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Biology and Fertility of Soils

Effect of encapsulated calcium carbide on dinitrogen, nitrous oxide, methane, and carbon dioxide emissions from flooded rice

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Summary. The efficiency of N use in flooded rice is usually low, chiefly due to gaseous losses. Emission of CH_4, a gas implicated in global warming, can also be substantial in flooded rice. In a greenhouse study, the nitrification inhibitor encapsulated calcium carbide (a slow-release source of acetylene) was added with 75, 150, and 225 mg of 75 atom % ^{15}N urea-N to flooded pots containing 18-day-old rice (*Oryza sativa* L.) plants. Urea treatments without calcium carbide were included as controls. After the application of encapsulated calcium carbide, 3.6 µg N_2, 12.4 µg N_2O-N, and 3.6 mg CH_4 were emitted per pot in 30 days. Without calcium carbide, 3.0 mg N_2, 22.8 µg N_2O-N, and 39.0 mg CH_4 per pot were emitted during the same period. The rate of N added had a positive effect on N_2 and N_2O emissions, but the effect on CH_4 emissions varied with time. Carbon dioxide emissions were lower with encapsulated calcium carbide than without. The use of encapsulated calcium carbide appears effective in eliminating N_2 losses, and in minimizing emissions of the "greenhouse gases" N_2O and CH_4 in flooded rice.

Key words: Denitrification – Flooded soil – ^{15}N – Urea – Wetland rice – *Oryza sativa* L.

Gaseous losses of N_2 and N_2O from denitrification, and NH_3 volatilization (De Datta 1981; Fillery et al. 1986; Mosier et al. 1989; Buresh and De Datta 1990), lead to low fertilizer-use efficiency in flooded rice. Stategies used to reduce these losses include slow-release urea (Carter et al. 1986), deep placement of urea supergranules (Cao et al. 1984), split applications of N (Cao et al. 1984), and amending urea fertilizer with urease and or nitrification inhibitors (Simpson et al. 1985; Buresh et al. 1988).

CH_4 emissions from rice, while not contributing to the N fertilizer loss, are of concern because CH_4 is an important "greenhouse gas", with 5 times more infrared sorbing capability than CO_2 (on a mole basis, considering the decay time of gases in the atmosphere; Rodhe 1990).

Bouwman (1990) has estimated that 20–45% of the total global emissions of CH_4 originate from flooded rice fields. Fertilizer N can increase CH_4 fluxes in rice (Cicerone and Shetter 1981).

Several workers have reported that the addition of nitrification inhibitors, such as nitrapyrin or C_2H_2, with urea indirectly reduces N_2O production in upland soils (Bremner and Blackmer 1979; Cribbs and Mills 1979; Aulakh et al. 1984). Banerjee and Mosier (1989) were the first to demonstrate that encapsulated calcium carbide is a slow-release source of C_2H_2 that inhibits nitrification and reduces N_2O fluxes in flooded soils. Acetylene also inhibits CH_4 production (Raimbault 1975; Knowles 1979) at 0.0101×10^6 Pa, a concept that has not been applied to flooded rice systems. In the present study, therefore, the use of encapsulated calcium carbide as an inhibitor of denitrification and CH_4 production was tested in a greenhouse study in flooded rice.

Materials and methods

Two g ground corn (*Zea mays* L.) straw (0.34% N and 42.9% C) was added to pots (16 cm high, 189 cm^2 in area) containing 2 kg Nunn clay loam soil (fine, montmorillonitic, mesic, Aridic Argiustoll). The soil had a pH of 7.9, 2.1% organic matter, 21 mg kg^{-1} NO_3^--N electrical conductivity 1.3 mmhos cm^{-1}, and medium to high levels of NH_4HCO_3-diethylenetriaminepentaacetic acid-extractable Ca, Mg, P, K, Zn, and Fe. The soil in the pots was flooded, and puddled by hand. Every 3–5 days for 19 days, and every 8–10 days thereafter, pH and redox potential (Eh) were measured at a depth of 5 cm, with pH and platinum electrodes in 6 of the 18 pots. Three 15-day-old rice (*Oryza sativa* L.) seedlings, cultivar 'IR 46', were transplanted to each pot 15 days after the start of permanent flooding. Three days later, 75, 150, or 225 mg (equivalent to 40, 80, and 120 kg N ha^{-1}) 75 atom % ^{15}N-labeled urea-N was added to the pots with or without encapsulated calcium carbide (0.25 g CaC_2 and 0.25 g coating). The 1–2 mm CaC_2 particles were coated first with a layer of carnuba wax (45% weight and CaC_2), secondly with a layer of beeswax (45% weight CaC_2), and final-

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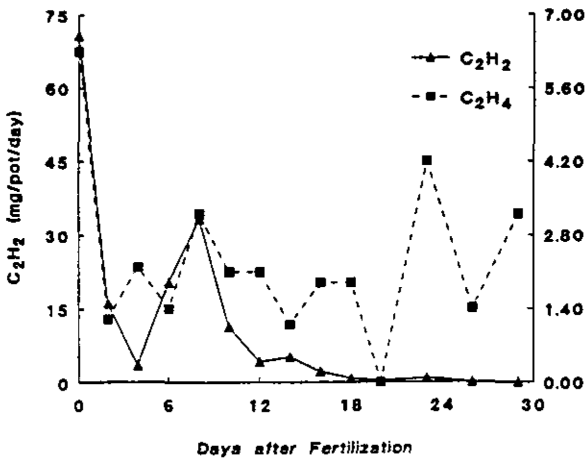

Fig. 1. C_2H_2 and C_2H_4 emissions from flooded rice after the application of encapsulated calcium carbide (CV 178%)

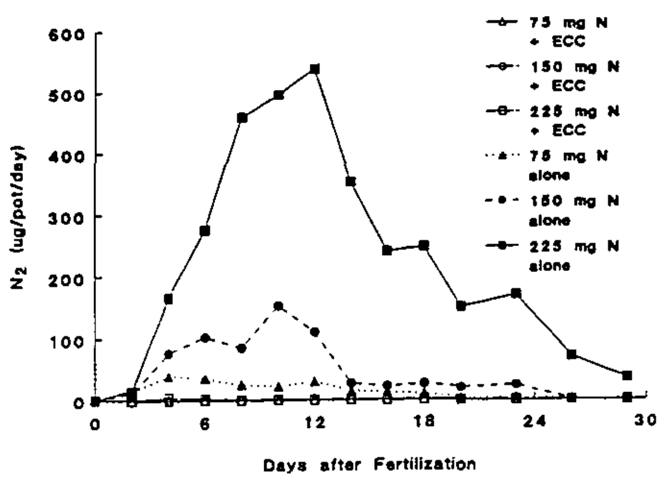

Fig. 2. N_2 emissions from flooded rice (CV 81%) as affected by N rate and the presence of encapsulated calcium carbide (*ECC*)

ly by a layer of shellac (10% weight of CaC_2). All treatments were replicated 3 times (i.e. 18 pots).

At 0, 2, 4, 6, 8, 10, and 12 days after fertilization, 3-liter vented chambers (Hutchinson and Mosier 1981) were placed over the pots from 9 to 10 a.m. At 14, 16, 18, 20, 23, 26, and 29 days after fertilization, 6-liter chambers were used for the same 1-h period. Fifty milliliter samples were taken from four of the pots at time zero and from all of the pots after 1 h.

N_2O was determined by gas chromatography as described by Mosier and Mack (1980). For N_2 analysis, the chambers were replaced on the pots and left overnight for 14–16 h. N_2 was determined by isotope ratio mass spectrometry (Mosier et al. 1986) on a VG-Micromass 903.

CH_4, C_2H_2, and C_2H_4 were measured by gas chromatography using a flame ionization detector (250 °C) and a 3-m stainless steel column (3.175 mm outside diameter) containing Porapak N (50 °C). Samples were analyzed for CO_2 on a Tracor MT-150 G gas chromatograph (Tracer Instruments, Austin, Texas, U.S.A.) fitted with a ultrasonic detector (145 °C) after passing through a 3-m stainless steel column (3.175 mm outside diameter) containing Porapak Q (75 °C). Eighteen days after fertilization, 10 mg 99.9 atom % $^{13}CH_4$ was injected into the soil of the pots fertilized with 225 mg urea-N pot^{-1}. $^{13}CH_4$ was injected through septa in fittings on the sides of the pots after the covers were put in place for the night. CO_2 was analyzed from the headspace of the covers after 16 h by gas chromatography as described above. For atom % $^{13}CO_2$ analysis, enough sample to contain 140 µg CO_2 was injected through a septum into an evacuated 500-ml glass jar that had a tin capsule containing 10 mg $Ca(OH)_2$, 10 mg V_2O_5, and 15 µl H_2O. After 24 h, the tin capsule was removed from the jar and analyzed for C and atom % ^{13}C on a Carlo Erba C/N analyzer (Carlo Erba Instruments, Rodano MI (Italy)) coupled to a VG-Micromass 903 mass spectrometer (VG Micromass LTO, VG Isogas, Middlewich, England) with a Europa Scientific Interface (Europa Scientific, Crewe, England).

Data analysis

Fluxes (*F*) of N_2, N_2O, CH_4, and CO_2 were calculated using the following equation (Rolston 1986):

$$F = \frac{V \Delta C}{At}$$

where *V* is the volume of the chamber (3 or 6 liters), ΔC is the change in concentration of the gas during time *t*, and *A* is the area of the chamber (189 cm^2).

The gas flux data were subject to analysis of variance for each date using the General Linear Models procedure in the Statistical Analysis System framework (SAS Institute 1985). Distributions were checked for normality ($P = 0.05$) using the Shapiro-Wilk statistic (Shapiro and Wilk 1965). If the normality assumption was not met, then treatment means were separated using the Kruskal-Wallis Test with $P = 0.05$ (Kruskal and Wallis 1952).

Results and discussion

The redox potential in the soil declined rapidly after flooding, probably due in part to addition of the readily decomposable corn straw. By 19 days after flooding, Eh (adjusted to pH 7) was -230 mV $\pm$ 11 (mean $\pm$ SD) and remained at this level throughout the study, low enough for CH_4 production (Ponnamperuma 1972).

Acetylene (C_2H_2) emitted from the treatments with encapsulated calcium carbide reached 71 mg pot^{-1} day^{-1} on the day of fertilization, then generally declined (Fig. 1). Between 14 and 26 days after fertilization, the C_2H_2 flux continued to decline from 5 to <0.1 mg pot^{-1} day^{-1}. Ethylene (C_2H_4) was produced in small amounts in the calcium carbide-treated pots only, probably from C_2H_2 reduction (Fig. 1). The flux of C_2H_4 was highest on the day of fertilization (6.3 µg pot^{-1} day^{-1}. For the first 14 days after fertilization, C_2H_4 emissions correlated well with the C_2H_2 emissions ($r = 0.90$, $P < 0.01$).

N_2 emissions from urea alone increased linearly ($P < 0.01$) with the N rate (Fig. 2). Without the calcium carbide, maximum fluxes of 40.1, 153.2, and 538.3 µg N_2 pot^{-1} day^{-1} (all different at $P = 0.05$) were measured with 75, 150, and 225 mg N pot^{-1}, respectively. With calcium carbide, N_2 was detected only at the highest N rate (maximum of 4 µg pot^{-1} day^{-1}). Averaged over the N rate, a total of 3.0 mg N_2 was emitted from urea alone in 30 days, while only 3.6 µg N_2 was lost with urea plus calcium carbide in the same time period. Mohanty and Mosier (1990) reported that encapsulated calcium carbide effectively eliminated N_2 losses from flooded rice in field and in greenhouse experiments.

N_2O emissions were low in all treatments (Fig. 3 a), although, the N rate had a positive effect ($P < 0.01$). A maximum flux (averaged over the N rate) of 1.2 and 2.1 µg N_2O-N pot^{-1} day^{-1} (different at $P = 0.05$) was

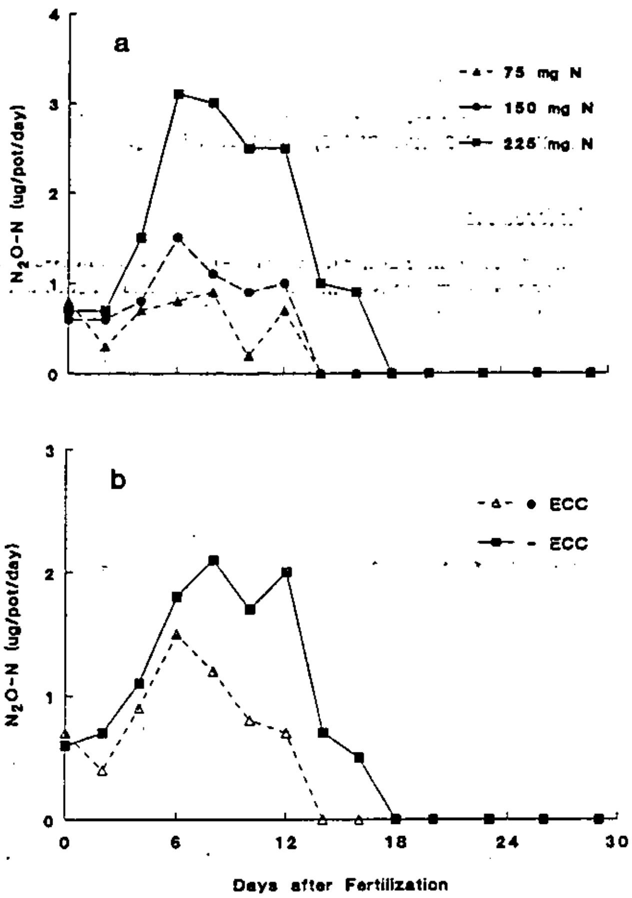

Fig. 3a, b. N_2O emissions from flooded rice (CV 70%) (a) as affected by N rate, average with and without encapsulated calcium carbide (*ECC*), and (b) as affected by *ECC*, averaged over N rate

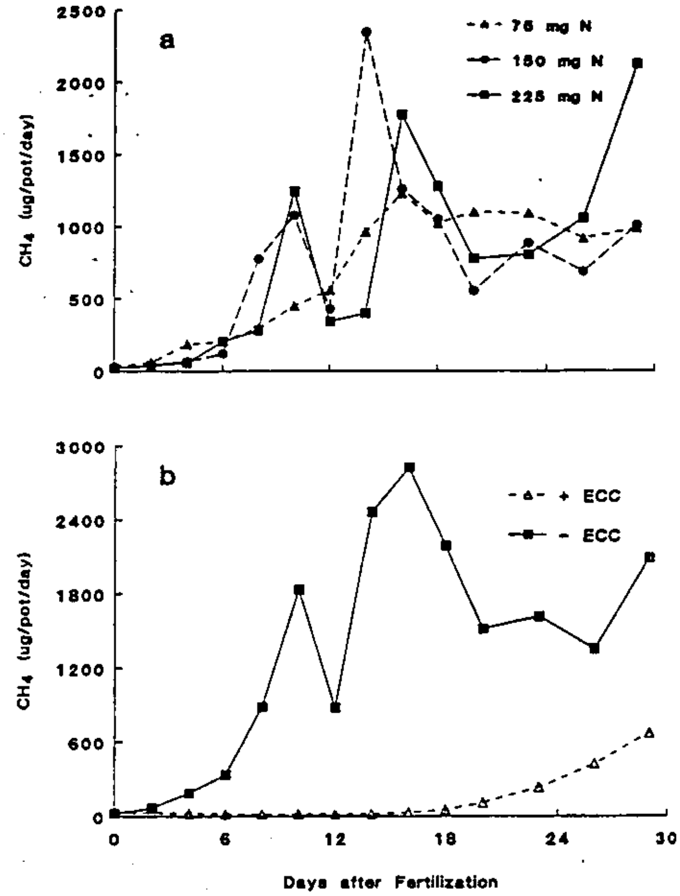

Fig. 4a, b. CH_4 emissions from flooded rice (CV 81%) (a) as affected by N rate, average with and without encapsulated calcium carbide (*ECC*), and (b) as affected by ECC, averaged over N rate

measured with and without encapsulated calcium carbide, respectively (Fig. 3b). The proportion of N_2O-N to (N_2O-N+N_2) over the 30-day period was <0.01%. Mosier et al. (1989, 1990) reported N_2O-N/(N_2O-N+N_2) emissions in flooded rice ranging from 1 to 6% in greenhouse and field studies. Freney et al. (1981) measured N_2O losses from flooded rice at only 0.1% of the N fertilizer applied. The small $N_2O/(N_2O+N_2)$ ratio measured in the present study was probably due to the low redox potential. There was no interaction between the N rate and the presence of encapsulated calcium carbide ($P>0.05$).

Seventeen days after flooding, small CH_4 emissions (35 µg pot^{-1} day^{-1}) began to appear in all pots; at the same time Eh neared −230 mV. The effect of the N rate on CH_4 emissions was not constant over the 30-day period (Fig. 4a). The N rate had a negative effect on CH_4 flux 0, 2, and 4 days after fertilization ($P<0.05$). In the period between 6 and 26 days after fertilization, the N rate had no effect on CH_4 emissions, but by 29 days after fertilization CH_4 evolution had begun to increase with the N rate ($P<0.01$). This trend agrees in part with that observed by Lindau et al. (1990), who reported in a field study that for up to 17 days after fertilization CH_4 fluxes were lower in plots given 120 kg urea-N ha^{-1} compared to unfertilized controls. By 21 days after fertilization in that study, the CH_4 emissions were higher from pots with urea than from those without. Many workers have studied the effects of N fertilizer on CH_4 emissions in flooded rice, with varying results. Holzapfel-Pschorn and Seiler (1986) used various N sources (including urea) but found no effect on CH_4 flux. Schütz et al. (1989a) observed either a positive or negative urea-N effect, depending on the method of fertilizer application.

CH_4 fluxes reached a maximum of 2816 µg pot^{-1} day^{-1} 16 days after fertilization without calcium carbide, while only 13.8 µg CH_4 pot^{-1} day^{-1} was emitted in the presence of encapsulated calcium carbide (Fig. 4b). After 18 days, CH_4 evolution in the calcium carbide treated pots began to increase, corresponding to a disappearance of C_2H_2. A total of 39.0 mg CH_4 (averaged over the N rate) was emitted with urea alone, and only 3.6 mg CH_4 was evolved with urea plus calcium carbide. No interaction between the N rate and the presence of encapsulated calcium was found ($P>0.05$).

N_2, N_2O, and CH_4 gases entrapped in the soil were assumed to be negligible in this rice-planted system. Rice plants serve as a conduit from flooded soil to the atmosphere for N_2 and N_2O (Mosier et al. 1990) and for CH_4 (Schütz et al. 1989b).

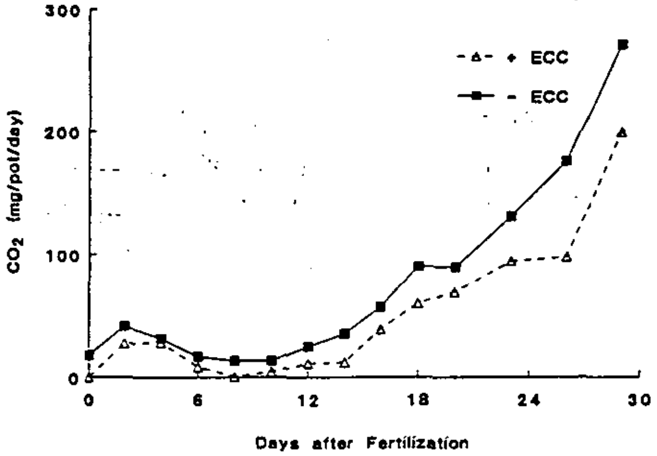

Fig. 5. CO_2 emissions from flooded rice (CV 62%) as affected by encapsulated calcium carbide (*ECC*), averaged over N rate

The N rate had no consistent effect on CO_2 fluxes, and therefore the data presented are averaged over the N rate (Fig. 5). CO_2 emissions were lower in the presence of C_2H_2 versus the controls for all dates except one ($P<0.05$). This may have been due to an actual suppression of soil and root respiration by C_2H_2. Within the encapsulated calcium carbide treatments, there was a negative correlation ($r = 0.32$, $P<0.01$) between CO_2 fluxes and the levels of C_2H_2. The higher CO_2 emissions in the absence of calcium carbide may also have been due to oxidation of a large part of the CH_4 produced. The CO_2 emissions were positively correlated ($r = 0.30$, $P<0.01$) with CH_4 emissions during the entire 30-day period, probably due to oxidation of CH_4, as mentioned above. Holzapfel-Pschorn and Seiler (1986) reported that 75% of the CH_4 produced in a reduced rice soil can be oxidized to CO_2. In the present study, $^{13}CH_4$ was added to the soil 18 days after fertilization and then the covers were installed. The atom % $^{13}CO_2$ of the initial headspace gas was 1.1219 ± 0.0020 (mean$\pm$SD). After 16 h, the atom % $^{13}CO_2$ content from pots given the high rate of urea-N with encapsulated calcium carbide was 1.1221 ± 0.0015, and 1.1492 ± 0.0081 from those with the high rate of urea-N without calcium carbide. The enrichment of CO_2 with ^{13}C indicated that oxidation of some of the added $^{13}CH_4$ occurred in the control pots, but not in the presence of encapsulated calcium carbide. Acetylene partial pressures of 0.0101×10^6 Pa inhibit CH_4 oxidation (De Bont and Mulder 1974; Knowles 1979).

Conclusion

The nitrification inhibitor, encapsulated calcium carbide, showed a strong mitigating effect on emissions of N_2 and CH_4. N_2O fluxes were also reduced with calcium carbide, but the magnitude of losses with urea alone were very small in flooded rice. Losses of N_2 and N_2O increased with the N rate. The effect of the N rate on CH_4 emissions was variable over the 30 days. More research is needed to determine the response of CH_4 fluxes to the N rate in flooded systems. In conclusion, encapsulated calcium carbide appears to be an effective tool in improving N-use efficiency in rice and in reducing emissions of the radiatively active gases, N_2O and CH_4.

References

Aulakh MS, Rennie DA, Paul EA (1984) Acetylene and N-Serve effects upon N_2O emissions from NH_4^+ and NO_3^- treated soils under aerobic and anaerobic conditions. Soil Biol Biochem 16:351–356

Banerjee NK, Mosier AR (1989) Coated calcium carbide as nitrification inhibitor in upland and flooded soils. J Indian Soc Soil Sci 37:306–313

Bouwman AF (1990) The role of soils and land use in the greenhouse effect. In: Bouwman AF (ed) Soils and the greenhouse effect. Chichester: John Wiley, pp 575

Bremner JM, Blackmer AM (1979) Effects of acetylene and soil water content on emission of nitrous oxide from soils. Nature (London) 280:380–381

Buresh RJ, De Datta SK (1990) Denitrification losses from puddled rice soils in the tropics. Biol Fertil Soils 9:1–13

Buresh RJ, De Datta SK, Padilla JL, Samson MI (1988) Field evaluation of two urease inhibitors with transplanted lowland rice. Agron J 80:763–768

Cao ZH, De Datta SK, Fillery IRP (1984) Effect of placement methods on floodwater properties and recovery of applied N [^{15}N-labeled urea) in wetland rice. Soil Sci Soc Am J 48:196–203

Carter MF, Vlek PLG, Touchton JT (1986) Agronomic evaluation of new urea forms for flooded rice. Soil Sci Soc Am J 50:1055–1060

Cicerone RJ, Shetter JD (1981) Sources of atmospheric methane: Measurements in flooded rice paddies and a discussion. J Geophys Res 86:7203–7209

Cribbs WH, Mills HA (1979) Influence of nitrapyrin on the evolution of N_2O from organic medium with and without plants. Commun Soil Sci Plant Anal 10:785–794

De Bont JAM, Mulder EG (1974) Nitrogen fixation and cooxidation of ethylene by a methane-utilizing bacterium. J Gen Microbiol 83:113–121

De Datta SK (1981) Principles and practices of rice production. John Wiley, New York

Fillery IRP, Simpson JR, De Datta SK (1986) Contribution of ammonia volatilization to total nitrogen loss after applications of urea to wetland rice fields. Fert Res 8:193–202

Freney JR, Denmead OT, Watanabe I, Craswell ET (1981) Ammonia and nitrous oxide losses following applications of ammonium sulfate to flooded rice. Aust J Agric Res 32:37–45

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

Hutchinson GL, Mosier AR (1981) Improved soil cover method for field measurement of nitrous oxide fluxes. Soil Sci Soc Am J 45:311–316

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

Kruskal WH, Wallis WA (1952) Use of ranks in one-criterion variance analysis. J Am Stat Assoc 47:583–621

Lindau CW, Delaune RD, Patrick Jr WH, Bollich PK (1990) Fertilizer effects on dinitrogen, nitrous oxide and methane emissions from lowland rice. Soil Sci Soc Am J 54:1789–1794

Mohanty SK, Mosier AR (1990) Nitrification-denitrification in flooded rice soils. Trans 14th Int Congr Soil Sci (Kyoto, Japan) IV:326–331

Mosier AR, Mack L (1980) Gas chromatographic system for precise, rapid analysis of N_2O. Soil Sci Soc Am J 44:1121–1123

Mosier AR, Guenzi WD, Schweizer EE (1986) Soil losses of dinitrogen and nitrous oxide from irrigated crops in Northeastern Colorado. Soil Sci Soc Am J 50:344–348

Mosier AR, Chapman SL, Freney JR (1989) Determination of dinitrogen emission and retention in floodwater and porewater of a lowland rice field fertilized with ^{15}N-urea. Fert Res 19:127–136

Mosier AR, Mohanty SK, Bhadrachalam A, Chakravorti SP (1990) Evolution of dinitrogen and nitrous oxide from soil to the atmosphere through rice plants. Biol Fertil Soils 9:61–67

Ponnamperuma FN (1972) The chemistry of submerged soils. Adv Agron 24:29–96

Raimbault M (1975) Étude de l'influence inhibitrice de l'acetylene sur la formation biologique du methane dans un sol de rizière. Ann Microbiol (Inst Pasteur) 126A:247–258

Rodhe H (1990) A comparison of the contribution of various gases to the greenhouse effect. Science 248:1217–1219

Rolston DE (1986) Gas flux. In: Klute A (ed) Methods of soil analysis: part 1, Physical and mineralogical methods. Am Soc Agron, Madison, Wisconsin, pp 1103–1119

SAS Institute (1985) SAS users' guide: Statistics, Version 5. Statistical Analysis System Institute Inc, Cary, North Carolina

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

Schütz H, Seiler W, Conrad R (1989b) Processes involved in formation and emission of methane in rice paddies. Biogeochemistry 7:33–53

Shapiro SS, Wilk MB (1965) An analysis of variance test for normality (complete samples). Biometrika 52:591–611

Simpson JR, Freney JR, Muirhead WA, Leuning R (1985) Effects of phenylphosphorodiamidate and dicyandiamide on nitrogen loss from flooded rice. Soil Sci Soc Am J 49:1426–1431