5:271–317

Holzapfel-Pschorn A, Seiler W (1986) Methane emission during a cultivation period from an Italian rice paddy. J Geophys Res 91:11803–11814

Holzapfel-Pschorn A, Conrad R, Seiler W (1985) Production, oxidation and emission of methane in rice paddies. FEMS Microbial Ecol 31:343–351

Holzapfel-Pschorn A, Conrad R, Seiler W (1986) Effects of vegetation on the emission of methane from submerged paddy soils. Plant and Soil 92:223–233

International Rice Research Institute (1988) Worldwide rice statistics 1987. IRRI, Los Baños, Philippines

Knowles R (1979) Denitrification, acetylene reduction, and methane metabolism in lake sediment exposed to acetylene. Appl Environ Microbiol 38:486–493

Kristjansson JK, Schonheit P, Thauer RK (1982) Different K_s values for hydrogen and methanogenic and sulfate-reducing bacteria: An explanation for the apparent inhibition of methanogenesis by sulfate. Arch Microbiol 131:278–282

Lindau CW, Bollich PK, DeLaune RD, Patrick WH Jr, Law VJ (1991) Effect of urea fertilizer and environmental factors on CH_4 emission from a Louisiana, USA rice field. Plant and Soil 136:195–203

Patrick WH Jr, DeLaune RD (1977) Chemical and biological redox systems affecting mutrient availability in coastal wetlands. Geosci Manage 18:131–137

Reddy KR, Patrick WH Jr (1984) Nitrogen transformations and loss in flooded soils and sediments. CRC Crit Rev Environ Control 13:274–309

Ryden JC, Rolston DE (1983) The measurement of denitrification. In: Freney JR, Sampson JR (eds) Gaseous loss of nitrogen from plant–soil systems. Martinus Nijhoff/Dr W Junk publishers, The Hague, pp 91–132

SAS Institute (1988) SAS/STAT User's Guide, Release 6.03 edn. SAS Institute Inc, Cary, North Carolina

Sass RL, Fisher FM, Harcombe PA (1990) Methane production and emission in a Texas rice field. Global Biogeochem Cycles 4:47–68

Schutz H, Holzapfel-Pschorn A, Conrad R, Rennenberg H, Seiler W (1989) A 3-year continuous record on the influence of daytime, season, and fertilizer treatment on methane emission rates from an Italian rice paddy. J Geophy Res 94:16405–16416

Seiler W, Holzapfel-Pschorn A, Conrad R, Scharffe D (1984) Methane emission from rice paddies. J Atmos Chem 1:241–268

United States Envrionmental Protection Agency (1990) Overview of methane's contribution to global warming. In: Methane emissions and opportunities for control. USEPA/Air and Radiation, EPA/400/9-90/007, Washington, DC, pp 2–24

United States Environmental Protection Agency (1991) Introduction. In: Braatz BV, Hogan KB (eds) Substainable rice productivity and methane reduction research plan. USEPA/Office of Air and Radiation, Washington, DC, pp 12–18

Van Breeman N, Feijtel TCJ (1990) Soil processes and properties involved in the production of greenhouse gases, with special relevance to soil taxonomic systems. In:Bouwmann AF (ed) Soils and the greenhouse effect. John Wiley, Chichester, pp 195–223