Methane Emission from Wetland Rice Fields

Promotor: Dr.ir. N. van Breemen
Hoogleraar in de Bodemvorming en Ecopedologie

Co-promotor: Dr. H.-U. Neue
Professor and Head of Soil Science Section, UfZ - Environmental Research Center Leipzig-Halle, Bad Lauchstaedt, Germany

Methane Emission from Wetland Rice Fields

H. A. C. Denier van der Gon

Proefschrift
ter verkrijging van de graad van doctor
op gezag van de rector magnificus,
dr. C.M. Karssen,
in het openbaar te verdedigen
op vrijdag 25 oktober 1996
des namiddags te half twee in de Aula
van de Landbouwuniversiteit te Wageningen

Guardati da colui che non ha letto che un libro solo

Giacomo Casanova, Memoires - Venetiaanse jaren 1753-1756
(Pas op voor iemand die maar één boek heeft gelezen)
(Beware of someone who read one book only)

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The study reported here results from the project "Soil parameters controlling methane production and emission in/from rice paddies", a collaboration between the department of Soil Science and Geology of the Wageningen Agricultural University, the International Rice Research Institute (IRRI), the Philippines and the Fraunhofer-Institut für Atmosphärische Umweltforschung, Garmisch-Partenkirchen, Germany. The research project was financed by the Dutch National Research Programme on Global Air Pollution and Climate Change (NRP-I). This thesis is an expanded version of the final report of NRP-project X103-1-B-90-9.

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Stellingen

1. Het domweg middelen van gemeten emissies uit rijstvelden zonder rekening te houden met verschillen in bodemtype, water management, klimaat en bemesting leidt tot enorme onzekerheden in de mondiale emissieschattingen.

2. Maatregelen gericht op vermindering van methaanproductie in rijstbodems leiden niet per definitie tot een proportionele afname in methaanemissie.

3. Het gebruik van een belangrijk proces als restpost in een balansstudie, zoals methaanoxydatie in de CH_4 balans van rijstvelden of denitrificatie in de N-balans van Nederlandse landbouwgronden, leidt tot overschatting van dit proces en verdoezelt onzekerheden in de quantificering van de overige processen.

4. Maatregelen voor het reduceren van broeikasgasemissies uit de landbouw middels algemeen toepasbare technieken zullen in een later stadium weer sneuvelen op hun slechte kosten-baten verhouding.

5. Het is zinniger gebieden met extreem hoge broeikasgasemissies te identificeren waar specifieke emissiereductiestrategiën op toegesneden kunnen worden dan het onderzoeken/ontwikkelen van algemeen toepasbare emissiereductietechnieken.

6. Een model om maatregelen ter beperking van methaanemissie uit natte rijstvelden te evalueren en hun effect te quantificeren zal enkel realistisch zijn als op voorhand het gebied waarop het model van toepassing moet zijn nauwkeurig wordt bepaald en niet te groot is (bijv. één delta of provincie).

7. De grote kloof tussen de schaal waarop biogene broeikasgasproductie plaatsvindt en de mondiale schaal waarop broeikasgassen het klimaatsysteem beïnvloeden kan alleen worden overbrugd door specifiek interdisciplinair onderzoek. Dit dient extra gestimuleerd te worden en niet te concureren met disciplinair onderzoek.

8. Methaanoxyderende bacteriën worden in zoute gronden sterker geremd dan methaanproducerende bacteriën.

9. In het onderzoek naar methaanemissie van biogene bronnen ligt de nadruk teveel op netto emissie en krijgt vooral methaanoxidatie binnen het bronsysteem onvoldoende aandacht.

10. De term "wacht"geld slaat niet op de reden waarom dit geld ontvangen wordt, maar de tijd die het duurt om het te krijgen.

11. Salarissen van contractonderzoekers dienen gebaseerd te zijn op functiewaardering en prestatie en niet op de geplande salarisontwikkeling voor vast personeel waarvan het salaris tot het 65ste jaar moet kunnen "doorgroeien".

12 De (ver)bouw van huis, dakkapel of schuurtje is in Nederland tot in het absurde beperkt door schoonheids- of welstandscommissies terwijl winkeliers via het aanbrengen van de meest monsterlijke gevelversieringen de Nederlandse binnensteden vrijelijk mogen ruïneren.

13 De titel, "Kunst, omdat het moet", en het tijdstip van uitzending (rondom middernacht) geven duidelijk aan hoe de Nederlandse "familie&gezelligheids" omroepen over kunst denken.

14 De beste manier om nieuwe Nederlandse kunst te subsidiëren is de aankoop daarvan (tot een bepaald maximum) aftrekbaar van de belasting te maken.

15 Het gaat in het leven niet om behoud maar om de voortzetting.
Joost Ritman, april 1995 (n.a.v. de gedwongen veiling van zijn kunstcollectie)

16 Het is niet te verwachten dat het gat in de ozonlaag ooit nog verdwijnt, zoals reeds vroeg door een groot Nederlands schrijver werd in gezien. "...het is prachtig weder, ongewoon warm nog steeds. Ik denk dat ze die gehele ozonlaag weggegooid hebben, omdat er toch al een groot gat in zat. Iets maken dat stuk is, dat is er vandaag de dag niet meer bij."
Gerard Reve - 1989 (in "Brieven van een Aardappeleter", 1993)

Abstract

Denier van der Gon, H.A.C., 1996, Methane Emission from Wetland Rice Fields, Doctoral Thesis, Agricultural University Wageningen, The Netherlands.

Methane (CH_4) is an important greenhouse gas and plays a key role in tropospheric and stratospheric chemistry. Wetland rice fields are an important source of methane, accounting for approximately 20% of the global anthropogenic methane emission. Methane fluxes from wetland rice fields in the Philippines were monitored with a closed chamber technique in close cooperation with the International Rice Research Institute (IRRI). The field studies were complemented by laboratory and greenhouse experiments. Up to 90 % of the methane emitted from a rice field may be transported from soil to atmosphere through the rice plant. It was shown that this plant-mediated transport is diffusion controlled. Methane emitted from a rice field is the net effect of methane production and methane oxidation. Methane oxidation in the rice rhizosphere depended on the growth stage of the rice plant and becomes of much less importance when the rice plant reaches the ripening stage. Maximum rhizospheric methane oxidation efficiency observed was about 30%, which is much lower than the 70-90% estimated from indirect measurements in previous studies. A higher percentage of oxygen in the air resulted in lower methane emission indicating that breeding rice cultivars that transport more oxygen to their rhizosphere may be a promising mitigation option. Field studies with several soil related factors that influence methane emission were conducted; salinity, sulfate availability, organic amendments and soil types. Organic amendments strongly stimulated methane emission. The impact of organic amendments on methane emission can be described by a dose-response curve. This approach proofed successful for data from various locations of the world. Salinity partly inhibited methane production but methane oxidation in the salt-amended plot was even more inhibited, indicating that a reduction in CH_4 production does not necessarily cause a proportional reduction in CH_4 emission. This illustrates the importance of both production and oxidation of methane when designing mitigation strategies to reduce methane emission. Different soil types had different methane emission levels. Wetland rice fields on saline, low-sulfate soils emit less methane than comparable non-saline rice fields. On soils high in sulfate or amended with large amounts of sulfate containing substances, methane emissions are reduced even more. Continuous monitoring of methane fluxes showed that upon soil drying considerable amounts of soil-entrapped methane may be released. In previous monitoring studies these periods were not included, which may cause an underestimation of total seasonal emission by 10-15%.

Additional key words: Global Change, Greenhouse Effect, Rice, Asia, Methane, Flooded soils

CONTENTS

Voor.....

Dit proefschrift is niet speciaal "voor iemand". Ik heb het vooral vanuit eigen motivatie gedaan, oftewel voor mijzelf. Om dan plots te zeggen, ik heb het voor deze en gene gedaan is op zijn zachtst gezegd wat eigenaardig. Wel is het zo dat de laatste jaren twee eigenschappen nadrukkelijk de kop op hebben gestoken; een interesse in de wetenschap en een sterke neiging tot verzamelen (en niet enkel van data). Dit overdenkend realiseer ik me dat in mij mijn beide grootvaders doorklinken. In die zin zou ik het aan hen willen opdragen. W.P.A. Ditmar (1910-1981) had (denk ik) weinig belangsteling voor wetenschap maar des te meer voor kunst en handel. Hij heeft mij doen inzien dat kunst beweegt, bereikbaar is en niet enkel in de kunstkoelkast, die museum heet, hoort. Helaas is hij te vroeg overleden om hier gezamelijk veel plezier aan te beleven. H.A.C. Denier van der Gon (1894-1945) is net voor het einde van de oorlog omgebracht omdat hij vasthield aan zijn principes en heb ik helaas nooit gekend. Het beeld dat ik heb is dat van een man met een grote wetenschappelijke, met name natuurkundige, en spirituele belangstelling. Mijn vader en broer zijn hem in die richting gevolgd en ook ik, hoewel wat minder zuiver in de leer, pas nu in die traditie.

Preface

Many people have helped me over the last 4-5 years, either with the research for this thesis or with enjoying live, which was essential to continue, or with both. Every thesis should have its preface in which tribute is payed to those people. Where to start? First you can't think of the words, next your lost in a spaghetti of memories where people helped you out, made you laugh when everything went wrong and, and, and. A wonderful feeling to have so many good things to remember. However, it does not give any structure to this preface, so, I will try the chronological approach. I will mention many people and not always add thank you but if you see your name listed in the coming pages, I mean to say thank you very much. Of course I am bound to forget a few people and of course I don't know yet who... I am sorry, it doesn't mean it was not important to me, o.k?

The story of a project - Acknowledgments

The project "Soil parameters controlling methane production and emission in/from rice paddies" started in 1990 but there are two important experiences I should mention that were well before this date. In '85-'86 I spend 9 months in Dr. W.H. Patrick Jr.'s Laboratory for wetland soils and sediments in Louisiana, USA. I think I worked quite hard while I was there, but there was still plenty of time to travel and to meet many people from various countries that I can still call my friends today. This made a great impression on me and I'm still grateful to Dr. Patrick for inviting me to work at LSU. Like everything that tastes good, this stay abroad made me hungry for more. From 1988-'90, I worked for Wil van Duijvenbooden at the National Institute for Public Health and Environmental Protection (RIVM). Wil gave me various research topics and lots of freedom to do it all in my own way. During this period I realized I liked doing research and, really quite a surprise for myself, that I was good at it. (I don't mean brilliant, just good). In 1990, I was looking for a new job and several people at RIVM offered me contracts of various length. Luxury. I was very happy about it but...... my stay in the US made me eager to go abroad again. I expressed this doubt and one of the people at RIVM that had actually offered me a job, Rob Swart, asked me if I knew prof. Nico van Breemen and tipped me to contact him. Something about a project in China. That sounded exciting and yes, I knew prof. van Breemen. Nico van Breemen had arranged my stay in Dr. Patrick's lab and the research I did in the US was more or less for him. Nico van Breemen immediately said he would be happy if I was willing to do the job. However, some investments were to be made because the project was still a proposal and not granted yet. Lex Bouwman, who had written the proposal, had

done a good job and although I adjusted the proposal somewhat to my own personal interests he had made all the contacts and had done most of the work. [Lex, thanks for writing a good proposal and then finding another job!] I am grateful to Nico for having enough confidence in me to simply say "I'll be happy if you want to take over from Lex". After some modifications the project was funded by the Dutch National Research Programme on Climate Change and Global Air pollution, better known as NOP-I or NRP-I. Lex Bouwman went to work for RIVM and managed to get his PhD well before me, so I guess he never needed the methane project anyway. No money, no research. Can you be grateful to a research programme? I think so, at least to all the people that make that programme possible. Moreover, the NOP-people (dr. T. Schneider, drs. S. Zwerver c.s.) accepted all changes in the project whenever I saw better ways to achieve my goals. They could also have made me stick to the original proposal and hassle me for 6-month progress reports. They didn't, and that made this thesis possible. I do hope they feel they got their money's worth of research and, looking back, do not consider it a tax payers fraud.

The project started in september 1990 and it was all about a gas, methane gas. I didn't know anything about gases, nor did anyone else in the Soil Science and Geology department. I always worked with touchable, visual things like soil and water. Luckily, the German partner in the project, the Fraunhofer Institute in Garmisch-PartenKirchen, had a lot of experience in this kind of work. Not only did they have a field site in China, where I was supposed to do my research, but also, a bit closer to home, in Italy. So, the first thing I did was visit prof. Heinz Rennenberg in Garmisch-Partenkirchen, who helped me to a general idea what it was all about, a suitcase full of literature and an introduction to their field site in Vercelli. I saw my first closed chambers. Helmut Schütz, Klaus Butterbach-Bahl and Wolfgang Lindig explained it all to me. I stayed two weeks in Vercelli with Klaus, Wolfgang and Shangguan Xing-jian a chinese student. It was not just us there. I met an enormous amount of little Italian mosquitos, the kind that bites through jeans and jackets and only stops when they are really really full or get squashed. I seriously doubted whether research in rice fields was such a brilliant idea. Vercelli was a strange place. We had a good time with crazy syringe water-battles, lambrusco & pizza's and a lot of work. After this stay I really knew what I was going to work on and it also began to dawn on me that just adding the soil component to other peoples field experiments might not be enough for a thesis. I teamed up with Margot and Robbie in Milan and we made a small Italian tour. This formula of where my work is, is our holiday was successful and to be repeated.

Back in Wageningen, it was time to read on my subject, do a first experiment and prepare for the field work in China. How to do an experiment involving plants and gases in a department equipped for soil and water analysis? The problem was solved by the friendly support from other departments. Rien van Beusichem allowed me access to the greenhouse of the department of Soil Science and Plant Nutrition, Fons Stams and Carolien Plugge from the Microbiology department provided the necessary know-how and materials for sampling and Ilion Wegh arranged access to a gas chromatograph at the department of Air Quality. Thomas van der Lijke, a student interested in this topic, helped with the experiment. Thanks for the support Thomas, it was a tough job. We were continuously on the bicycle with little vials going from one department to another. The results were a nightmare and never yielded anything publishable. Everything that could possibly interfere interfered. However, I had gained very valuable experience in sampling, analysis and experimental set-up for methane emission problems. It was now about time for my first field experiments. Go east young man. The original idea was to participate in the experiments of the Fraunhofer Institute and prof. Wang Ming-Xing at the Tao Yuan field station in Hunan Province, China. However, no exact information on the facilities at the field site were available since it was a new site and very remote. Nico had met Dr. Uli Neue, head of the Soil and Water sciences division of the International Rice Research Institute (IRRI) at a conference and found out that at IRRI a large methane monitoring programme would start in 1991. Dr. Neue had said that if desired it would be possible to do my research at IRRI. This was of course very tempting, IRRI is a well-known and well-equipped institute. In November 1990, I made a 2-week trip to IRRI to discuss the possibilities. A very successful trip. The facilities and possibilities at IRRI looked very good, the people were very friendly and, after loosing a foul game of lying poker and paying (or better performing) the prize, I was immediately adopted by a large crowd of international students, many of whom became very good friends over the next years. Dr. Neue agreed with having me around and so the decision to concentrate my work on the Philippines instead of China was quickly made. I still wanted to go to China because maybe I could work on both sites, there was an interesting conference in Beijing and it was still not decided what kind of research I was really going to do. Looking around at the Chinese station might bring some new ideas to mind. I met Reiner Wassmann for the first time in Tao Yuan. Tao Yuan, a five hour drive from Changsha, really was remote but very impressive. The Chinese were good hosts, showed us many things and served excellent food. How impressive? Well, I never write dairies, here, as an urge to express my amazement, I easily wrote 80 pages in one month time. I hope to make it into a book one day. I had long discussions with Reiner about research possibilities and absorbed his vast experience with trace gas measurements. Uli Neue was also at the Conference in Beijing, so there was time (probably more than at IRRI) to discuss matters with him. During this stay in China the rough idea of what my research would be about materialized. It appeared to be possible to build my own low-budget version of the closed chamber set-up to monitor methane emissions and use the computer controls from the IRRI experimental set-up. This way I could do my own experiments and would be less reliable on other peoples experiments. Reiner Wassmann and Herbert Hoffmann came from Garmisch to IRRI to assemble the IRRI-EPA methane monitoring equipment. They taught me the basics of pressure lines, magnetic valves, 10-port sampling valves and what have you. Herbert arranged shippings from Germany with copies of special parts that were constructed for their monitoring system only. It's clear that without the help of Reiner and Herbert I would have measured nothing at all. At the same time the chambers had to be designed and build with products that were locally available. How much support can one get? I don't know but I got lots of it. I think Uli Neue and Rhoda Lantin told everyone at IRRI that I was on a special mission and had their blessings. The people from Purchasing helped me, whenever they had a car going to Manila I was welcome to join. Numerous missions to Manila followed with Tony Tanzo and Felix, the driver, to buy materials. Sometimes they dropped me in China town (the place where you can buy e-v-e-r-y-t-h-i-n-g) but often Tony took me to his special addresses. We even went to Clarke air base and bought, after long bargaining, 10 pneumatic cylinders designed for opening the roof of a convertible Chevrolet or Cadillac. They made a dent in my budget and... I never used them. It turned out it costs a fortune worth of car batteries (and a running engine to recharge the batteries) to operate the cylinders every 20 minutes. There are plenty more stories like that but we managed to buy all necessities. Well, not everything. There was one thing I really couldn't find. Nothing expensive, just simple rubber draught-excluder tape. I suppose people want all the draught they can get in the Philippines, no market for draught-excluder. Fortunately, the Netherlands is a different story. So, everyone coming from the Netherlands to IRRI had to bring me rolls of draught-excluder tape. The people at Carpentry constructed my chambers and did a great job (although no wood was involved). Ric Eugenio and his army of field workers helped me installing everything and, finally, after days (and yes, like PhD's go, sometimes weekends, evenings or nights) of connecting, soldering, applying Reiner's tips, tuning, checking: it worked! A few weeks later than planned but still in time to monitor most of the 1991 wet season. I now had my own semi-continuous automatic methane monitoring set-up. I quickly learned that automatic means that you are automatically continuously fixing things that block, break, explode etc. The bright side was that it offered an opportunity to pay some of my debts back. Reiner and Herbert were back in Germany but since I had, with their help, constructed a whole system I could now help keeping the IRRI-EPA system going. Never a dull moment, all continuous measurement systems are continuous problem generators.

I did many more experiments at IRRI, always the same story. If you asked people to help you, no one refused. The National staff but also several of the International staff. Marco van den Berg arranged computer facilities, Marco Wopereis helped me with materials and drove me to work at night when I didn't have transport and and and....Thank you all. A special thank you for the people of dr. Neue's methane research group at IRRI who helped me tremendously. Never failed me, never refused a favour. Rhoda Lantin, Maricar Alberto, Elyn Aduna, Jane Tan, Ric and the other field workers and later on also Lenny Bueno, Diane Llenaresas and Eddy. And of course Dr. Uli Neue, who always supported my work, encouraged my ideas (and laughed when I was disappointed when something wasn't successful at once). This thesis would not have been possible without their support. [Diane died in 1995 of cancer. It's not all fun. Diane, wherever you are, thanks for helping me and devoting some of your precious time to my work. We never knew how precious your time really was.] In the wet season of 1992, Yne Meindertsma came as a student from Wageningen and took over some of my experiments while I went back to Wageningen. Yne and I discussed several alternative experiments and Yne decided to try it all. This was an enormous amount of work but he did it. Good job, Yne. As research goes, we found out that several things had to be done slightly different but I am glad to say that several parts of his work found there way into publications and chapters of this thesis. The other people at the soils department Bebot, Charo, Joey, Mang-boy, Ely, Corintha and others were always willing to go out of their way to help me with something, what a wonderful place to work (I mean it). But life in Los Baños was not only work. Bitzi, Boru, Benoit, Caroline, Dylan, Edna, Genna, Gon, Hans, Hilary, Ian, Jeff, John, Jon, July-Ann, Kathy, Lucille, Marco (2x), Myra, Martin (2x), Mavick, Mike, Marz, Nynke, Olivier, Riza and all others around when I was around. Thanks for doing one or more of the following activities with me; partying, sporting, diving, living, gossiping, travelling, buying, jamming, cooking or pokering. It was good good fun. Every now and then, life in the Philippines really was a beach, a wonderful beach. I spend most of 1991 and 1992 in the Philippines, working hard but also able to see a fair bit of a beautiful country. Margot and Robbie came over 2 times and one time Jan, my father, joined as well. We made exciting trips to the Ifugao rice terraces, Palawan or just relaxed at El Galleon enjoying the beauty of a tropical beach and coral reefs. These visits of my closest friends and my father made my "Filipino episode" a shared memory and not something outside of my Dutch life. Many things in our houses, jokes and stories we tell still echo the good times we had while in the Philippines.

After the fieldwork and experiments at IRRI I went back to the Soil Science and Geology department to work on the data and write the oh so desired papers. This was a bit of a shock. Suddenly I was no longer part of an active and inspiring research group but became a lone ranger, the methane man. Fortunately, this sometimes depressing situation was compensated by the friendly attitude of my colleagues in the department. Especially my office mates, Harry Booltink and Jan Verhagen offered a lot of relief, and now we even have our own department indoor soccer team, what else can a scientist desire? And there was my promoter Nico van Breemen with an amazing talent to review papers, separating sense and nonsense, proper reasoning from yapping away. Every manuscript clearly improved after being "Breemenized". (maybe Breemen stems from to broom?) Nico's reviews quickly became my only internal standard and were highly appreciated. Sometimes a manuscript returned so blue with ink that I started to wonder whether I could write at all. However, this way I was convinced the white parts just had to be good. I am glad to conclude that in my next job, a spin-off of the current thesis, my research will have more in common with that of my colleagues in the department and at the same time some of the new research in the department comes closer to what I am doing. Thus providing links for fruitful cooperations within the department.

The IRRI connection remained important. Thanks to the e-mail system I had instant access to the Soil and Water Science division and could pester Uli Neue, Rhoda Lantin, Elyn, Maricar or Ely for additional information, opinions, documents. Sometimes fast, sometimes a bit later but I always got what I needed. This made it possible to successfully write in the Netherlands on everything I did in the Philippines. At the end of '93 I tried to create analytical facilities in the department for additional experiments. However, when I explained that methane is analyzed with a hydrogen flame, people seemed to have recollections of the Hindenburg exploding. I quickly learned I was much better off buying a ticket to the Philippines. So, back to IRRI in March '94, where everyone still remembered me and again was willing to help me out.

In December 1994 Dido was born and she turned me into a PhD student classic; writing your thesis while changing nappies and preparing milk. We both enjoyed it, Dido was sitting in her chair on my desk and always laughed at what I was typing. Sometimes she fell asleep and it is true, science is not always exciting it has its boring moments. It's healthy when someone points that out to you every now and then. A last but one acknowledgment goes to Hanni and Jan, my parents. Of course you encouraged me in what I was doing over the last years but I am old enough to make my own plans and have quite a good idea of what I can. Your major contribution to this thesis was much earlier. I am not talking about raising me, although I am grateful for that as well. In my second year as an undergraduate student in Wageningen, I was convinced I should quit university. Too difficult, too theoretical for me. You always told me that that was not a problem but that I should at least try as hard as I could now so that (1) if I failed I could at least say I tried and never think if only... and (2) if I made it through this year and decided to stop it would be fully my own choice. I saw the sense of that reasoning, worked hard (Jan explaining all the mathematics) and suddenly had amazing grades (Yes, amazing... a "9" for statistics). Never a serious problem with my study after that, and I never considered to quit again. A special *thank you* is reserved for Margot. She had made up her mind to live with me and I said "great" and was gone. For quite some time we had a P.L.A.N.T. relationship (Permanently Living Apart Not Together) - It was not easy. There must have been many times you thought "why don't I find someone who stays (a bit closer to) home"......... I am very glad you didn't.

Utrecht 1996,

Hugo Denier van der Gon

Most other chapters of this thesis have been published, or will be published in the near future, as individual research papers. Therefore, each of the Chapters 2 through 8 has a separate introduction to the subject of that particular chapter. In Chapter 2, the results of monitoring methane emission from rice fields on three different soil types are presented. The approach involving different soil types proved hard to control and results were difficult to interpret. An alternative was to verify the effect of one soil variable only, e.g., sulfate content (Chapter 3) or salinity (Chapter 4) on CH_4 emission. The effect of incorporation of organic matter in a rice field on CH_4 emission was studied in Chapter 5. Continued monitoring of methane emissions from the rice fields after harvest revealed that CH_4 emissions may continue substantially longer than just the rice growing season (Chapter 6). In addition to these field studies, greenhouse studies were performed to answer specific questions concerning gas transport in rice plants (Chapter 7) and possible oxidation of methane in the rice rhizosphere (Chapter 8). The last chapter, general discussion, tries to live up to its title.

Chapter 1

General Introduction

General introduction

The greenhouse effect

The fundamental process driving the global climate system is heating by incoming short-wave solar radiation and cooling by long-wave infrared radiation in to space (Figure 1.1). The average global temperature is determined by the equilibrium between incoming energy from the sun and outgoing energy as heat from the earth. Part of the outgoing infrared radiation is trapped by radiatively active gases, the so-called greenhouse gases, in the lower atmosphere and then re-emitted. This process, generally referred to as the greenhouse effect, adds to the net energy input of the lower atmosphere and thus leads to an increased global temperature. The existence of this basic greenhouse effect is widely accepted. The absorption of radiation emitted from the Earth's surface by greenhouse gases has been demonstrated with satellite measurements. Furthermore, calculations on the basis of the greenhouse effect theory can explain the very different surface temperatures of Venus, Earth and Mars (Table 1.1). In fact, the basic greenhouse effect is highly appreciated since the mean global temperature of the Earth would be about −18 °C without the greenhouse effect, making life virtually impossible. The concentrations of greenhouse gases are increasing since pre-industrial times due to human activities. This is likely to cause an enhanced greenhouse effect.

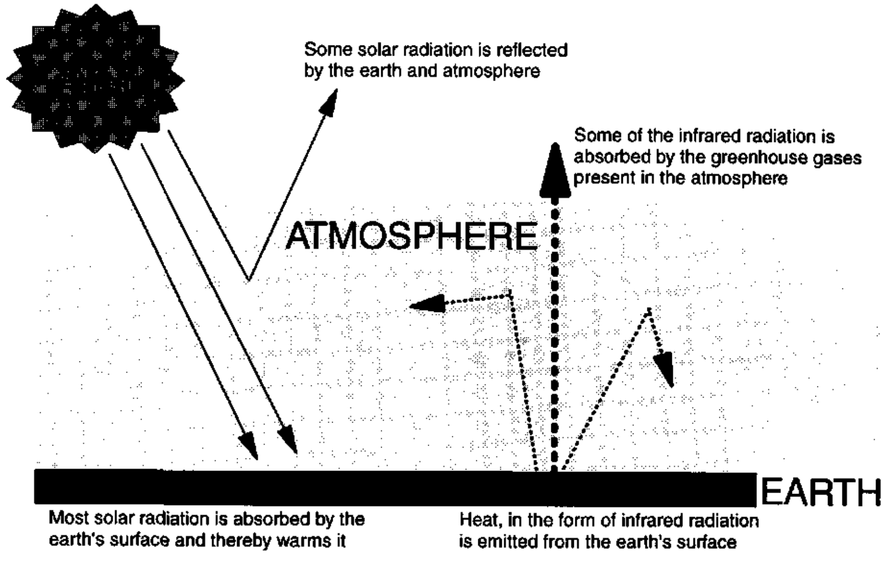

Figure 1.1 A simplified diagram illustrating the greenhouse effect (adapted from IPCC, 1990).

Table 1.1 Surface temperatures of Venus, Earth and Mars with and without the greenhouse effect (adapted from IPCC, 1990).

	Surface temperature in absence of greenhouse effect	Observed surface temperature	Warming due to greenhouse effect
Venus	−46 °C	477 °C	523 °C
Earth	−18 °C	15 °C	33 °C
Mars	−57 °C	−47 °C	10 °C

This enhanced greenhouse effect, usually referred to as *the* greenhouse effect, is a major cause of concern and discussion among scientists and politicians alike because it may raise global temperature ("global warming"), change weather patterns and cause more extreme weather events like storms and floods. However, this is theory and not fact. The enhanced greenhouse effect is difficult to detect (or "prove") because 1) it is relatively small compared to the background of the much larger basic greenhouse effect and, 2) the natural variation in weather patterns and temperature is large. One needs long time series to observe significant changes. By the time we have such proof of the enhanced greenhouse effect, it may be too late to do anything about it. Obviously it is advisable and safer to act now, try to reduce greenhouse gas emissions where possible and decrease uncertainties about what might happen in the future. Unfortunately, there is a price to be paid, an economic price. The key greenhouse gases responsible for the enhanced greenhouse effect, carbon dioxide (CO_2, by far the most important), methane (CH_4), nitrous oxide (N_2O) and the man-made chlorofluorocarbons (CFC's) are associated with economic activities and food production. Reducing or even stabilizing their emissions would slow down economic growth. This would be unacceptable for many countries, especially since the exact hazards of the enhanced greenhouse effect are not yet known.

Methane

Methane has been recognized as one of the principal greenhouse gases, second only to CO_2. The first evidence that the concentration of atmospheric CH_4 is increasing was presented in the early 1980's (Graedel and McRae, 1980; Rasmussen and Khalil, 1981). Its estimated contribution to the enhanced greenhouse effect varies between 15-20% (IPCC, 1990), depending on the time window for which the calculation is made. Methane is not only a potent greenhouse gas, it is also chemically active in the atmosphere thus influencing atmospheric concentrations of several important species, e.g., hydroxyl radicals, ozone and carbon monoxide. [For more information on the

Table 1.2 Estimated sources and sinks of methane in $Tg.yr^{-1}$ (1 Tg = 10^{12} g) (Adapted from IPCC, 1994).

Sources	**Estimate**	**Range**	**Total**
Natural			
Wetlands	115	55-150	
Termites	20	10-50	
Oceans	15	5-50	
Other	15	10-40	
Total		110-210	160
Anthropogenic			
Fossil fuel related	100	70-120	
Cattle (Enteric fermentation)	85	65-100	
Rice paddies	60	20-100	
Biomass burning	40	20-80	
Landfills	40	20-70	
Animal waste	25	20-30	
Domestic sewage	25	15-80	
Total		300-450	375
Total identified sources		410-660	535
Total sinks		430-600	515
Atmospheric increase		35-40	37
Implied total sources (sinks + atmospheric increase)			552

chemistry of atmospheric methane and its biogeochemical sources I refer to Cicerone and Oremland (1988)]. Over the past two decades several global methane budgets have been constructed. The most recent IPCC global methane budget is presented in Table 1.2. Since it is a budget, total sources should equal total sinks + atmospheric increase. Although this is accomplished in Table 1.2, the estimates of individual source strengths is still highly uncertain (as indicated by the ranges in Table 1.2). About 70% of the estimated global CH_4 emission is anthropogenic, and therefore, on principle manageable.

Methane is produced by strict anaerobic bacteria (methanogens). Anaerobic conditions occur in, for example, aquatic sediments, natural wetlands, and wetland rice fields (Cicerone and Oremland, 1988; Conrad, 1989). An extensive review of the biogeochemistry of methanogenic bacteria is given by Oremland (1988).

Wetland rice fields as a source of methane emission

Rice is one of the world's most important food crops. From 1951 to 1990 the harvested area of rice increased from 104 to 146 million ha and rough rice production increased from 171 to 519 million tons (IRRI, 1991). Rice growing systems include wetland rice and upland rice. Upland rice contributes about 14% to total rice production (Neue and Roger, 1994). Upland rice fields are never flooded, do not have the anaerobic conditions essential for methanogenic bacteria and thus are not a source of CH_4. Anaerobic conditions do occur in wetland rice fields, that are flooded for at least part of the rice growing season. Wetland rice fields may account for approximately 20% of the global anthropogenic methane annually produced (Table 1.2). Wetland rice systems are separated in irrigated rice, rainfed rice and deepwater rice, a description and further classification of rice systems is given by Neue (1989) and Neue and Roger (1994). In irrigated rice fields the floodwater is controlled and usually maintained throughout the growing season. These conditions are favourable for both rice production (irrigated rice is grown on about 50% of the harvested area but contributes about 70% to total rice production) and methane production. In the last decades many rainfed rice fields have been transformed in to irrigated rice fields to increase rice production. The field studies described in this thesis were all done in irrigated rice fields. The potential for methane release from rice fields was already noted by Harrison and Aiyer in 1913 (quoted in Neue, 1993). In the 1930's, Acharya did extensive studies on the degradation of organic materials, such as rice straw, in wetland rice fields. He observed that in wetland rice fields, organic matter is degraded to the gaseous end-products CO_2 and CH_4 and that the ratio between those two gases depended on several factors such as temperature and *p*H (Acharya, 1935a; 1935b). The first global estimate of the methane source strength of rice paddies, 190 $Tg.yr^{-1}$, was based on anaerobic incubation of paddy soil samples (Koyama, 1963). The first field measurements were done in California by Cicerone and Shetter (1981), followed by extensive studies in Spain (Seiler et al., 1984) and Italy (Holzapfel-Pschorn and Seiler, 1986; Schütz et al., 1989). The findings of these field experiments reduced the global estimate to about 100 $Tg.yr^{-1}$ and stressed the importance of the rice plant as a conduit for CH_4 transport from soil to atmosphere. At present, the CH_4 source strength of wetland rice fields is estimated at 60 $Tg.yr^{-1}$. However, this estimate is still highly tentative.

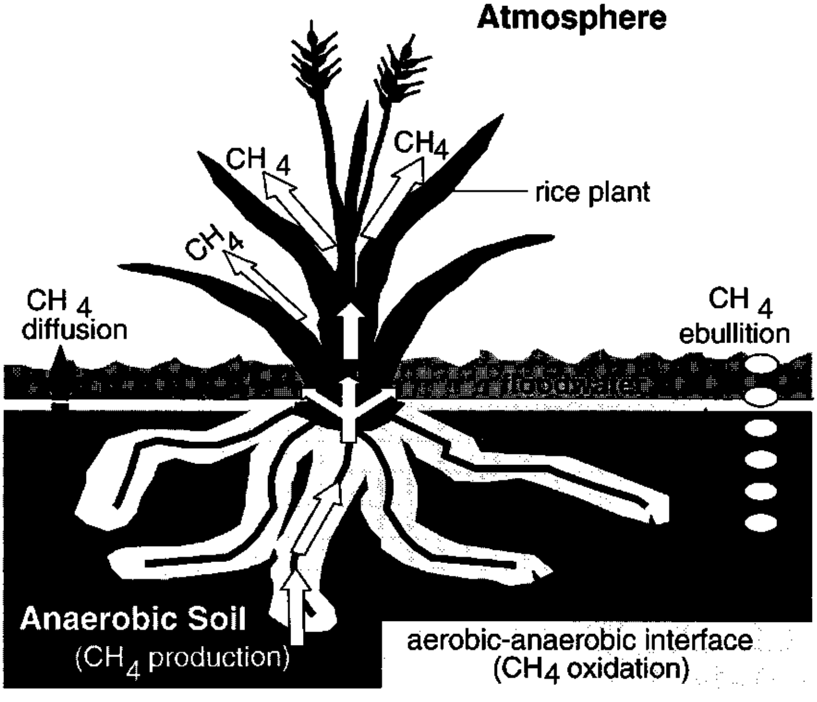

Figure 1.2 A Schematic reprentation of the soil-water-rice plant ecosystem showing the transport pathways of methane produced in the soil to the atmosphere.

A more accurate estimate of the global CH_4 source strength of wetland rice fields is needed, not only to evaluate the impact and cost-benefit ratio of mitigating technologies on CH_4 from rice fields but also to reduce uncertainty in the estimates of other CH_4 sources. In 1990, when the project started, the estimates of the contribution of rice agriculture to atmospheric methane were largely based on field measurements in subtropical regions of California, Spain and Italy, although over 90% of the world's rice is produced in Asia. No reports were available for the tropics, although the majority of wetland rice is grown there. The research described in this thesis aims at contributing to improved estimates at a global scale by investigating (soil) factors that control the emission level from rice fields in a tropical Asian country (The Philippines). A model of the soil-water-plant ecosystem emitting methane to the atmosphere is shown in Figure 1.2. Methane is produced by methanogens in the anoxic soil of the flooded rice field. It can escape to the atmosphere, in order of importance, by plant-mediated transport, ebullition and diffusion through soil and floodwater. A considerable part of the methane produced in the soil may be oxidized by methane oxidizing bacteria (methanotrophs) before reaching the atmosphere. Methanotrophs need free oxygen to oxidize methane and are active in oxic-anoxic interfaces such as the soil-water interface and root-soil interface (rhizosphere). A number of factors influence the capacity of the rice ecosystem to emit methane, e.g., hydrology of the field, temperature, soil type, cultural practices (including application of organic amendments and fertilizer). Several of these factors are subject of study in the following chapters.

References

Acharya, C.N., Studies on the anaerobic decomposition of plant materials, I, The anaerobic decomposition of rice straw (*Oryza sativa*), Biochem. J., 29, 578-541, 1935a.

Acharya, C.N., Studies on the anaerobic decomposition of plant materials, II, Some factors influencing the anaerobic decomposition of rice straw (*Oryza sativa*), Biochem. J., 29, 953-960, 1935b.

Cicerone, R.J. and R.S. Oremland, Biogeochemical aspects of atmospheric methane, Global Biogeochem. Cycles, 2, 299-327, 1988.

Cicerone, R.J., and J.D. Shetter, Sources of atmospheric methane: Measurements in rice paddies and a discussion, J. Geophys. Res., 86, 7203-7209, 1981.

Conrad, R., Control of methane production in terrestrial ecosystems, in Exchange of trace gases between terrestrial ecosystems and the atmosphere, edited by M.O. Andrae and D.S. Schimmel, Wiley and Sons Ltd, pp. 39-58, 1989.

Graedel, T.E. and J.E. McRae, On the possible increase of the atmospheric methane and carbon monoxide concentrations during the last decade, Geophys. Res. lett., 7, 977-979, 1980.

Holzapfel-Pschorn, A. and W. Seiler, Methane emission during a cultivation period from an Italian rice paddy, J. Geophys. Res., 91, 11,803-11,814, 1986.

Intergovernmental Panel on Climate Change (IPCC), Climate Change: Intergovernmental Panel on Climate Change - Scientific Assessment, (edited by J.T. Houghton, G.J. Jenkins and J.J. Ephraums), Cambridge University Press, Cambridge, 1990.

Intergovernmental Panel on Climate Change (IPCC), Climate Change 1994, Radiative forcing of climate change and an evaluation of the IPCC IS92 emission scenarios, Cambridge University Press, New York, 1994.

International Rice Research Institute (IRRI), World Rice Statistics 1990, P.O. Box 933, Manila, Philippines, 1991.

Koyama, T., Gaseous metabolism in lake sediments and paddy soils and the production of atmospheric methane and hydrogen, J. Geophys. Res., 68, 3971-3973, 1963.

Neue, H.U., Rice growing soils: Constraints, utilization and research needs. In: Classification and management of rice growing soils. FFFTC Book Series, Food and Fertilizer Technology Center for the ASPAC region, Taiwan, pp. 1-14, 1989.

Neue, H.U. and P.A. Roger, Potential of Methane Emission in major Rice Ecologies In: Climate Biosphere Interaction, R.G. Zepp (Ed.), pp. 65-93, Wiley and Sons, New York, 1994.

Neue, H.U. Methane Emission from Rice Fields, Bioscience 43, 466-474, 1993.

Oremland, R.S., Biogeochemistry of methannogenic bacteria, In: Biology of anaerobic microorganisms, A.J.B. Zehnder (Ed.), pp. 641-705, Wiley and Sons, New York, 1988.

Rasmussen, R.A. and M.A.K. Khalil, Increase in the concentration of atmospheric methane, Atmos. Environ., 15, 883-886, 1981.

Schütz, H., A. Holzapfel-Pschorn, R. Conrad, H. Rennenberg, and W. Seiler, A 3-year continuous record on the influence of daytime, season, and fertilizer treatment on methane emission rates from an Italian rice paddy, J. Geophys. Res., 94, 16,405-16,416, 1989.

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

Chapter 2

Influence of Various Soil and Climate Factors on Methane Emission from Rice Fields

Influence of various soil and climate factors on methane emission from rice fields

Abstract

Three soils, ranging from acidic via near-neutral to calcareous, differed largely in their capacity to produce CH_4 in laboratory incubations. Addition of rice straw to the incubated soils enhanced CH_4 production in all three soils and reduced the differences in CH_4 productivity of the soils. It appeared that in one soil, Maahas clay, the native soil organic matter was protected against anaerobic microbial decomposition. The relative CH_4 production of the soils in incubations with organic matter addition showed a good correlation with the relative seasonal CH_4 emission from these soils when planted to rice but a quantitative relationship could not be derived. Production and emission of CH_4 from a calcareous sandy loam planted to rice and fertilized with urea was higher than from a near-neutral, non-calcareous clay soil under otherwise similar conditions. Incorporation of organic matter at the start of the growing season overruled the influences of $CaCO_3$ and/or texture and led to similar production and emission of CH_4 from these two soil types. Methanotrophs in the soil-water interface of wetland rice fields typically oxidize 70-90% of the diffusive flux of CH_4 to the atmosphere. However, in the calcareous soil only 33% of the CH_4 was oxidized at the soil-water interface, indicating that a high pH or free $CaCO_3$ hinders CH_4 oxidation. CH_4 emission from the rice fields showed a positive correlation with air temperature and solar radiation on a time scale of hours or days, irrespective of the soil type. The stimulating effect of air temperature and/or solar radiation is probably caused by a plant related process because the change in soil temperature was relatively small and often out of phase with the large diurnal variation in CH_4 emission.

Introduction

Methane (CH_4) is the most abundant greenhouse gas after water vapor and CO_2. Furthermore, CH_4 is a reactive gas, both in the troposphere and the stratosphere, influencing atmospheric concentrations of other greenhouse gases such as ozone (IPCC, 1990). Wetland rice fields are an important source of methane, with an estimated source strength of 60 ± 40 $Tg.yr^{-1}$ (IPCC, 1994). Since the first measurements of CH_4 emission from a Californian rice field (Cicerone and Shetter, 1981) numerous studies showed that CH_4 emissions from rice fields are influenced by climate, organic amendments, water regime, agronomic practices, soil characteristics, rice variety and fertilizer application. Despite the identification of controlling variables the uncertainty in the global CH_4 source strength estimate from rice paddies is still among the highest of all CH_4 sources (IPCC, 1994). This uncertainty needs to be narrowed if we want to have a reliable global CH_4 budget and are to develop effective, cost-efficient mitigation options to stabilize the atmospheric CH_4 concentration. The large uncertainty in the source strength estimate of rice fields is a scale-related problem. The scale at which we want global or regional CH_4 emission estimates (> km) is much larger than the scale of the emission measurements (~1 m). This problem may partly be overcome by empirical relationships linking data from benchmark sites to larger areas but unfortunately geo-referenced databases on CH_4 emission controlling factors are not available. A digitized FAO soil-map-of-the-world database (e.g., Zobler, 1986) can potentially be used to predict regional or global CH_4 emission estimates if we know 1) where rice fields are located, 2) how various soil types influence CH_4 emission from a rice field, and 3) have reliable regional information on other modifying factors (e.g., organic amendments, fertilizer inputs). The first can be achieved by using a combination of remote sensing, satellite imagery and land use maps. The latter by compilation of regional statistics although this may be problematic and deserves further attention. This paper concentrates on the influence of soil types on CH_4 emission.

The potential importance of differentiating soil types when estimating CH_4 emission from rice fields was illustrated by Bachelet and Neue (1993) who introduced a correction factor for CH_4 emission from rice grown on soil types that were expected to be low CH_4-producing soils. After accounting for differences in soil types, previous estimates for CH_4 emission from Asian rice fields were reduced by 28% (Bachelet and Neue, 1993). That CH_4 emissions from rice fields on different soil types do differ was observed in Japan (Yagi and Minami, 1990) and the USA (Sass et al., 1990; 1991). Furthermore, anaerobic incubation of a range of rice soils revealed high variations in the potential of these soils to produce CH_4 (Denier van der Gon et al., 1992; Wang et al., 1993b). If the potential of a soil to produce CH_4 correlates with the CH_4 emission from that soil when planted to rice than regional and/or global CH_4 emission estimates from rice agriculture could greatly improve by linking potential CH_4 production of rice soils to a geo-referenced soil database. Incubation experiments in microcosms had shown that CH_4 production in reduced soils is very sensitive to pH (optimum pH 6.9-7.1; Wang et al., 1993a). Therefore, the first objective of this study was to measure CH_4 emission from rice growing on soils ranging from acidic (Luisiana; low pH and high active Fe) via near neutral pH (Maahas) to an alkaline soil (Pila, high pH and presence of $CaCO_3$). Second, temperature is a factor with a well-known influence on microbial processes, that are the source of CH_4 production. We therefore also investigated the influence of climate variables such as temperature and solar radiation on CH_4 emission from rice fields.

Table 2.1 Characteristics of the selected soils, originating from Luzon, Philippines.

Soil	Maahas	Luisiana	Pila
pH 1:1 H_2O	5.9	4.5	7.8
CEC (meq.100 g^{-1})	40.2	24.9	27.2
Org. C (%)	1.97	1.84	1.47
N (%)	0.166	0.180	0.182
Olsen P (ppm)	2.5	5.9	24
Active Fe (%)	1.53	4.63	0.800
Active Mn (%)	0.090	0.109	0.058
Clay (%)	66	56	21
Silt (%)	28	40	40
Sand (%)	6	4	39

Materials and methods

All field experiments were performed at the International Rice Research Institute (IRRI), Los Baños, Philippines. Three soils were used in this study (Table 2.1). Maahas is the soil originally present at the IRRI research farm. Luisiana and Pila are soils from neighboring districts. The 0-20 cm surface soil from farmers fields in Luisiana and Pila was collected and transported to the IRRI research farm. The original 0-20 cm topsoil from 3 x 5 m plots was removed, and replaced by Luisiana or Pila soil. The newly placed soils were separated from the original subsoil by a plastic sheet. The rice fields were located next to each other, fertilized with urea or green manure (Table 2.2) and subject to the same management practices. Maahas is a near-neutral clay soil, Luisiana is an acidic clay soil with high iron content and Pila is a calcareous sandy loam containing, partly fragmented, mollusc shells. All plots were planted to rice variety IR72 at a spacing of 25x25 cm (1991) or 20x20 cm (1992).

Capacity of the soils to produce CH_4

Potential CH_4 production rates of the three soils before the start of the season, with and without organic amendment, were measured in triplicate by weighing 20 g of air-dry, 80 mesh soil into a 100 ml spoutless beaker containing a magnetic bar.

Table 2.2 Overview of field experiments performed in 1991 and 1992.

Soil type	Fertilizer		Straw yield ($t.ha^{-1}$)		CH_4 emission ($g.m^{-2}$)	
	Type	kg N ha^{-1}	in[a]	out[a]	Vegetation period	Total season[b]
Wet season 1991						
Maahas	Urea	55.2	2.3	3.9	4.0	na[c]
Pila	Urea	55.2	1.7	2.7	5.6	na[c]
Luisiana	Urea	55.2	1.4	2.3	8.6	na[c]
Dry season 1992						
Maahas	Urea	146	5.8	6.2	17.2	20.1
Pila	Urea	146	5.0	3.9	30.5	36.1
Luisiana	Urea	146	8.3	6.9	23.6	28.7
Wet season 1992						
Maahas	Urea	115	7.7	5.5	7.9	na[c]
Maahas	Green manure[d], Urea	160	11.1	7.8	47.1	55.6
Pila	Green Manure[d], Urea	160	10.0	6.9	42.3	51.7

[a] in = inside flux chamber; out = outside flux chamber
[b] Vegetation period and post harvest emissions
[c] na = not available; post harvest CH_4 emissions were not recorded
[d] 20 t ha^{-1} fresh *Sesbania rostrata* as green manure (≈ 100 kg $N.ha^{-1}$)

The organic amendment consisted of a 1% addition of ground rice straw (0.2 g) mixed in to the soil. After adding 40 ml of distilled water, the beaker was covered with a rubber stopper equipped with gas inlet/outlet, a platinum electrode and an electrode opening. The beaker was stirred, deaerated by flushing with N_2 for 3 minutes (N_2 rate, 200 $ml.min^{-1}$) and incubated at 30 °C. The CH_4 production rate was measured after stirring and flushing the beaker with N_2 for 3 minutes one day before actual sampling. On the sampling day, the beaker was stirred for 3 minutes and a 1 ml gas sample was withdrawn from the headspace (the headspace gas was mixed thoroughly by pushing the syringe plunger up and down at least 10 times). The gas sample is analyzed on a gas chromatograph with flame ionization detector using Porapak N column (100/120 mesh) at 45°C with N_2 as carrier gas. After sampling the headspace composition was refreshed by flushing with N_2 while stirring for 3 minutes, and incubation was continued. The CH_4 production rate of the soil is determined 0.5, 1, 2, 3, 4, 5, 6, 7 and 8 weeks after the start of the incubation.

Climate data

Daily temperature, rainfall, solar radiation, sunhours and evaporation were recorded at the experimental farm by the IRRI climate unit. In the experimental plots the temperature of the ambient air, floodwater and soil (at 5 or 10 cm depth) was monitored continuously.

Experimental apparatus

Methane emission rates from rice field plots were monitored with an automatic measurement system based on the closed chamber technique as developed by Schütz *et al.* (1989a). The system allows 24-hour semi-continuous determination of CH_4 emission rates. Measurements were performed in 2-hour cycles, providing 12 flux measurements per day for the entire growing season. The chambers were made of smooth colorless plexiglass and equipped with lids that are opened and closed by time-controlled pneumatic cylinders. Two electrical fans (12 or 24 V DC) were mounted inside the boxes to ensure rapid mixing of the air within the chamber when closed during sampling and with the ambient air when the cover was open. Air samples from the individual closed chambers were analyzed for CH_4 with a gas chromatograph (GC) equipped with a 6-port valve, sample loop, and flame ionization detector (FID). The large number of samples made it necessary to install one GC with two channels and an extra GC with one channel. Further details of the measurement system are given by Schütz et al. (1989a) and International Atomic Energy Agency (IAEA) (1992). Modifications of the system used in this study were (1) the closing time of the chambers during sampling was reduced from 48 min in 1991 to 24 min in 1992 to reduce plant stress, and (2) the supply of calibration gas from a separate container, resembling the chambers in the field rather than directly from a gas cylinder, to ensure equal pressure in the gas flow system during sampling and calibration of the system. Methane emission rates were calculated from the slope of a linear regression over the sampling interval of the CH_4 concentration inside the chamber against time. Four samples were taken per interval. This regression had almost always $r^2 > 0.95$. An extra check on the raw data was performed if r^2 is < 0.9, because this often indicated technical problems with gas sampling or injection; such data were discarded. Daily CH_4 emission rates were calculated from the 12 flux measurements in 24 hours.

Soil pH and soil redox potential (Eh)

After transplanting, six Pt electrodes were permanently installed in each plot. Every 3 days soil Eh was measured against a Ag/AgCl reference electrode. In the direct vicinity of the Pt electrode soil pH was measured at 3-5 cm depth with a combination electrode, equipped with a protection cap.

CH_4 production and CH_4 oxidation in intact soil columns

In the 1992 dry season during the last 4 weeks before harvest, triplicate soil cores of about 10 cm length were taken from each treatment plot between the rows (10 cm from a hill), using 4.4 cm inner diameter acrylic core tubes with a length of 25 cm. The intact soil cores were brought immediately to the laboratory and assayed 1-2 hours later. The thickness of the layer of flood water above the sediment surface was decreased with a pipette to 2-3 mm to provide a diffusive boundary layer which allowed quick exchange between soil and gas phase (King et al., 1990). The core tubes were sealed with rubber stoppers to provide a headspace of 100-200 cm^3 and incubated at a temperature of 29 - 31 °C. The top rubber stopper contains two septa, so, the headspace could be flushed through syringe needles with either air or N_2 to create an oxic or anoxic incubation, respectively (King et al., 1990). After flushing with either air or N_2 for about 40 minutes, gas samples (2.5 mL) from the headspace above the cores were taken repeatedly and injected immediately in a sample loop of 2 mL, connected to a 6-port valve with manual switch. CH_4 was analyzed on a gas chromatograph equipped with a FID. After taking a sample the headspace pressure was readjusted by injecting the same amount of either air or N_2. The temporal increase of the CH_4 concentration in the headspace was corrected for the dilution and used to calculate the CH_4 flux per surface area from the soil cores with linear regression ($r^2 > 0.95$).

After measuring the CH_4 emission from intact cores, CH_4 production at different depths was measured. The cores were sliced into 2.5 cm thick segments resulting in four different depth intervals; 0-2.5, 2.5-5, 5-7.5 and 7.5-10 cm. Each segment was mixed with 30 mL of demineralized water and transferred to a 125 mL erlenmeyer flask of a known total volume. The flasks were sealed with suba-seals, flushed with N_2 and placed in a waterbath shaker (T = 30 °C) for pre-incubation overnight. The following day the flasks were purged with N_2. Headspace gas samples were taken repeatedly (every 2 hours) and analyzed for CH_4. After each sampling the headspace volume was readjusted by injecting a sample volume of N_2 in to the erlenmeyer flask. CH_4 production rates were calculated, after correction for dilution, from the increase over time of CH_4 in the headspace.

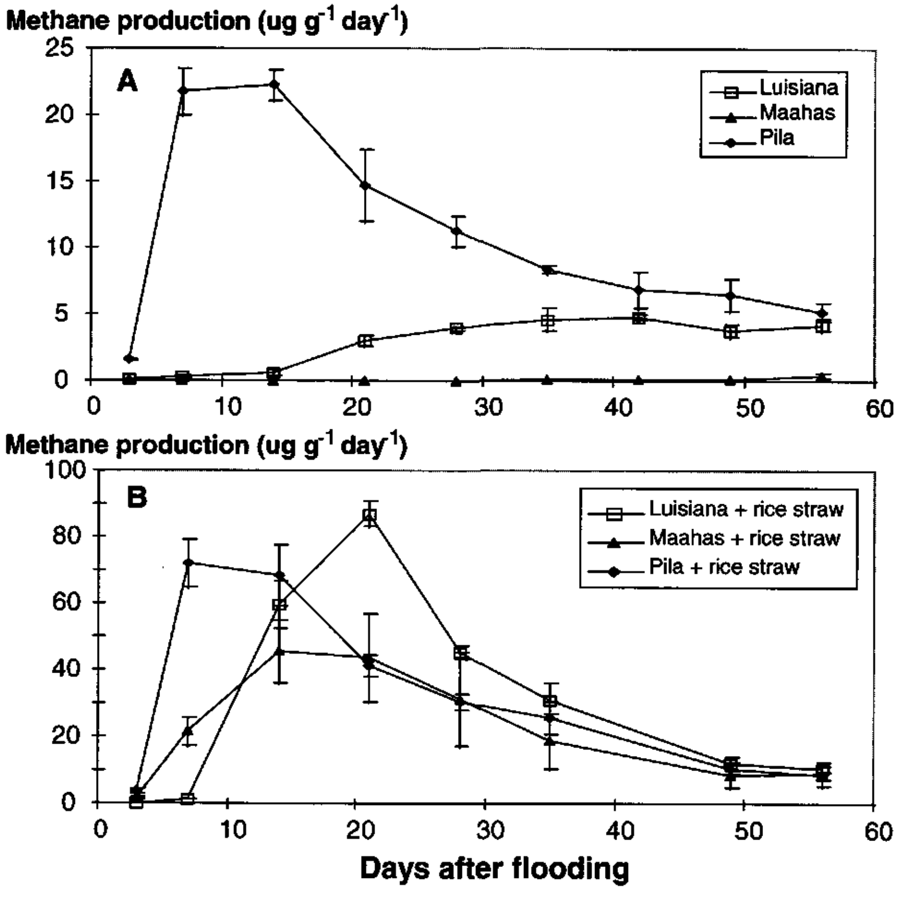

Figure 2.1 CH_4 production rate of three soils incubated under anoxic, flooded conditions in the laboratory without (a) and with addition of rice straw (b).

Results and discussion

Capacity of the soils to produce CH_4

Incubation of soil samples collected before land preparation and rice planting revealed a large difference in the capacity of the three soils to produce CH_4 (Figure 2.1a). CH_4 production in Pila soil peaked immediately after flooding. This is typical for a calcareous soil (Neue and Roger, 1994). CH_4 production in the Luisiana soil started 2 weeks later and became rather constant from 5 weeks onward. There are no obvious trends of increasing CH_4 production as a function of pH, soil organic carbon or other soil characteristics. The CH_4 production rate of Maahas soil was much lower than in Pila and Luisiana, which is remarkable since the Maahas soil has intermediate

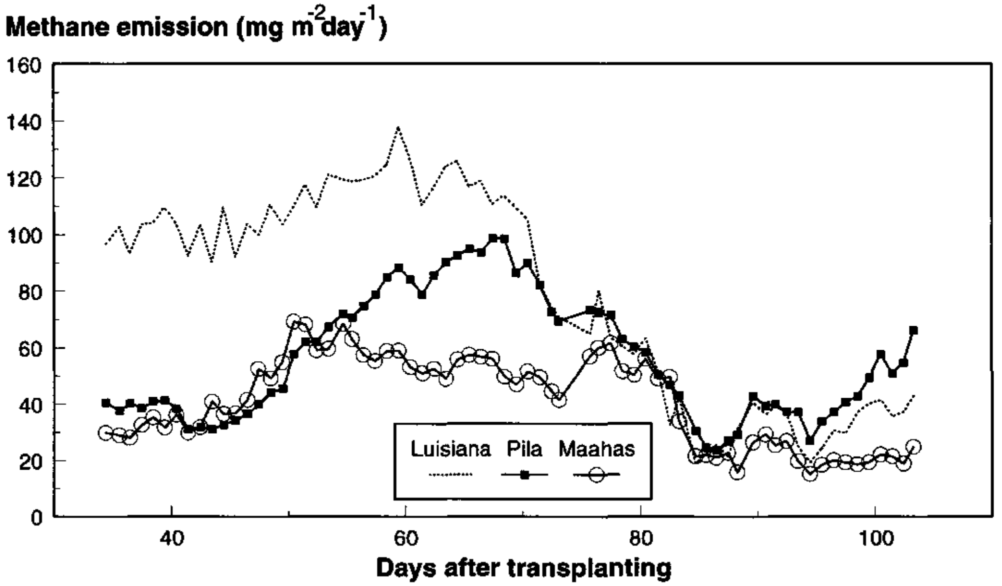

Figure 2.2 Methane emission from Philippine rice fields on three different soil types fertilized with urea in the wet season of 1991.

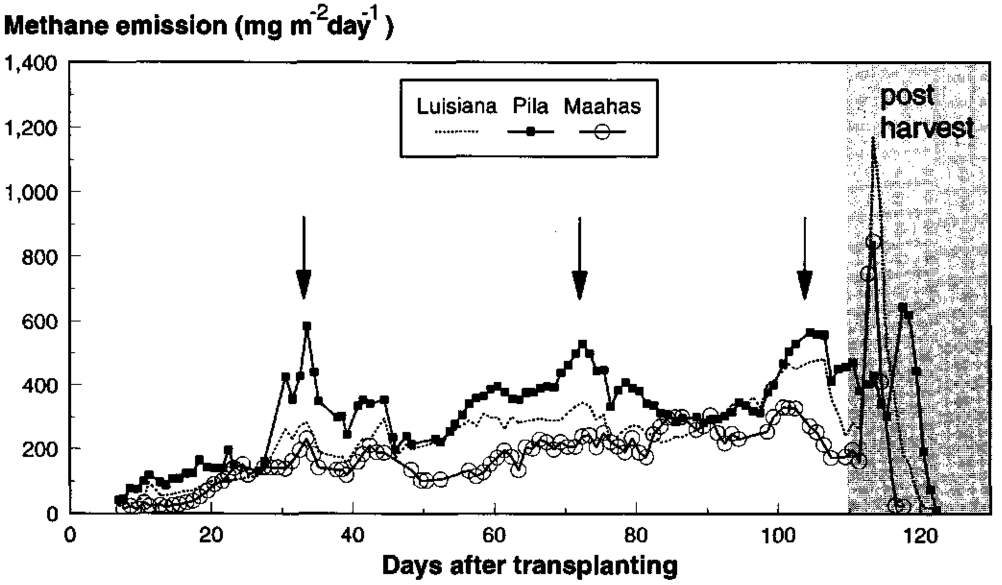

Figure 2.3 Methane emission from Philippine rice fields on three different soil types fertilized with urea in the dry season of 1992. Shaded area indicates emission during the post-harvest period.

values for many important soil characteristics (Table 2.1). Incubation of Maahas soil with a slightly different incubation technique in a previous study had a similar result (soil # 11, Denier van der Gon et al., 1992). Tsutsuki and Ponnamperuma (1987) also observed CH_4 production rate in the order Pila soil > Luisiana soil > Maahas soil. Addition of rice straw enhanced CH_4 production in all soils (Figure 2.1b). The CH_4 production in Pila soil and Luisiana soil was about equal with a slightly higher production in the latter. CH_4 in the Maahas soil was still significantly lower than in the other two soils in accordance with Tsutsuki and Ponnamperuma (1987) who reported that the decomposition rate of both native soil organic matter and added organic materials in the Maahas soil was about half that of the Pila and Luisiana soil for unknown reasons. However, the response of Maahas soil to the addition of rice straw clearly showed that the soil itself contained no inhibitors for CH_4 production. The absence of CH_4 production upon soil incubation without organic amendment suggests that the native soil organic carbon of Maahas soil is protected against microbial decomposition.

The influence of soil parameters on CH_4 emission in field plots

The average daily CH_4 fluxes in the 1991 wet season (WS), 1992 dry season (DS) and 1992 wet season (WS) are shown in Figures 2.2 to 2.4, respectively. The average daily CH_4 fluxes in the first 2 weeks of the 1992 WS are plotted separately in Figure 2.4a because the CH_4 emission level was much higher at this early stage, and the seasonal pattern would become less clear if the data were plotted in the same figure. Unfortunately, the potential effect of the different soil pH values on CH_4 emission could not be properly assessed because the alkaline floodwater probably influenced the acidic Luisiana soil and neutralizes adverse effects of low pH and high dissolved Fe on rice growth. This was concluded from the good rice growth on the Luisiana soil which is otherwise known as a problem soil for rice. The high CH_4 emissions up to about 70 days after transplanting (DAT) from the Luisiana plot in the 1991 WS (Figure 2.2) could be due to additional substrate that came available from increased microbial breakdown following pH increase. From 70 DAT onwards the Luisiana soil apparently reached a new equilibrium with CH_4 emissions in between the Maahas and Pila soil. Clearly, the results for the Luisiana plot cannot be extrapolated to acidic rice growing soils and interpretation of the CH_4 emission curve and its relation to soil characteristics is difficult. The experiments with Luisiana soil were stopped after the 1992 DS, the CH_4 emission from the Luisiana plot is plotted as a dotted line in Figures 2.2 and 2.3 for comparison only. When fertilized with urea, CH_4 emission from rice on the Maahas plot was lower than from Luisiana or Pila plots but not proportional to the large

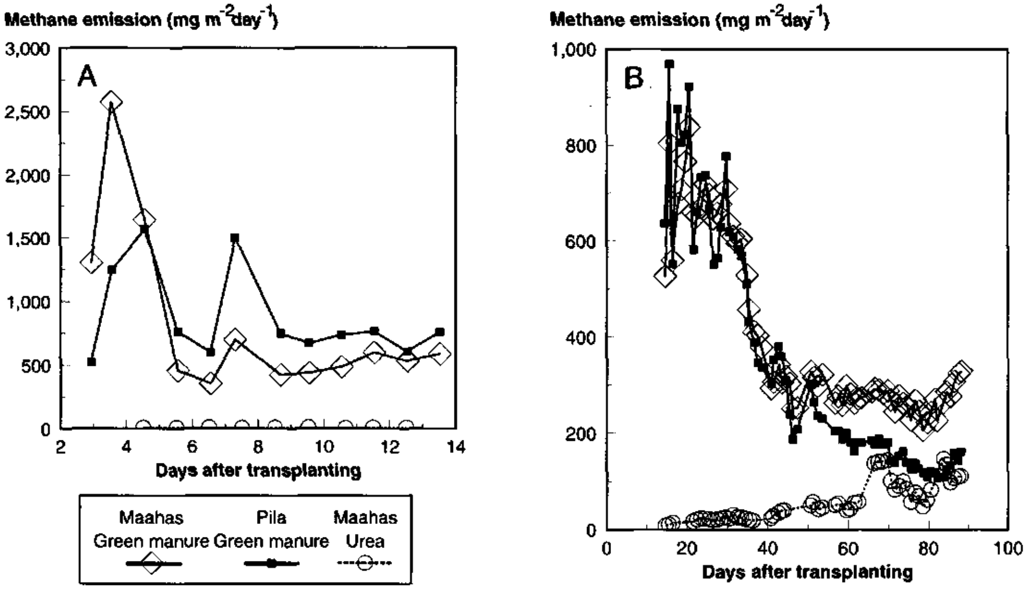

Figure 2.4 Methane emission from Philippine rice fields on two different soil types fertilized with urea or green manure in the wet season of 1992. (a) in the first 2 weeks after transplanting and (b) from 2 weeks after transplanting up to harvest.

differences observed in the soil incubations (Figure 2.1). If the low CH_4 emission from Maahas in the soil incubation study was related to low substrate supply to methanogens than the presence of rice plants creates an almost equal substrate supply to methanogens in all three soils.

Soil pH and Eh Average field soil pH after flooding in the 1991 wet season for the Luisiana, Maahas and Pila soil was 6.7 (± 0.5), 7.0 (± 0.4), and 7.5 (± 0.5), respectively. So, the soils were in the near-neutral pH range, which is the optimum range for CH_4 production (Wang et al. 1993a). In the following dry season the pH values after flooding narrowed even further to 6.8 ± 0.4 in all three soils. While flooding usually causes the soil pH to stabilize between 6.5 and 7.2, Eh falls to levels that depend on the electron acceptors present (Ponnamperuma, 1972). Upon flooding the Eh dropped from > 350 mV in the aerated state to 60 mV (± 40) in Maahas, -58 mV (± 68) in Luisiana and -61 mV (± 64) in Pila. In the 1992 DS average Eh values were lower; 0 mV (± 50) in Maahas, -142 mV (± 89) in Luisiana, and -180 mV (± 63) in Pila. In green manure fertilized fields Eh values dropped to -200 mV or below (data not shown). In laboratory incubation studies CH_4 production was observed only at Eh values < -150 mV (Wang et al. 1993a). The higher Eh values at which we recorded

CH_4 emission were also observed by Yagi and Minami (1990) in some rice fields without organic amendments. There are several possible explanations for this observation 1) CH_4 production occurs at micro sites where the Pt electrodes do not properly penetrate, 2) the 3-5 mm long tips of the Pt electrodes are larger than micro sites where CH_4 production occurs and therefore "touch" spots with various redox potentials, the highest value will be recorded, and 3) CH_4 production already starts at Eh values > -150 mV. The last explanation contradicts the sequential oxidation-reduction theory in flooded soils (Ponnamperuma 1972, Patrick 1981). However, Fetzer and Conrad (1993) recently showed that inhibition of CH_4 production at a redox potential higher than -150 mV is caused by introduction of free O_2 in the system. In an O_2 free medium CH_4 production already started at + 50 mV, and once started even continued until Eh = +420 mV (Fetzer and Conrad, 1993). This is not necessarily in contradiction with thermodynamics because microorganisms may well be able to lower their internal redox potential. Wang et al. (1993) used O_2 (or air) to control Eh in studying methanogenesis. Thus the inhibitory or toxic effect of O_2 on methanogens may interfere with the study of Eh effects on methanogenesis. A redox potential of +420 mV would, under field conditions, always include presence of free O_2 but at Eh values of +50 mV no free O_2 is present and according to the observations of Fetzer and Conrad (1993) CH_4 production could start. The effect of Eh and introduction of O_2 on methanogenesis in flooded soils planted to rice warrants further research because this concept is important for future process modelling. For example, in the rhizosphere where O_2 diffuses from the rice roots a lower Eh may be required to start CH_4 production than in the bulk soil. A lower average soil Eh correlated with higher seasonal CH_4 emission but the temporal pattern of Eh during the growing season did not correspond with emission levels (data not shown).

Other soil characteristics CH_4 emission from the Pila soil was higher than CH_4 emission from Maahas soil both in the 1991 WS and 1992 DS. The higher emission is largely due to more pronounced emission peaks (Figures 2.2, 2.3). Furthermore, CH_4 production in soil cores just before harvest in the '92 DS was about three times higher in the Pila soil than in the Maahas soil (Table 2.3). The main differences between Pila and Maahas soil are soil texture and presence of $CaCO_3$ in Pila soil. In the '92DS we observed total seasonal CH_4 emissions of 20.1 and 36.1 $g.m^{-2}$ from fields with 66% and 21% clay, respectively, which is remarkably similar to the results of Sass and Fisher (1994) who reported a negative correlation between CH_4 emission and clay content. On the other hand, calcareous soils show rapid formation of CH_4 upon flooding (Neue and Roger 1994), perhaps because presence of $CaCO_3$ buffers

Table 2.3 Potential methane production in 15 cm field soil cores of rice fields on different soil types fertilized with urea or green manure in the dry season and wet season of 1992. Standard deviation in parentheses.

		CH_4 production in the dry season ($mg.m^{-2}.day^{-1}$)		
Soil		Maahas	Luisiana	Pila
Fertilizer		Urea	Urea	Urea
Growth stage	Harvest	440 (52)	672 (74)	1217 (354)
		CH_4 production in the wet season ($mg.m^{-2}.day^{-1}$)		
Soil		Maahas	Maahas	Pila
Fertilizer		Urea	GM[a]+ Urea	GM[a]+ Urea
Growth stage	Tillering	45 (23)	1043 (103)	1527 (311)
	Panicle Initiation	146 (72)	1047 (230)	962 (192)
	Harvest	431 (35)	975 (116)	1583 (72)

[a] GM = Green Manure

Table 2.4 Methane fluxes under oxic and anoxic headspace conditions, CH_4 oxidation rate and percentage of CH_4 oxidized in soil cores of wetland rice fields on different soil types.

Soil type	number of cores	CH_4 flux ($ng.min^{-1}.cm^{-2}$)		CH_4 oxidation rate[a] ($ng.min^{-1}.cm^{-2}$)	CH_4 oxidized (% of anoxic flux)
		Oxic	Anoxic		
Maahas	9	0.50 (0.38)	4.95 (1.54)	4.45 (1.29)	91 (5)
Luisiana	6	0.40 (0.32)	3.09 (0.79)	2.69 (0.68)	87 (10)
Pila	6	9.14 (7.20)	12.35 (8.40)	3.21 (3.38)	33 (30)
Vercelli, Italy[b]	5	0.34 (0.51)	1.74 (1.20)	1.40 (0.84)	81 (15)

[a]difference between anoxic and oxic flux
[b]Sandy loam, data from Conrad and Rothfuss (1991)

the pH at micro sites where methanogenesis occurs. When the soils were fertilized with green manure, as in the '92 WS, the difference in CH_4 emission between the Maahas and Pila soil disappeared. This is confirmed by the similar CH_4 production in the soil columns of Maahas and Pila soil in the '92 WS (Table 2.3).

CH_4 production and CH_4 oxidation in the soil column A summary of the oxic and anoxic CH_4 fluxes from intact soil cores of rice fields with different soil types is presented in Table 2.4. An advantage of using intact soil cores instead of soil slurries to assay the production and oxidation of CH_4 at the soil-water interface is that the CH_4 and O_2 gradients that control microbial activity are comparable to field conditions (King, 1990; King et al., 1990). This technique was previously used to show inhibition of CH_4 oxidation in the soil surface layer of a rice field by ammonium (Conrad and Rothfuss, 1991) and salinity (Denier van der Gon and Neue, 1995b). CH_4 oxidation requires free oxygen, so, the difference between the CH_4 flux from cores with anoxic and oxic headspaces can be attributed to CH_4 oxidized in the floodwater-soil interface. CH_4 oxidation occurred in all cores, indicated by an increased CH_4 flux under N_2 incubation for each individual core. For a detailed description on the reversibility of oxic and anoxic incubations and interpretation of fluxes from individual cores we refer to King et al., (1990), Conrad and Rothfuss (1991) and Denier van der Gon and Neue (1995b). Potential CH_4 emission was higher in the tropical soils than in the Italian soil used by Conrad and Rothfuss (1991) although incubations were done at the same temperature. The Italian soil (Vercelli) was a sandy loam (60% sand, 25% silt and 12% clay) with 2.5% organic C, 0.15% total N and pH 6.5-7.0 under flooded conditions. The C:N ratio of the Vercelli soil is higher than the other soils which generally makes a soil less favorable for microbial activity. The texture of the Italian soil is similar to the Pila soil. The higher CH_4 production from the Pila soil is probably caused by the presence of $CaCO_3$. The efficiency of methanotrophs present in the oxic surface layer is indicated by the percentage of the anoxic CH_4 flux that is oxidized (Table 2.4). The fraction of the CH_4 oxidized varies much less than the absolute production or oxidation of CH_4 within a rice field. The CH_4-oxidizing bacteria in the soil-water interface of Maahas and Luisiana soils are very efficient (70-90% of the diffusive CH_4 flux is oxidized) which is similar to the CH_4 oxidation efficiency of the Vercelli soil (Conrad and Rothfuss, 1991). Remarkably, the efficiency of CH_4-oxidizers in the soil-water interface of the Pila soil is much lower (33%) and highly variable. Low CH_4 oxidation rates were also reported for marl sediments of the Florida Everglades (King et al. 1990), indicating that high pH or presence of $CaCO_3$ in the water-soil interface may inhibit CH_4 oxidation.

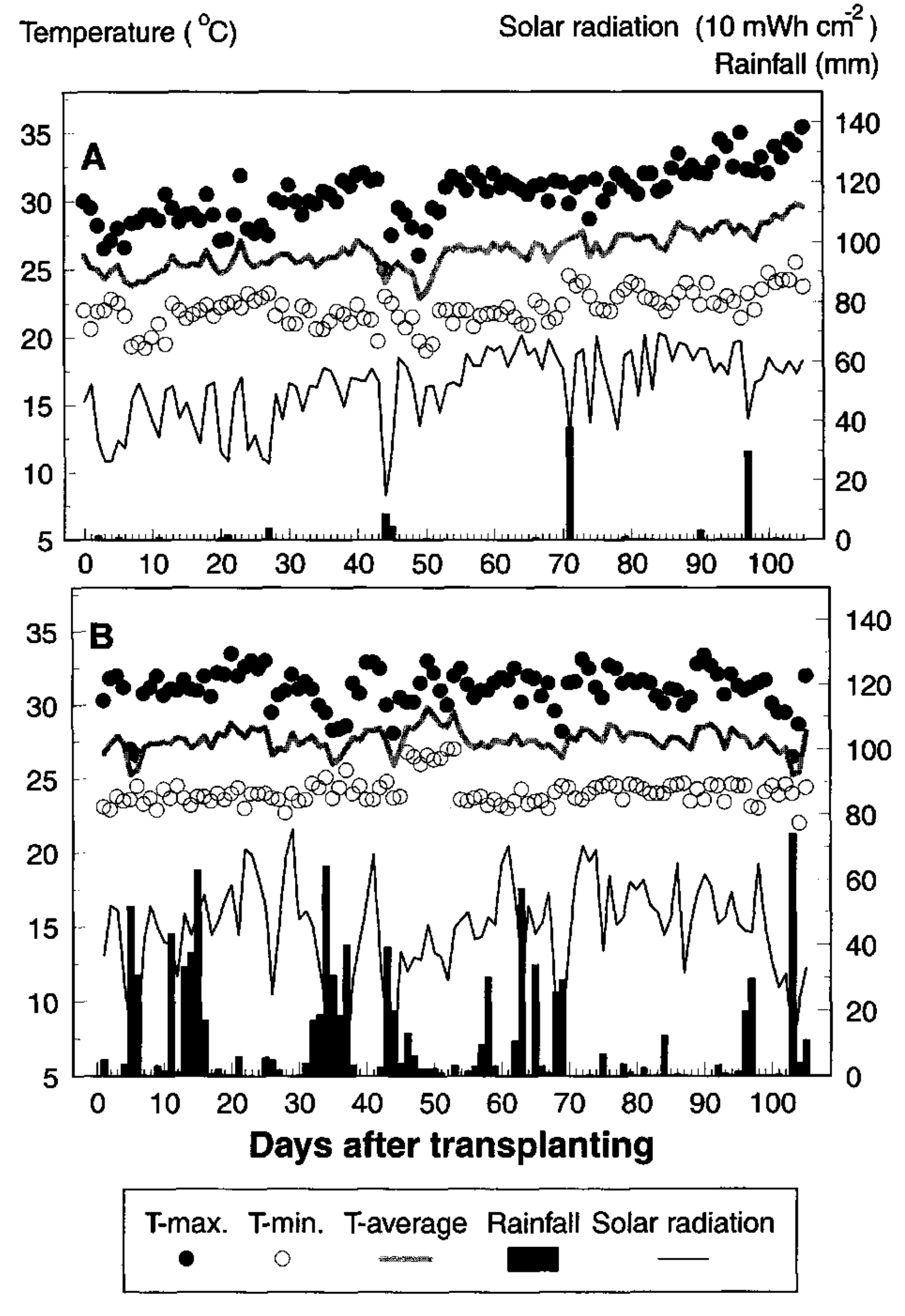

Figure 2.5 Temperature, rainfall and solar radiation in the 1992 dry season (a) and 1992 wet season (b).

Seasonal variation of CH_4 emission in field plots

During the growing season of the 1992 DS three emission peaks can be observed; around 35 DAT, 55-80 DAT, and from 100 DAT up to harvest (indicated by arrows in Figure 2.3). The second and third CH_4 emission peak are also observed in the urea fertilized plots of the '91 and '92 WS. Due to technical problems monitoring in the 1991 WS started only at 35 DAT, thus the first peak may have been missed in this season. Two or three seasonal peaks have been observed in most field studies e.g., USA (Cicerone et al., 1983; Sass and Fisher, 1994), Italy (Schütz et al., 1989a) and Japan (Yagi and Minami, 1990). The first peak is associated with the decomposition of soil organic matter or plant material from the previous season. This peak is not always observed, depending on local conditions. The second and third CH_4 emission peaks are associated with the rice plants since they are not observed in unplanted fields (Schütz et al., 1989a). Suggested causes for these emission peaks are increased root exudation, providing substrate for methanogens (second peak) and turnover of root litter at the end of the season (third peak) (e.g., Schütz et al., 1989b). A change in rhizospheric CH_4 oxidation is probably involved as well since rhizospheric CH_4 oxidation varies with the plant growth stage (Denier van der Gon and Neue, 1996). Monitoring of CH_4 emission continued after harvest of the 1992 DS crop and a fourth emission peak was observed. The peaks during the post-harvest period are due to the release of entrapped CH_4 upon soil drying (Denier van der Gon et al. 1995). The largest CH_4 emissions are observed from green manure fertilized plots (Table 2.2, Figure 2.4). Application of green manure enhanced CH_4 emission in general and also drastically changed the seasonal methane emission pattern by causing an extremely high CH_4 emission peak early in the season. The impact of green manure application on CH_4 emission was discussed in a separate paper by Denier van der Gon and Neue (1995a).

Influence of climate on CH_4 emission

The climate of the wet and dry season is different and may influence CH_4 emission. The wet season is characterized by higher rainfall and corresponding lower sunhours but temperature differences between the wet and the dry season are rather small (Figures 2.5a and 2.5b). In our study the rice fields were kept flooded by irrigation in rainless periods. Therefore, rainfall did not control the water status of the field. Obviously, without irrigation rainfall may make the difference between a flooded and a dry field and will have a distinct influence on production and emission of CH_4. The impact of other climate variables on CH_4 emission differs with the time scale studied.

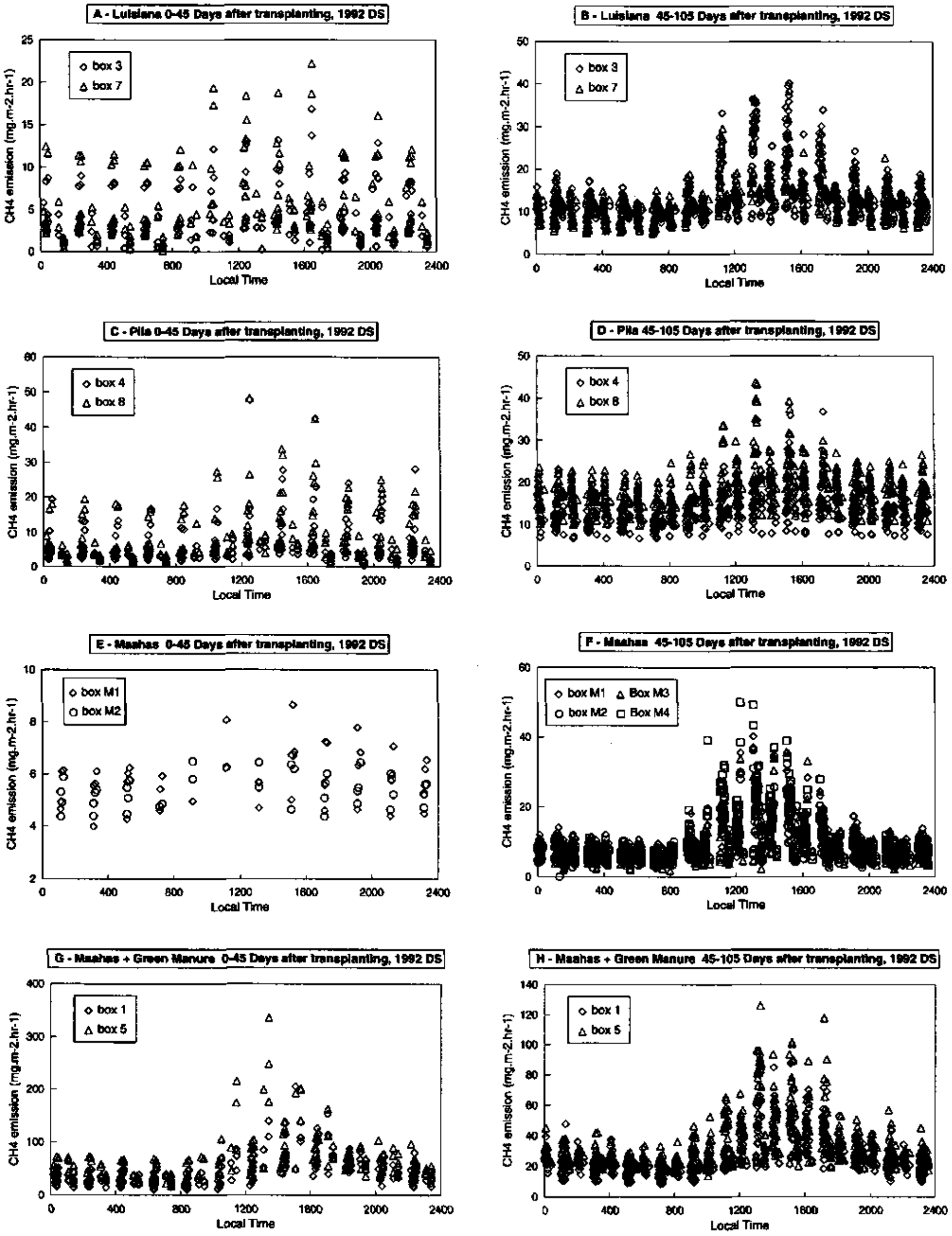

Figure 2.6 Methane emission data for the 1992 dry season from individual closed chambers in rice fields on three different soil types fertilized with urea (a-f) or green manure (g-h, data from Denier van der Gon and Neue, 1995a) plotted as a function of time of day.

Diurnal variation Plotting all CH_4 emission measurements of the 1992 dry season against the time of day in (Figure 2.6) revealed a weak diurnal pattern during the first 45 days after transplanting in the urea fertilized plots (Figures 2.6a, 2.6c and 2.6e). The green manure fertilized field showed a strong diurnal variation in this early period (Figure 2.6g). This indicates that additional substrate input is a prerequisite for strong diel emission peaks early in the season. After 45 days after transplanting CH_4 emission from all fields showed a strong diel fluctuation (Figures 2.6b, 2.6f and 2.6h) although the pattern was less pronounced in the sandy loam (Pila soil, Figure 2.6d). The diel CH_4 emission pattern roughly correlated with the diel temperature pattern (Figure 2.7). In Texan rice fields, variations in CH_4 emission correlated well with soil temperatures and this relation could be described by the Arrhenius equation (Sass et al., 1991). However, applying the Arrhenius equation to our data set yielded poor

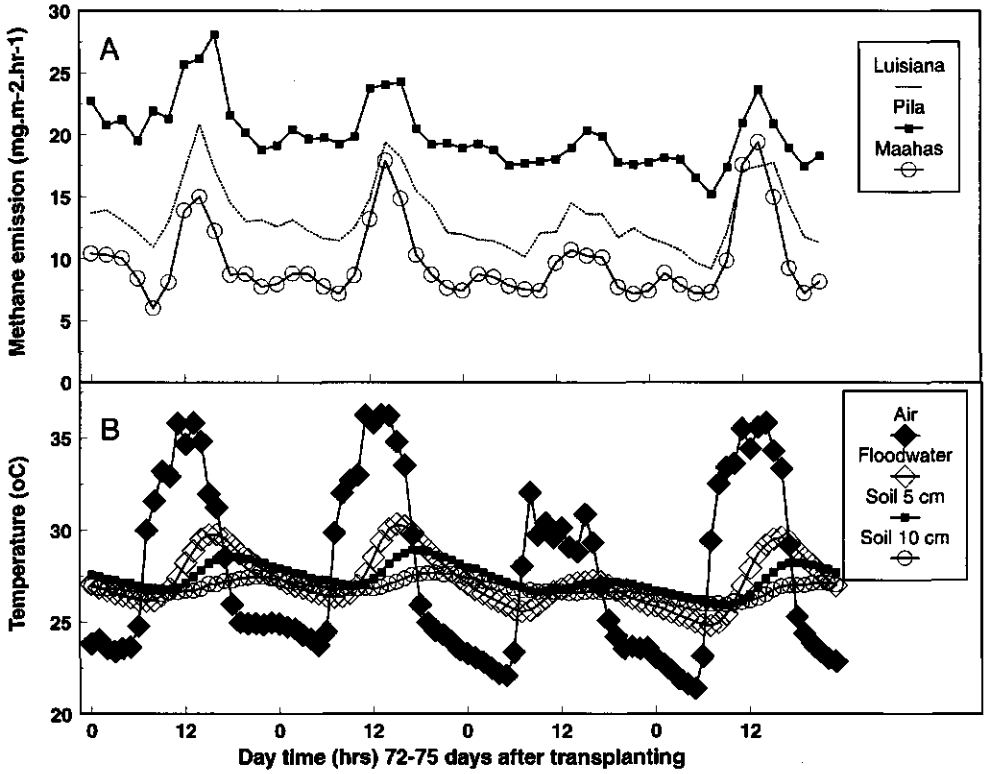

Figure 2.7 Diurnal pattern of CH_4 emission (a) and temperature (b) from 72-75 days after transplanting in the 1992 dry season.

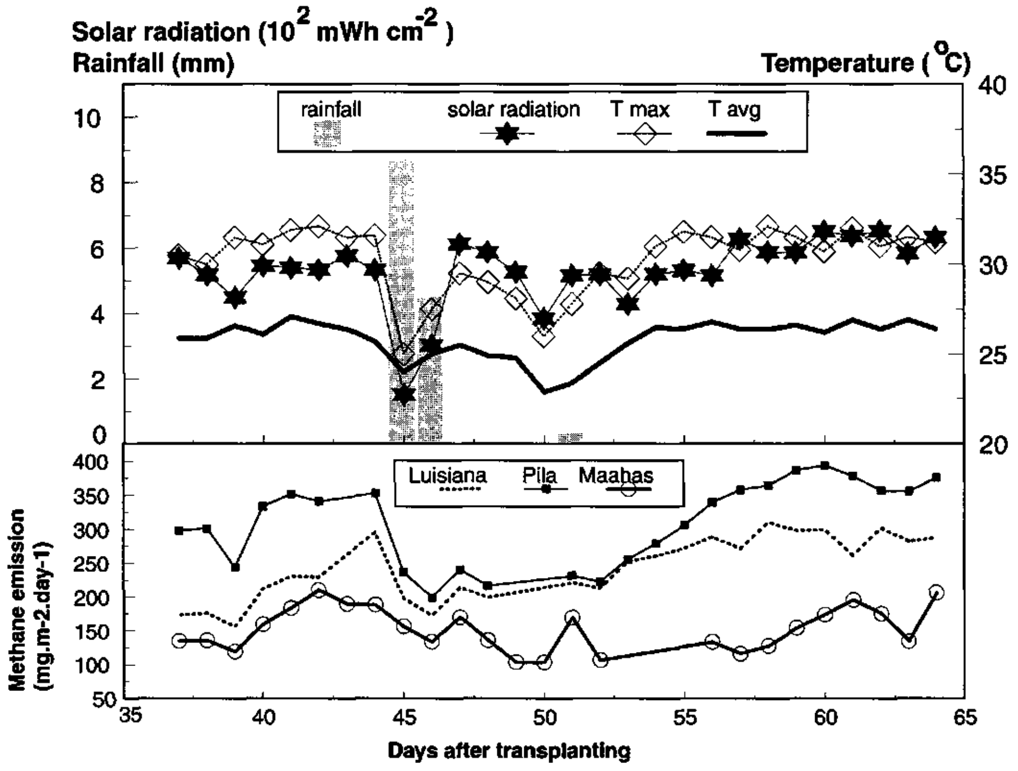

Figure 2.8 A climatic event in the 1992 dry season illustrating the correlation between solar radiation, air temperature and CH_4 emission in the 1992 dry season.

results. This can be explained by a difference in the timing of the diel CH_4 emission peak. Diel CH_4 emission peaks in Texan rice fields occurred at 19:00-21:00 local time (Sass et al., 1991), several hours later than in our fields (Figure 2.6). In our fields CH_4 emissions peaked often distinctly earlier than soil temperature peaks, making a causal relationship between soil temperatures peaks and CH_4 emission peaks unlikely. Diel CH_4 emissions from our fields correlate best with a 2-4 hour shifted air temperature curve or, in other words, CH_4 emission correlates with the air temperature observed 2-4 hours earlier. Of course air temperatures are highly correlated with other processes that follow day-night patterns (e.g. solar radiation, photosynthesis), so no causal relationships can be deduced from this observation.

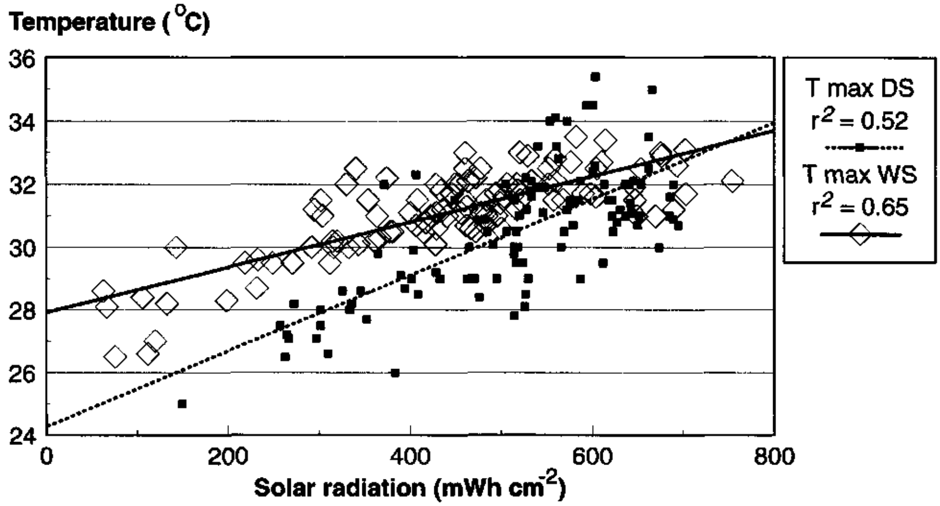

Figure 2.9 Correlation between temperature and solar radiation for the dry season and wet season of 1992.

Variation on a scale of days In periods with a climatic event, while other non-climate variables remained relatively constant (e.g., total root length, plant biomass), a positive correlation between average daily CH_4 emission, maximum daily temperature and solar radiation can be observed (e.g., Figure 2.8). The correlation with average daily temperature and minimum daily temperature (=night temperature) was smaller. Maximum daily temperature and solar radiation were highly correlated in both seasons (Figure 2.9). Controlled experiments with variations in maximum temperature under constant radiation and vice versa are desired to elucidate the relationship between daily CH_4 emission and these climate variables.

Seasonal variation CH_4 emissions were not correlated with temperature over a full growing season, probably because 1) the variation in daily temperature within a season is small and, as will be discussed below, 2) the growing rice plant with its increasing root system and biomass is the main factor controlling the seasonal emission pattern. Seasonal CH_4 emission for comparable fertilizer treatments was lower in the wet season. This is not a temperature effect because average temperatures of the 1992 dry season and wet season were not significantly different (26.3 ± 1.4 °C and 27.6 ± 0.8 °C, respectively). Total number of sunhours was about double in the dry season (816) compared to the wet season (447) but the difference in total solar radiation was less pronounced. During the first 40 days after transplanting solar radiation was equal in both seasons, from 40 days onward total solar radiation was 25% higher in the dry season. Such climate variables may affect CH_4 emission e.g., through effects on net primary production and root exudation.

Influence of biomass on CH_4 emission

Aselman and Crutzen (1989) calculated that 3-7% of the net primary production (NPP) in a wetland rice field was emitted as CH_4. In one of two Texan rice fields studied, CH_4 emission was strongly correlated with above ground biomass (Sass et al. 1990). So, NPP, or a correlated parameter such as straw yield, is an important parameter when studying CH_4 fluxes from rice fields. When using a closed chamber technique with fixed chambers as in our study both the NPP (or straw yield) inside the chambers and in the surrounding field should be recorded to link measured emissions to the field. CH_4 fluxes measured in the 1991 wet season probably underestimate the emissions from the surrounding field because the biomass inside the flux chambers was about half that of the surrounding field (Table 2.2). The low straw yields in the 1991 wet season may be caused by 1) low fertilizer input and, 2) the flux chambers were closed for 48 minutes every 2 hours which may have hindered plant growth. In 1992 fertilizer application was adjusted and closure of the boxes during a measurement cycle was reduced to 24 minutes. Straw yields doubled in 1992 and, in the dry season, straw yields inside and outside the gas collector chambers were not significantly different. The straw yields in the 1992 wet season inside the gas collector chambers were higher than outside the chambers, because the plants growing inside were protected against a typhoon which damaged the plants outside. So, CH_4 fluxes measured in the 1992 wet season may slightly overestimate CH_4 emissions from the surrounding field. CH_4 emissions in the 1991 wet season were lower than in the other seasons for all three soils. In urea fertilized fields, low CH_4 emissions correlate with low biomass production for each soil type. Green manure fertilized fields should be considered separately because the input of fresh organic matter strongly enhances CH_4 emission and changes the seasonal emission pattern (Denier van der Gon and Neue, 1995a). NPP or straw yield may be a useful proxy for predicting CH_4 emission, once a baseline emission is known. However, CH_4 emission from the urea fertilized Maahas plots in the dry season was about 3 times higher than in the 1992 wet season while straw yields were comparable so additional variables need to be included.

Conclusions

The large difference in CH_4 production of the three soils as observed in the laboratory incubation study without organic amendment was not proportional to the CH_4 emission from these soils when planted to rice. When planted to rice the Maahas soil, with a very low CH_4 production rate in the incubation experiment, was only 1.4-1.8 times lower in CH_4 emission than the other two soils. A similar difference was observed in the incubation study with organic amendment. The most likely explanation for this observation is that the rice plants generate a large supply of substrate for microbial decomposition, thus making the methanogens less dependable on substrate from native soil organic carbon. Including an incubation with organic amendment was found to be very valuable, especially if soil incubations are to be used for prediction of CH_4 emission from rice fields. To link soil incubation results to actual CH_4 emissions requires additional research with a strong emphasis on process modeling.

There appears to be no causal relationship between the diel soil temperature pattern and the diel CH_4 emission pattern in our fields. This is in contradiction with Sass et al. (1991) but Schütz et al. (1990) also suggested that diel changes of soil properties other than temperature affect CH_4 emission rates (e.g. root exudation). A positive correlation between maximum air temperature, solar radiation and CH_4 emissions can be observed both on a time scale of hours (diurnal variation) and on a time scale of days if there is a climatic event. On a longer time scale (e.g., months, the growing season) no correlation between temperature, and CH_4 emission was observed probably because average daily temperatures on our field site are relatively stable year round. Nevertheless, recording of temperature and solar radiation remains important because it may help explaining differences in CH_4 emission from different locations of the world. Field measurements of pH and Eh in a planted rice fields appear to be of limited value to predict CH_4 emission perhaps because it is not possible to precisely measure Eh and pH at microsites where CH_4 production occurs.

Methane oxidation is an important process which reduces the CH_4 flux from wetland rice fields. Methanotrophs typically oxidize 70-90% of the CH_4 diffusing upward through the oxic soil surface layer in most rice soils. However, exceptions to this rule do exist. So far, lower CH_4 oxidation efficiencies in the soil-water interface of rice fields have been found when ammonium (Conrad and Rothfuss, 1991), salinity (Denier van der Gon and Neue, 1995b) or calcareous material (this study) is present. Apparently a high pH or free $CaCO_3$ hinders CH_4 oxidation too. Whether this is due to a direct or indirect effect (e.g. complexation of trace elements important for methanotrophs) needs further study. Furthermore, we do not know whether a calcareous soil also reduces CH_4 oxidation in the rhizosphere. The rhizosphere environment differs considerably from the bulk soil and it is not unlikely that soil properties are of limited influence in the rhizosphere.

CH_4 emission from rice planted on a calcareous sandy loam was higher than CH_4 emission from a clay soil if mineral fertilizer was applied. CH_4 production in the calcareous soil was higher and CH_4 oxidation was hindered. Although we cannot separate the impact of calcareous material and texture in our study, incubation studies show that presence of $CaCO_3$ stimulates CH_4 production (Neue and Roger, 1994). We therefore assume that presence of $CaCO_3$ was mostly responsible for the higher CH_4 emission of the calcareous sandy loam. However, clay minerals can protect organic matter from breakdown (Jenkinson, 1977; Oades, 1988) and higher clay content may promote soil entrapment of CH_4 (Wang et al. 1993b) indicating that the soil texture of the calcareous sandy loam was also more favorable for CH_4 emission. Production and emission of CH_4 from plots on different soil types increased strongly and became similar upon incorporation of green manure. So, in our study incorporation of organic carbon in the rice fields was a more important variable controlling CH_4 emission than presence of $CaCO_3$ or variation in texture.

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References

Aselman, I. and P. Crutzen, Global distribution of natural freshwater wetlands and rice paddies: Their net primary productivity, seasonality and possible methane emissions, J. Atmos. Chem., 8, 307-358, 1989.

Bachelet, D. and H.U. Neue, Methane emission from wetland rice areas of Asia, Chemosphere, 26, 219-238, 1993.

Cicerone, R.J., and J.D. Shetter, Sources of atmospheric methane: Measurements in rice paddies and a discussion, J. Geophys. Res., 86, 7203-7209, 1981.

Cicerone, R.J., J.D. Shetter, and C.C. Delwiche, Seasonal variation ofmethane flux from a California rice paddy, J. Geophys. Res., 88, 11022-11024, 1983.

Conrad, R. and R. Rothfuss, Methane oxidation in the soil surface layer of a flooded rice field and the effect of ammonium, Biol. Fert. Soils, 12, 28-32, 1991.

Denier van der Gon, H.A.C. and H.-U. Neue, Impact of gypsum application on the methane emission from a wetland rice field, Global Biogeochem. Cycles., 8, 127-134, 1994.

Denier van der Gon, H.A.C. and H.-U. Neue, Influence of organic matter incorporation on the methane emission from a wetland rice field, Global Biogeochem. Cycles., 9, 11-22, 1995a.

Denier van der Gon, H.A.C. and H.U. Neue, Methane emission from a wetland rice field as affected by salinity, Plant and Soil, 170, 307-313, 1995b.

Denier van der Gon, H.A.C. and H.U. Neue, Oxidation of methane in the rhizosphere of rice plants, Biol. Fert. Soils, 22, 359-366, 1996.

Denier van der Gon, H.A.C., H.-U. Neue, R.S. Lantin, R. Wassmann, M.C.R. Alberto, J.B. Aduna, and M.J.P. Tan, Controlling factors of methane emission from rice fields, In: Proceedings of WISE workshop, ISRIC, Wageningen, The Netherlands, 1992.

Denier van der Gon, H.A.C., N. van Breemen H.-U. Neue, R.S. Lantin, R. Wassmann, J.B. Aduna, and M.C.R. Alberto, Release of entrapped methane from wetland rice fields upon soil drying, Global Biogeochem. Cycles., 10, 1-9, 1996.

Fetzer, S. and R. Conrad, Effect of redox potential on methanogenesis by methanosarcina barkeri, Arch. Microbiol., 160, 108-113, 1993.

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

International Atomic Energy Agency (IAEA), Manual on measurement of methane and nitrous oxide emissions from agriculture, IAEA-TECDOC-674, Int. At. Energ. Agency, Vienna, Austria, 1992.

Intergovernmental Panel on Climate Change (IPCC), Climate Change, The IPCC scientific assessment, edited by J.T. Houghton, G.J. Jenkins and J.J. Ephraums, Cambridge University Press, New York, 1990.

Intergovernmental Panel on Climate Change (IPCC), Climate Change 1994, Radiative forcing of climate change and an evaluation of the IPCC IS92 emission scenarios, Cambridge University Press, New York, 1994.

Jenkinson, D.S., Studies on the decomposition of plant material in soil. V. The effects of plant cover and soil type on the loss of carbon from ^{14}C labelled ryegrass decomposing under field conditions, J. Soil Sci., 28, 424-434, 1977.

King, G.M., Dynamics and controls of methane oxidation in a Danish wetland sediment, FEMS Microbiol. Ecol., 74, 309-324, 1990.

King, G.M., P. Roslev, and H. Skovgaard,, Distribution and rate of methane oxidation in sediments of the Florida Everglades, Appl.Environmen. Microbiol., 56, 2902-2911, 1990.

Neue, H.U. and P.A. Roger, Potential of Methane Emission in major Rice Ecologies, in: Climate Biosphere Interaction, edited by R.G. Zepp, pp. 65-93, Wiley and Sons, New York, 1994.

Oades, J.M., The retention of organic matter in soils, Biogeochem., 5, 35-70, 1988.

Patrick, W.H., Jr., The role of inorganic redox systems in controlling reduction in paddy soils, In: Proceedings of Symposium on Paddy Soil, pp. 107-117, Science Press, Beijing, Springer Verlag, Berlin, 1981.

Ponnamperuma, F.N., The chemistry of submerged soils. Adv. Agr. 24, 29-96, 1972.

Sass, R.L. and F.M. Fisher, CH_4 emission from paddy fields in the United States Gulf Coast Area, in: CH_4 and N_2O: Global emissions and controls from rice fields and other agricultural and Industrial sources, edited by K. Minami, A. Mosier, and R. Sass, pp. 65-77, National Institute of Agro-Environmental Sciences, Tsukuba, Japan, 1994.

Sass, R.L., F.M. Fisher, P.A. Harcombe, and F.T. Turner, Methane production and emission in a Texas rice field, Global Biogeochem. Cycles, 4, 47-68, 1990.

Sass, R.L., F.M. Fisher, F.T. Turner, and M.F. Fund, Methane emission from rice fields as influenced by solar radiation, temperature, and straw incorporation, Global Biogeochem. Cycles, 5, 335-350, 1991.

Schütz, H., A. Holzapfel-Pschorn, R. Conrad, H. Rennenberg, and W. Seiler, A 3-year continuous record on the influence of daytime, season, and fertilizer treatment on methane emission rates from an Italian rice paddy, J. Geophys. Res., 94, 16,405-16,416, 1989a.

Schütz, H., W. Seiler, and R. Conrad, Processes involved in formation and emission of methane in rice paddies, Biogeochem., 7, 33-53, 1989b.

Schütz, H., W. Seiler, and R. Conrad, Influence of soil temperature on methane emission from rice paddy fields, Biogeochem., 11, 77-95, 1990.

Tsutsuki, K., and F.N. Ponnamperuma, Behaviour of anaerobic decomposition products in submerged soils, Effects of organic material amendment, soil properties and temperature, Soil Sci. Plant Nutr., 33, 13-33, 1987.

Wang, Z.P., R.D. DeLaune, P.H. Masscheleyn, and W.H. Patrick, Jr., Soil redox and pH effects on methane production in a flooded soil, Soil Sci. Soc. America J., 57, 382-385, 1993a.

Wang, Z.P., C.W. Lindau, R.D. Delaune, and W.H. Patrick, Jr., Methane emission and entrapment in flooded rice soils as affected by soil properties, Biol. Fertil. Soils, 16, 163-168, 1993b.
Yagi, K., and K. Minami, Effect of organic matter application on methane emission from some Japanese paddy fields, Soil Sci. Plant Nutr., 36, 599-610, 1990.
Zobler, L., A world soil file for global climate, NASA technical memorandum 87-802, 1986.

Chapter 3

Impact of Gypsum Application on the Methane Emission from a Wetland Rice Field

H.A.C. Denier van der Gon and H.-U. Neue

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

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 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} gypsum ($CaSO_4.2H_2O$). 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} gypsum). 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 is based on four samples, and r^2 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 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 3.1).

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 3.1a and 3.1b 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 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 3.2, 3.3a, and 3.3b). 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 3.2). 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 3.2 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 3.2).

Table 3.1 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.

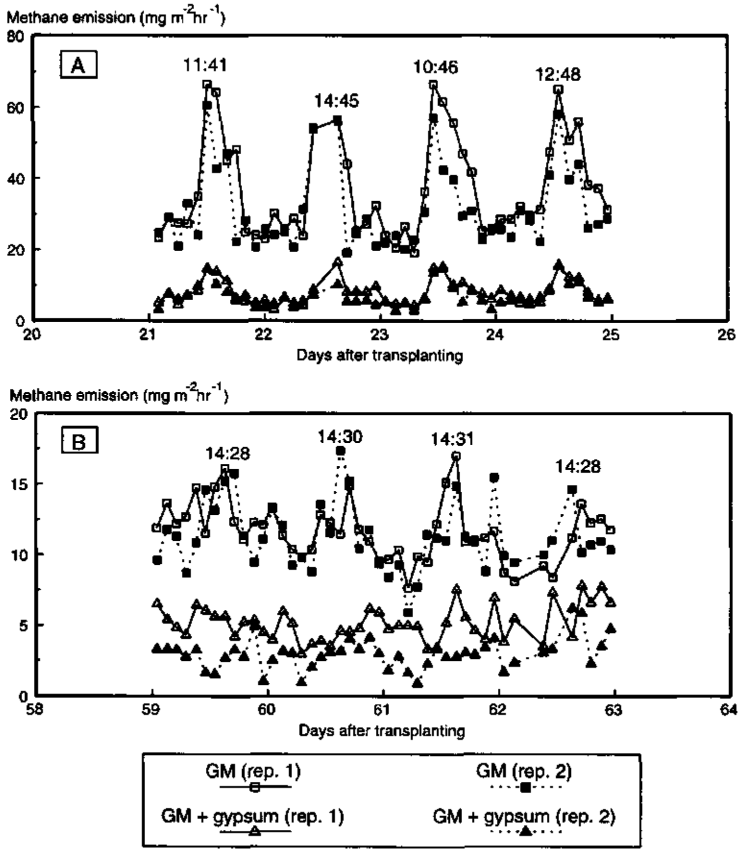

Figure 3.1 Diurnal variation in methane emission from green manure fertilized rice fields, with and without gypsum amendment, approximately (a) three weeks after transplanting and (b) nine weeks after transplanting.

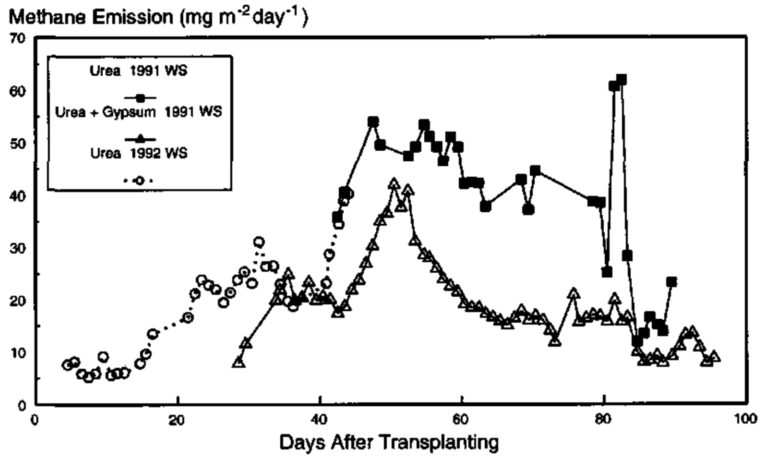

Figure 3.2 Methane emission from urea fertilized rice fields, with and without gypsum amendment, in the 1991 wet season.

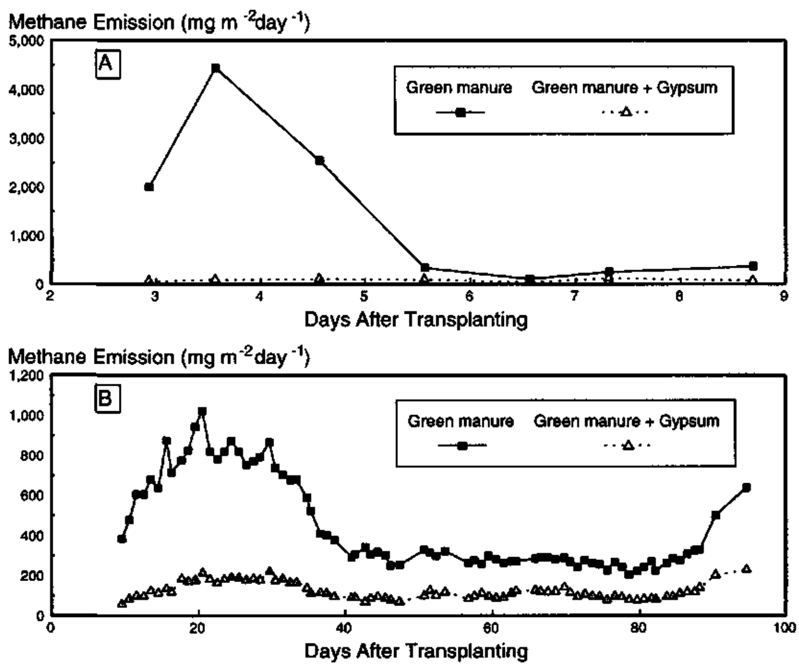

Figure 3.3 Methane emission from green manure fertilized rice fields, with and without gypsum amendment, in the 1992 wet season (a) during the first week after transplanting and (b) from the second week after transplanting onward.

Table 3.2 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 3.3a.

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 3.2). 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 3.1; 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 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 3.3a).

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 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 3.3. 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.

Table 3.3 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.

Table 3.4 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.

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 3.4). 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 3.3). The data in Table 3.3 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-} concentration in the soil solution remained high throughout the growing season (Table 3.4). 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.

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References

Abrol, I.P., D.R. Bhumbla, and O.P. Meelu, Influence of salinity and alkalinity on properties and management of ricelands, in Soil Physics and Rice, pp. 183-198, Int. Rice Res. Inst., Los Banos, Philippines, 1985.

Anastasi, C., M. Dowding, and V.J. Simpson, Future CH_4 emissions from rice production, J. Geophys. Res., 97, 7521-7525, 1992.

Bachelet, D., and H.U. Neue, Methane emission from wetland rice areas of Asia, Chemosphere, 26, 219-238, 1993.

Bhumbla, D.R., and I.P. Abrol, Saline and sodic soils, in Soils and Rice, pp. 719-738, Int. Rice Res. Inst., Los Banos, Philippines, 1978.

Bouwman A.F. (Ed.) , Soils and the Greenhouse Effect, 575 pp., John Wiley, New York, 1990.
Cappenberg, T. E., Interrelations between sulfate-reducing bacteria and methane-producing bacteria in bottom deposits of a fresh-water lake, I, Field observations, Anthonie van Leeuwenhoek, 40, 285-295, 1974.
Cicerone, R.J., and R.S. Oremland, Biogeochemical aspects of atmospheric methane, Global Biogeochem. Cycles, 2, 299-327, 1988.
Cicerone, R.J., and J.D. Shetter, Sources of atmospheric methane: Measurements in rice paddies and a discussion, J. Geophys. Res., 86, 7203-7209, 1981.
Conrad, R., Control of methane production in terrestrial ecosystems, in Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere, edited by M.O. Andrae and D.S. Schimmel, pp. 39-58, John Wiley, New York, 1989.
DeLaune, R. D., C. J. Smith and W. H. Patrick, Jr., Methane release from Gulf coast wetlands, Tellus, 35B, 8-15, 1983.
Delwiche, C.C. and R.J. Cicerone, Factors affecting methane production under rice, Global Biogeochem. Cycles, 7, 143-155, 1993.
Freney, J.R., V.A. Jacq, and J.F. Baldensperger, The significance of the biological sulfur cycle in rice production, in Microbiology of Tropical Soils and Plant Productivity, edited by Y.R. Dommerques and H.G. Diem, pp. 271-313, Nijhoff/Junk, Boston, Mass., 1982.
Hines, M.E., and J.D. Buck, Distribution of methanogenic and sulfate-reducing bacteria in near-shore sediments, Appl. Environ. Microbiol., 43, 447-453, 1982.
International Atomic Energy Agency (IAEA), Manual on measurement of methane and nitrous oxide emissions from agriculture, IAEA-TECDOC-674, Vienna, Austria, 1992.
Intergovernmental Panel on Climate Change (IPCC),Climate Change: Intergovernmental Panel on Climate Change-Scientific Assessment, edited by J.T. Houghton, G.J. Jenkins, and J.J. Ephraums, Cambridge University Press, New York, 1990.
Intergovernmental Panel on Climate Change (IPCC), Climate Change. The Supplementary Report to the IPCC Scientific Assessment, edited by J.T. Houghton, B.A. Callander, and S.K. Varney, 200 pp., Cambridge University Press, New York, 1992.
International Rice Research Institute (IRRI), Program report for 1992, Los Baños, Philippines, 1993.
Lelieveld, J., P.J. Crutzen and C. Brühl, Climate effects of atmospheric methane, Chemosphere, 26, 739-768, 1993.
Logan, J.A., M.J. Prather, S.C. Wofsy, and M.B. McElroy, Tropospheric chemistry: A global perspective, J. Geophys. Res., 86, 7210-7254, 1981.
Lovley, D.R., and M.J. Klug, Model for the distribution of sulfate reduction and methanogenesis in freshwater sediments, Geochim. Cosmochim. Acta, 50, 11-18, 1986.
Lovley, D.R., and M.J. Klug, Sulfate reducers can outcompete methanogens at freshwater sulfate concentrations, Appl. Environ. Microbiol., 45, 187-192, 1983.
Lovley, D.R., D.F. Dwyer, and M.J. Klug, Kinetic analysis of competition between sulfate reducers and methanogens for hydrogen in sediments, Appl. Environ. Microbiol., 43, 1373-1379, 1982.
Martens, C.S., and R.A. Berner, Methane production in the interstitial waters of sulfate-depleted marine sediments, Science, 185, 1167-1169, 1974.
Motomura, S., Dynamic behaviour of ferrous iron in paddy soils, JARQ, 4, 12-17, 1969.
Novozamsky, I., J. Beek, and G.H. Bolt, Chemical equilibria, in Soil Chemistry, A, Basic Elements, edited by G.H. Bolt and M.G.M. Bruggenwert, pp. 13-41, Elsevier Science, New York, 1978.
Oremland, R.S., Biogeochemistry of methannogenic bacteria, in Biology of Anaerobic Microorganisms, edited by A.J.B. Zehnder, pp. 641-705, John Wiley, New York, 1988.
Patrick, W.H., Jr., and C.N. Reddy, Chemical changes in rice soils, in Soils and Rice, pp. 361-376, Int. Rice Res. Inst., Los Banos, Philippines, 1978.
Robles, A.M., The effect of flood and dry fallow rice cropping systems on the kinetics and plant availability of Fe and Mn, M.S. thesis, Univ. of the Philippines at Los Banos, 1989.
Sass, R.L., F.M. Fisher, P.A. Harcombe, and F.T. Turner, Methane production emission in a Texas rice field, Global Biogeochem. Cycles, 4, 47-68, 1990.

Schütz, H., A. Holzapfel-Pschorn, R. Conrad, H. Rennenberg, and W. Seiler, A 3-year continuous record on the influence of daytime, season and fertilizer treatment on methane emission rates from an Italian rice paddy, J. Geophys. Res., 94, 16,405-16,416, 1989a.

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

Schütz, H., W. Seiler, and R. Conrad, Influence of soil temperature on methane emission from rice paddy fields, Biogeochemistry, 11, 77-95, 1990.

Sharma, P.K., and S.K. De Datta, Effects of puddling on soil physical properties and processes, in Soil Physics and Rice, pp. 217-234, Int. Rice Res. Inst., Los Banos, Philippines, 1985.

Van Breemen, N., and L.J. Pons, Acid sulfate soils and rice, in Soils and Rice, Int. Rice Res. Inst., Los Banos, Philippines, 1978.

Wang, W.C., Y.L. Yung, A.A. Lacis, T. Mo, and J.E. Hansen , Greenhouse effects due to man-made perturbations of trace gases, Science, 194, 685-690, 1976.

Wassmann, R., H. Schütz, H. Papen, H. Rennenberg, W. Seiler, A.G. Dai, R.X. Shen, X.J. Shangguan, and M.X. Wang, Quantification of methane emissions from chinese rice fields (Zhejiang Province), Biogeochemistry 20, 83-101, 1993.

Wiebe, W.J., R.R. Christian, J.A. Hansen, G. King, B. Sherr, and G. Skyring, Anaerobic respiration and fermentation, in The Ecology of a Salt Marsh, edited by L.R. Pomeroy and R.G. Wiegert, pp. 137-159, Springer-Verlag, New York, 1981.

Yagi, K., and K. Minami, Effect of organic matter applica-tion on methane emission from some Japanese paddy fields, Soil Sci. Pl. Nutr., 36, 599-610, 1990.

Yamane, I., and K. Sato, Initial drop in oxidation-reduction potential in submerged, air-dried soils, Soil Sci. Plant Nutr. Tokyo, 14, 68-72, 1968.

Chapter 4

Methane Emission from a Wetland Rice Field as Affected by Salinity

H.A.C. Denier van der Gon and H.-U. Neue

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Methane emission from a wetland rice field as affected by salinity

Abstract

The impact of salinity on CH_4 emission was studied by adding salt to a Philippine rice paddy, increasing pore water EC to approx. 4 $dS.m^{-1}$. Methane emission from the salt-amended plot and adjacent control plots was monitored with a closed chamber technique. The addition of salt to the rice field caused a reduction by 25% in CH_4 emission. Rates of methane emissions from intact soil cores were measured during aerobic and anaerobic incubations. The anaerobic CH_4 fluxes from the salt-amended soil cores were three to four times lower than from cores of the control plot, whereas the aerobic CH_4 fluxes were about equal. Measurements of the potential CH_4 production with depth showed that the CH_4 production in the salt-amended field was strongly reduced compared to the control field. Calculation of the percentage CH_4 oxidized of the anaerobic flux indicated that CH_4 oxidation in the salt-amended plot was even more inhibited than CH_4 production. The net result was about equal aerobic CH_4 fluxes from both salt-amended plots and non-amended plots. The data illustrate the importance of both CH_4 production and CH_4 oxidation when estimating CH_4 emission and show that the ratio between CH_4 production and CH_4 oxidation may depend on environmental conditions. The reduction in CH_4 emission from rice paddies upon amendment with salt low in sulfate is considerably smaller than the reduction in CH_4 emission observed in a similar study where fields were amended with high-sulfate containing salt (gypsum). The results indicate that CH_4 emissions from wetland rice fields on saline, low-sulfate soils are lower than CH_4 emissions from otherwise comparable non-saline rice fields. However, the reduction in CH_4 emission is not proportional to the reduction in CH_4 production.

Introduction

Atmospheric methane concentrations have increased from about 0.8 to 1.7 ppmv since pre-industrial times (Blake and Rowland, 1988; Khalil et al., 1989). Methane is an important greenhouse gas and plays a key role in tropospheric and stratospheric chemistry (Wang et al., 1976; Lelieveld et al., 1993). The rate at which atmospheric methane concentrations increase has slowed down in recent years (Steele et al., 1992; Dlugokencky et al., 1994). To understand the observed trends and predict future atmospheric methane concentrations an accurate budget of the sources and sinks of atmospheric CH_4 is required. To achieve this uncertainties in individual CH_4 sources need to be reduced.

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 may account for about 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). Various parameters that influence CH_4 emission from rice fields have been identified but only few have been tested under field conditions. These include incorporation of organic matter, which stimulates CH_4 emissions (e.g., Schütz et al., 1989; Yagi and Minami, 1990) and high concentrations of sulfate, which reduce CH_4 emissions (Denier van der Gon and Neue, 1994). For an extensive review of parameters controlling CH_4 emission from wetland rice fields we refer to Neue and Sass (1994) and Rennenberg et al. (1993).

Salinity is among the factors suggested to influence CH_4 emission from wetland rice fields (Bachelet and Neue, 1993; Neue and Sass, 1994). A soil is called saline if the electrical conductivity of its saturation extract exceeds 4 $dS.m^{-1}$ (US Salinity Laboratory Staff, 1954). Saline soils are widely distributed in arid and semi-arid areas and in coastal areas. Boje-Klein (1986) estimated the total area of saline soils and sodic soils in South and South-east Asia as 16.2 and 7.2 million ha, respectively. Approximately 9.5 million ha of this acreage could be grown to saline and/or sodic soils-tolerant rice varieties (Boje-Klein, 1986). This may even be an underestimate since no data for Indonesia were available. We estimate that 4-5 million ha saline soils is grown to rice at present. This estimate is based on the estimated coastal saline soils grown to rice in India, Bangladesh, Thailand, Burma, Vietnam and Malaysia (Garrity et al., 1986) and adding 1 million ha of coastal saline soils in Indonesia and about 2 million ha of inland saline soils grown to irrigated rice in India and Pakistan. Thus, saline soils contribute significantly to the total rice soil acreage. Combination of the estimated area of saline soils grown to rice at present and the potential saline soil-area for rice cultivation indicates that in the future another 4-5 million ha of saline and/or sodic soils may be reclaimed for rice production.

The predominant anions in saline soils are chloride, sulfate and carbonate. Microbial incubation studies demonstrated that sulfate-reducing bacteria (in the presence of sulfate) can outcompete methanogens for substrate (Lovley and Klug, 1983). The annual CH_4 flux from coastal salt marshes in the USA showed a strong negative correlation with soil salinity which was mainly attributed to increasing sulfate concentrations along the salinity gradient (DeLaune et al., 1983; Bartlett et al., 1987). A 50-72 % reduction in CH_4 emission was reported for wetland rice fields amended with gypsum ($CaSO_4$), most likely caused by competition between methanogenic and sulfate-reducing bacteria (Denier van der Gon and Neue, 1994). Although salinity is often accompanied by high sulfate concentrations, this is not necessarily the case. Unfortunately there is no soil classification that separates saline soils high in sulfate from other saline soils. Often these soils are classified as sodic soils (soils with an exchangeable sodium percentage (ESP) > 15, US Salinity Laboratory Staff, 1954) but the definition of sodic soils gives no information on the sulfate content of the soil. Whether non-sulfate salts (notably NaCl or Na_2CO_3), important in many non-coastal salt affected regions, also reduce CH_4 fluxes cannot be deduced from experiments where sulfate is present in high concentrations. In pure cultures of methanogens, NaCl inhibited microbial growth and CH_4 production (Patel and Roth, 1977) indicating that non-sulfate salinity may also reduce CH_4 emission. However, some strains showed inhibition only at high concentrations (>0.17 M), well above the concentrations normally found in saline rice soils (0.04-0.1 M).

CH_4 emission is the net result of CH_4 production and CH_4 oxidation. The mechanism behind changes in CH_4 emission can only be understood if information on CH_4 production and CH_4 oxidation is obtained. King et al. (1990) introduced a method to study the production and oxidation of CH_4 in intact soil cores from natural wetlands. This method was successfully applied by Conrad and Rothfuss (1991) in an Italian rice field. Furthermore, potential CH_4 production in the total soil column can be measured by incubating soil samples from different layers under a N_2 atmosphere (Sass et al., 1990). By comparing the CH_4 production with the CH_4 actually emitted an estimate of CH_4 oxidation in the field can be obtained.

Bachelet and Neue (1993) proposed a classification of rice soils, based on so-called "expert judgement", to categorize rice growing locations from potentially methane producing to non-methane producing areas. They found that global emissions from rice fields were reduced by 25% if a distinction according to soil type was made. This indicates that including soil characteristics in the global estimates could significantly alter the global estimate. To study the impact of non-sulfate salinity on CH_4 emissions we amended a rice field with salt in the 1991 wet season. The monitored CH_4 flux was compared with the CH_4 flux from neighbouring non-amended plots. Although we observed no strong reduction in CH_4 emission from the saline plot, the results could not be properly interpreted because 1) a part of the saline plot was severely damaged by insects and 2) heavy rains in the wet season made it very difficult to control the salinity level. Therefore the experiment was repeated in the 1992 dry season. The objective of this paper is to study the impact of non-sulfate salinity on CH_4 emission and to understand the mechanism controlling CH_4 emission by measuring CH_4 production and CH_4 oxidation.

Materials and methods

Field preparations

Field measurements of CH_4 emission are performed during the 1992 dry season (January-April) in wetland rice fields of the International Rice Research Institute, Los Baños, Philippines. The soil at the field site is an Andaqueptic Haplaquoll. Its texture is 66% clay, 28% silt and 6% sand and the soil has 1.97% organic C, 0.166% total N and a pH-H_2O of 5.9. The plots (3x5 m or 5x5 m), adjacent to each other, are planted with rice variety IR72 at a plant spacing of 20x20 cm. The plots received 146 kgN.ha^{-1} as urea. In addition to this, one plot is amended with 0.66 kg salt m^{-2} at the start of the growing season. The full analysis of 1g salt used in the field experiment is 350 mg Na, 2 mg K, 8 mg Ca, 11 mg Mg, 550 mg Cl and 3 mg SO_4. The salt is broadcast and incorporated at final harrowing. The electrical conductivity (EC) of the salt-amended plot is measured every 2-3 weeks. If the EC of the soil solution dropped below 4 dS.m^{-1} additional salt is broadcast (0.13 kg salt m^{-2}) and the EC measured again 3 days after broadcasting. Hereby the average EC of the amended plot is kept between 3-6 dS.m^{-1}, making it a moderately saline soil (U.S. Salinity laboratory staff, 1954). The EC of the non-amended plots is 0.8 ± 0.1 dS.m^{-1}.

Experimental set-up

Methane emission rates are monitored with an automatic measurement system based on the closed chamber technique as developed and described by Schütz et al. (1989) with small modifications. The system allows 24-hour semi-continuous determination of CH_4 emission rates from different gas collector chambers. Measurements are performed in 2-hour cycles, allowing 12 flux measurements per day of each chamber. The baseline emission data from the urea fertilized plots are measured in 4 separate plots with one gas collector chamber each (1x1x1.2 m). Two chambers (0.6x0.6x1.2 m) are placed in the amended plot. All chambers are made of smooth colourless plexiglass and equipped with a plexiglass cover which could be opened and closed by a time-controlled pneumatic cylinder. To stabilize the boxes, each corner of a box has a 20 cm aluminum extension which is placed in the soil. The lower sides of the boxes are hanging a few cm in the floodwater, providing a gastight seal between inside and outside the boxes. So, free exchange of floodwater, soil fauna and roots between inside and outside the boxes is possible. Inside the boxes two electrical fans (12 V DC) are mounted to ensure rapid mixing of the air inside the closed chamber during sampling and with the ambient air when the cover is open. Air samples from the individual closed chambers are analyzed for CH_4 on a gas chromatograph equipped with a 6-port valve, sample loop and a flame ionization detector (FID). For a schematic overview and technical details of the measurement system we refer to Schütz et al. (1989) and IAEA (1992). Modifications of the system used in this study are 1) closing time of the chambers during sampling is 24 min. and 2) injection of calibration gas 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 is calculated with linear regression from the temporal increase of the CH_4 concentration in the chamber. Each emission rate is based on 4 samples, r-squared of the linear regression of the CH_4 concentration against time is typically > 0.95.

CH_4 production and CH_4 oxidation in soil columns

Triplicate soil cores of approx. 10 cm length are taken from each treatment plot between the rows (10 cm from a hill), using 4.4 cm inner diameter acrylic core tubes with a length of 25 cm. The intact soil cores are collected at 75, 96 and 110 days after transplanting (the latter date being 1 week after harvest). The cores are immediately brought to the laboratory and assayed 1-2 hours later. The thickness of the layer of flood water above the sediment surface is decreased with a pipette to 2-3 mm to provide a diffusive boundary layer which allowed quick exchange between soil and gas phase (King et al., 1990). The core tubes are sealed with rubber stoppers to provide a headspace of 100-200 cm^3 and incubated under a dim light at a temperature of 29 - 31 °C. The top rubber stopper contains 2 septa, so, the headspace could be flushed through syringe needles with either air or N_2 to create an aerobic or anaerobic incubation, respectively (King et al., 1990). CH_4 is analyzed on a gas chromatograph equipped with a FID. Samples of 2.5 mL from the headspace above the cores are taken repeatedly and immediately injected in a sample loop of 2 mL, connected to a 6-port valve with manual switch. After taking a sample the headspace pressure is readjusted by injecting the same amount of either air or N_2. The temporal increase of the CH_4 concentration in the headspace is corrected for the dilution and used to calculate the CH_4 flux per surface area from the soil cores with linear regression (r-squared > 0.95). Since CH_4 oxidation can occur only if oxygen is available, the difference between the CH_4 flux from cores during anaerobic and aerobic incubation can be attributed to CH_4 oxidized in the floodwater-soil interface (King et al., 1990; Conrad and Rothfuss, 1991). [It is important to note that the term anaerobic incubation or aerobic incubation as used here refers to the headspace above the soil core. Therefore the anaerobic status inside the intact soil core does not change and CH_4

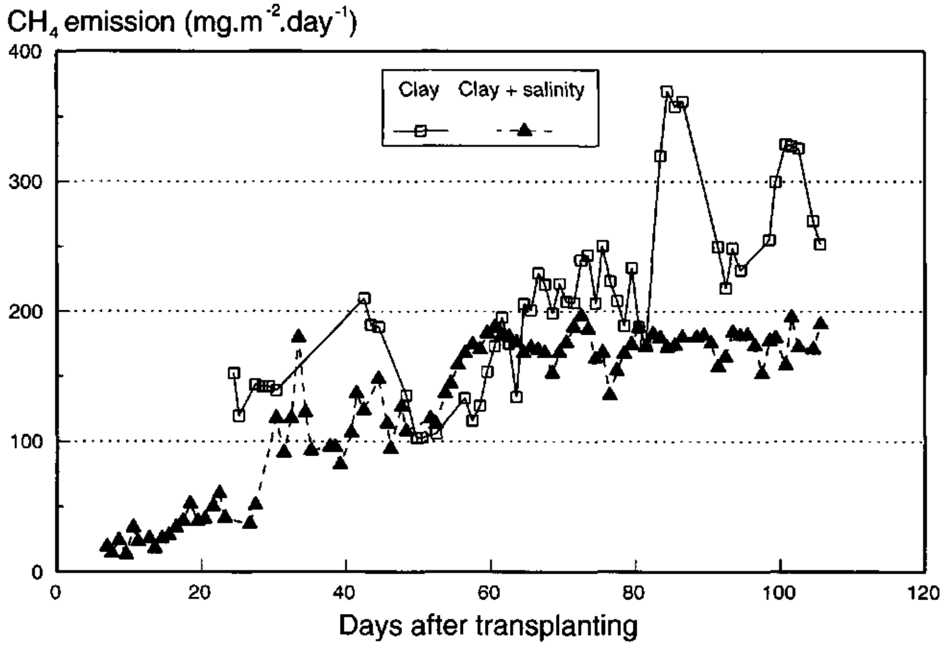

Figure 4.1 Methane emission from rice fields, with and without salt amendment, in the 1992 dry season.

Table 4.1 Average methane flux from triplicate soil cores of rice fields with and without salt amendment, during anaerobic and aerobic incubation, and percentage CH_4 oxidized (standard deviation in brackets).

Date[a]	Treat-ment	CH_4 flux (nmol.cm^{-2}.hr^{-1})		CH_4 oxidized	
		anaerobic	aerobic	(nmol.cm^{-2}.hr^{-1})	(% of anaerobic flux)
76 DAT	no salt	11.02 (1.29)	1.31 (0.33)	9.71 (1.07)	88 (2)
96 DAT	no salt	24.53 (1.62)	3.29 (1.39)	21.24 (1.27)	88 (5)
110 DAT[b]	no salt	20.82 (4.78)	2.75 (1.28)	18.07 (3.82)	87 (5)
76 DAT	salt	2.75 (0.42)	1.32 (0.46)	1.43 (0.54)	52 (15)
96 DAT	salt	7.04 (3.48)	2.17 (0.98)	4.87 (2.63)	70 (10)
110 DAT[b]	salt	7.42 (0.53)	2.99 (0.81)	4.43 (0.74)	60 (10)

[a] DAT = days after transplanting
[b] 110 DAT is 1 week after harvest.

production in the intact core is constant.]

After measuring the CH_4 fluxes of the intact cores under aerobic and anaerobic incubation, CH_4 production at different depths is measured in the cores collected at 96 and 110 days after transplanting. The cores are sliced into 2.5 cm thick segments resulting in four different depth intervals; 0-2.5, 2.5-5, 5-7.5 and 7.5-10 cm. Each segment is mixed with 30 mL of demineralized water and transferred to a 125 mL erlemeyer flask of a known total volume. The flasks are sealed with suba-seals, flushed with N_2 and placed in a waterbath shaker (T = 30 °C) for pre-incubation overnight. The following day the flasks are purged with N_2. Headspace gas samples are taken repeatedly (every 2 hours) and analyzed for CH_4. After each sampling the headspace volume is readjusted by injecting a sample volume of N_2 in to the erlemeyer flask. CH_4 production rates are calculated, after correction for dilution, from the increase over time of CH_4 in the headspace.

Results and discussion

The average CH_4 flux in $mg.m^{-2}.day^{-1}$ for the 1992 dry season is calculated from the 2-hourly flux measurements. Average daily CH_4 emission for the salt amended and non-amended plots are shown in Figure 4.1. Total seasonal CH_4 flux from the amended plots (12.8 ± 1.9 g $CH_4.m^{-2}$) is lower than from non-amended plots (17.0 ± 1.5 g $CH_4.m^{-2}$) but a significant difference is observed only from 70 days after transplanting onwards. Straw yield in the salt-amended plots is reduced by 18%. Root exudates and root litter can be important substrates for methanogens, especially at the end of the growing season (Schütz et al., 1989). So, lower plant biomass may lead to lower CH_4 emissions. The observed reduction in plant growth is most likely caused by the salt-amendment since all other factors influencing CH_4 emission, such as climate, temperature and fertilization, are the same as for the control plot.

The effects of salt addition on total CH_4 production and emission (CH_4 production minus CH_4 oxidation) are investigated by taking soil cores and measuring the aerobic and anaerobic CH_4 flux. Typical experimental results for two soil cores, collected from the salt-amended field and control field, are shown in Figure 4.2. The results are independent of whether the experiment is started under aerobic or anaerobic headspace composition, in line with the observations of Conrad and Rothfuss (1991). The results for triplicate soil cores collected on different dates are summarized in Table 4.1. For each individual core the CH_4 flux under aerobic incubation is always smaller than under anaerobic incubation. The anaerobic CH_4 flux from cores of the salt-amended field is strongly reduced compared to that of cores from the non-amended field. This indicates that CH_4 production is depressed by

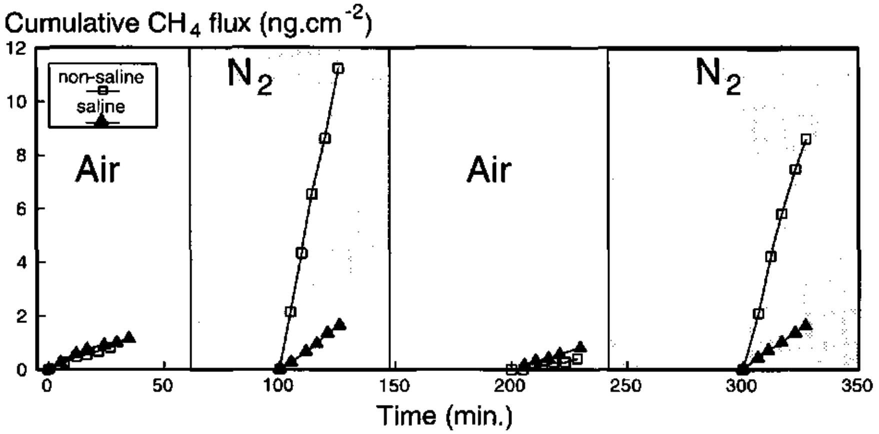

Figure 4.2 Cumulative CH_4 flux from intact soil cores, collected 96 days after transplanting from rice filelds with and without salt amendment, during aerobic and anaerobic incubations.

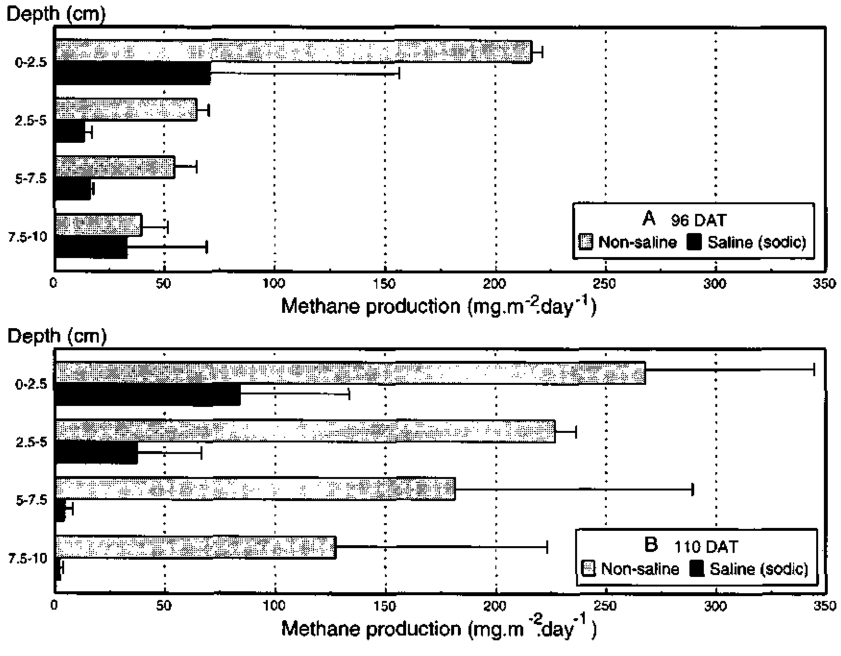

Figure 4.3 Average potential methane production in 2.5 cm segments of triplicate 10 cm soil cores, collected 96 days after transplanting (A) and 110 days after transplanting (B, 1 week after harvest) from rice fields with and without salt amendment (Error bars indicate standard deviation).

salinity. However, the aerobic CH_4 flux from cores sampled in plots with and without salt amendment did not differ significantly despite the large difference in anaerobic CH_4 flux (Figure 4.2 and Table 4.1). This apparent discrepancy can be explained by lower rates of CH_4 oxidation in saline than in non-saline plots. The lower CH_4 oxidation rate in the salt-amended plot is a result of the lower anaerobic CH_4 flux because if less CH_4 is produced, less can be oxidized. However, the percentage of the anaerobic CH_4 flux oxidized is also significantly lower in the salt-amended plot (Table 4.1). This suggests that the methanotrophic community is either less efficient at lower CH_4 concentrations or that the methanotrophs are more inhibited by the salt effect than methanogens are. The percentage of the anaerobic CH_4 flux oxidized in the non-amended field is similar to values reported by Conrad and Rothfuss (1991) for an Italian rice field, although the absolute values of the CH_4 fluxes in our study are higher.

The observed differences in anaerobic CH_4 flux are further investigated by measuring the potential CH_4 production with depth in the cores sampled on 96 and 110 days after transplanting (Figure 4.3a and 4.3b). The total CH_4 production as well as the CH_4 production in separate layers is significantly lower in the salt-amended plot, confirming the reduced anaerobic fluxes observed earlier. The CH_4 production in the non-saline field increases strongly after harvest (110 days after transplanting), probably as a result of increased root litter becoming available to the microbial community. The increased CH_4 production is primarily located in the deeper layers, which may explain why no increase in the anaerobic CH_4 flux from the intact cores is observed after harvest (Table 4.1). The CH_4 production in the salt-amended plot did not change significantly before and after harvest, although here too litter would have increased. Furthermore, straw yield decreases by 18% only in the salt-amended plot but CH_4 production by a factor 3-4. This suggests that the reduction in CH_4 emission by 25% in the salt-amended plot mainly results from inhibition of methanogens and/or microorganisms producing substrates for methanogens to grow on and is not caused by lower organic matter availability. On the other hand, the rice plants are the main conduct for CH_4 transport from soil to atmosphere (Cicerone and Shetter, 1981; Holzapfel-Pschorn et al., 1986). Lower biomass production may reduce the gas transport capacity which could result in lower CH_4 emission. Further research is necessary to elucidate the relationship between gas transport capacity and total emission. In rice fields that are amended with gypsum, increasing pore water EC to 2 $dS.m^{-1}$, CH_4 emission is reduced by 50-72 % (Denier van der Gon and Neue, 1994) probably because sulfate-reducing bacteria outcompete methanogens. Although the EC in the gypsum-amended fields is a factor 2 lower, the reduction in CH_4 emission is much stronger than in our salt-amended fields. This indicates that salinity accompanied by high sulfate levels will reduce CH_4 emission much stronger than salinity caused by non-sulfate containing salts.

The total CH_4 production as measured 96 days after transplanting (Figure 4.3a) can be compared to the CH_4 emission at that date (Figure 4.1). The sampled soil cores have a length of 10 cm but CH_4 production in the field is not limited to the top 10 cm of the soil. The puddled layer in our fields has a varying thickness of 15-20 cm. We assume an average depth of 17.5 cm and calculate the CH_4 production in the layer from 10-17.5 cm by extrapolating the measured values in the layer from 7.5-10 cm. The validity of this procedure is supported by occasional CH_4 production measurements in the layer of 10-12.5 cm (data not shown) which show no significant difference with values for the layer of 7.5-10 cm. The average potential CH_4 production amounts to 494 and 232 mg $CH_4.m^{-2}.day^{-1}$ for the control field and salt-amended field, respectively. Comparison of these values with the daily CH_4 emission (average for 95-97 days after transplanting), indicates that 47% of the produced CH_4 is oxidized in the control field against 28% in the salt-amended field. So, the CH_4 oxidation efficiency in the salt-amended field is much lower. The percentage of the produced CH_4 that is oxidized in our experiment is low compared to observations in rice fields elsewhere; 58% (Sass et al., 1990) up to 90% (Holzapfel-Pschorn et al., 1986). The cores in our study are taken between the rows of rice plants, 10 cm from a hill, which is the maximum distance from the rice plant in a field with a plant spacing of 20x20 cm. The CH_4 production in the soil decreases with the distance from the rice plant (Sass et al., 1990). Therefore, the potential CH_4 production in our fields may be underestimated, indicating that the calculated percentage CH_4 oxidized in our fields is a lower limit.

Conclusions

The addition of salt (mainly NaCl) to a rice field, increasing pore water EC to approx. 4 $dS.m^{-1}$, reduced CH_4 emissions by 25%. The reduction in CH_4 emission is much smaller than the reduction in total CH_4 production, showing that CH_4 emission is not necessarily proportional to CH_4 production. Reduced CH_4 production has a limited impact only on CH_4 emission because CH_4 oxidation is even stronger reduced.

Bachelet and Neue (1993) suggested "soil type" correction factors when estimating CH_4 emission from rice agricultural areas to improve current global estimates of CH_4 emission from rice fields. Our results support such an approach and show that saline soils with a high sulfate content need a higher reduction factor than saline soils with low sulfate concentrations. To improve the current global estimates of CH_4 emission from rice agriculture CH_4 emission measurements from various soil types and ecosystems are required.

The salt-amendment of our plot started in the 1991 wet season and the measurements presented here are done in the second season of moderate salinity. However, the ecosystem of natural saline rice fields has a much longer time to adapt to salinity stress. This may change, amongst other things, the soil microbial community active in CH_4 production and CH_4 oxidation. Further research in long-term saline and sodic rice fields is necessary to confirm the impact of salinity/sodicity on production, oxidation and emission of CH_4.

The results stress the importance of both production and oxidation of CH_4 in determining the net CH_4 emission from soils and show that a reduction in CH_4 production alone does not necessarily result in lower CH_4 emission. When developing adequate mitigation strategies to reduce the CH_4 source strength of wetland rice fields or estimating source strengths from different regions in the world both CH_4 production and CH_4 oxidation should be taken in to account.

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References

Anastasi, C., M. Dowding, and V.J. Simpson, Future CH_4 emissions from rice production, J. Geophys. Res., 97, 7521-7525, 1992.

Bachelet, D., and H.U. Neue, Methane emission from wetland rice areas of asia. Chemosphere, 26, 219-237, 1993.

Bartlett, K.B., D.S. Bartlett, R.C. Harriss, and D.I. Sebacher, Methane emissions along a salt marsh salinity gradient, Biogeochem., 4, 183-202, 1987.

Blake, D.R., and F.S. Rowland, Continuing worldwide increase in tropospheric methane, Science, 239, 1129-1131, 1988.

Boje-Klein, G., Problem soils as potential areas for adverse soil tolerant rice varieties in South and South-east Asia, IRRI Research Paper Series No. 119. IRRI, P. O. Box 933, Manila, Philippines, 43 p, 1986.

Cicerone, R.J., and J.D. Shetter, Sources of atmospheric methane: measurements in rice paddies and a discussion, J. Geophys. Res., 86, 7203-7209, 1981.

Cicerone, R.J., and R.S. Oremland, Biogeochemical aspects of atmospheric methane, Global Biogeochem. Cycles, 2, 299-327, 1988.

Conrad, R., and F. Rothfuss, Methane oxidation in the soil surface layer of a flooded rice field and the effect of ammonium, Biol. Fert. Soils, 12, 28-32, 1991.

Delaune, R.D., C.J. Smith, and W.H. Patrick, Jr., Methane release from Gulf coast wetlands, Tellus, 35B, 8-15, 1983.

Denier van der Gon, H.A.C., and H.U. Neue, Impact of gypsum application on the methane emission from a wetland rice field, Global Biogeochem. Cycles, 8, 127-134, 1994.

Dlugokencky, E.J., K.A. Masarie, P.M. Lang, P.P. Tans, L.P. Steele, and E.G. Nisbet, A dramatic decrease in the growth rate of atmospheric methane in the northern hemisphere during 1992, Geophys. Res. Lett., 21, 45-48, 1994.

Garrity, D.P., L.R. Oldeman, and R.A. Morris, Rainfed lowland rice ecosystems, characterization and distribution, in Progress in Rainfed Lowland Rice, pp 3-23. International Rice Research Institute, P. O. Box 933, Manila, Philippines, 1986.

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

IAEA, Manual on measurement of methane and nitrous oxide emissions from agriculture, IAEA-TECDOC-674, IAEA, Vienna, Austria, 1992.

IPCC, Climate Change 1992. The supplementary report to the IPCC scientific assessment, Cambridge University Press, Cambridge, 200 p, 1992.

King, G.M., P. Roslev, and H. Skovgaard, Distribution and rate of methane oxidation in sediments of the Florida Everglades, Appl. Environ. Microbiol., 56, 2902-2911, 1990.

Khalil, M.A.K., R.A. Rasmussen, and M.J. Shearer, Trends of atmospheric methane during the 1960s and 1970s, J. Geophys. Res., 94, 18279-18288, 1989.

Lelieveld, J., P.J. Crutzen, and C. Brühl, Climate effects of atmospheric methane, Chemosphere, 26, 739-768, 1993.

Lovley, D.R., and M.J. Klug, Sulfate reducers can outcompete methanogens at freshwater sulfate concentrations, Appl. Environ. Microbiol., 45, 187-192, 1983.

Neue, H.U., and R. Sass, Trace gas emissions from rice fields, in Global Atmospheric-Biospheric Chemistry, edited by R.G. Prinn, pp 119-148, Plenum Press, New York, 1994.

Oremland, R.S. Biogeochemistry of methanogenic bacteria, in Biology of anaerobic microorganisms, edited by A.J.B. Zehnder, pp. 641-705. Wiley and Sons, New York 1988.

Patel, G.B., and L.A. Roth, Effect of sodium chloride on growth and methane production of methanogens, Can. J. Microbiol. 23, 893-897, 1977.

Rennenberg, H., R. Wassmann, H. Papen, and W. Seiler, Trace gas exchange in rice cultivation, Ecol. Bull., 42, 164-173, 1992.

Sass, R.L., F.M. Fisher, P.A. Harcombe, and F.T. Turner, Methane production and emmision in a texas rice field, Global Biogeochem. Cycles 4, 47-68, 1990.

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

Steele, P., E.J. Dlugokencky, P.M. Lang, P.P. Tans, R.C. Martin, and K.A. Masarie, Slowing down of the global accumulation of atmospheric methane during the 1980s, Nature, 358, 313-316, 1992.

U.S. Salinity Laboratory Staff, Diagnosis and improvement of saline and alkali soils, United States Department of Agriculture, Washington DC, 1954.

Wang, W.C., Y.L. Yung, A.A. Lacis, T. Mo, and J.E. Hansen, Greenhouse effects due to man-made perturbations of trace gases, Science, 194, 685-690, 1976.

Yagi, K. and K. Minami, Effect of organic matter application on methane emission from some Japanese paddy fields, Soil Sci. Pl. Nutr., 36, 599-610, 1990.

Chapter 5

Influence of Organic Matter Incorporation on the Methane Emission from a Wetland Rice Field

H.A.C. Denier van der Gon and H.-U. Neue

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Influence of organic matter incorporation on the methane emission from a wetland rice field

Abstract

Methane (CH_4) emission from Philippine rice paddies was monitored with a closed chamber technique during the 1992 dry and wet season. CH_4 emissions were significantly higher in the dry season. Application of green manure stimulated CH_4 emissions. In plots that received more than 11 t ha^{-1} of fresh green manure, CH_4 emission was highest during the first half of the growing season. Significant amounts of CH_4 may evolve during or immediately after transplanting, if the organic amendments are incorporated 1 to 3 weeks before transplanting. Laboratory incubations of soil cores show that CH_4 production is highest near the soil surface. CH_4 production in green manure treated fields is higher than in urea-fertilized fields, but toward the end of the season this difference is less pronounced. Around panicle initiation, the fraction of CH_4 produced, which was emitted to the atmosphere, is lower than at tillering or ripening. The impact of organic amendments on CH_4 emissions at different locations of the world can be described by a dose response curve, if CH_4 emission from organically amended plots is expressed relative to CH_4 emission from mineral fertilized plots of the same location and season. Various organic amendments (e.g., straw, fermented residues) have a similar effect on CH_4 emissions after correction for differences in easily decomposable carbon content.

Introduction

Atmospheric methane concentrations have increased from about 0.8 to 1.7 parts per million by volume (ppmv) since preindustrial times (Blake and Rowland, 1988; Khalil et al., 1989). Although the atmospheric CH_4 concentration is much lower than the atmospheric concentrations of the most important greenhouse gases, H_2O and CO_2, the rising atmospheric methane concentration may significantly affect global temperature. The importance of CH_4 as a greenhouse gas is due to its relatively large annual concentration increase of approximately 0.8% (Intergovernmental Panel on Climate Control (IPCC), 1992) and its high global warming potential (GWP) of 26.9 for a 10-year integration period (Lelieveld et al., 1993). Furthermore, CH_4 merits attention due to its relatively short atmospheric lifetime compared to other greenhouse gases such as CO_2, N_2O, and CFCs. To stabilize the atmospheric CH_4 concentration, a reduction of about 10% in anthropogenic emission would be required, whereas for other gases much higher reductions would be required (Lelieveld et al., 1993). Such a decrease in an anthropogenic source may be the cause for the dramatic decrease in the growth rate of atmospheric CH_4 in 1992 (Dlugokencky et al., 1994). Studies on the atmospheric CH_4 cycle have stressed the need for identification of individual CH_4 sources and their source strength. Wetland rice fields are an important source of methane, accounting for approximately 20% of the global anthropogenic methane emission (IPCC, 1992).

Methane is produced by strict anaerobic bacteria (methanogens). Anaerobic conditions occur in, for example, aquatic sediments, natural wetlands, and wetland rice fields. Under such conditions, organic matter is degraded to the gaseous end-products known as CO_2 and CH_4 (Acharya, 1935a,b). Acharya (1935a,b) found that the rate at which anaerobic decomposition of rice straw proceeds, as well as the ratio of CO_2 to CH_4 produced, depended on several factors such as temperature and *p*H. Two major pathways in submerged soils produce CH_4 (Takai, 1970; Neue and Scharpenseel, 1985).

1. Reduction of CO_2 with H_2 or organic molecules (H_2A) as the H donor.

$$CO_2 + 4H_2A \rightarrow CH_4 + 2H_2O + 4A \tag{1}$$

2. Decarboxylation (transmethylation) of acetic acid.

$$CH_3COOH \rightarrow CH_4 + CO_2 \tag{2}$$

Various factors influence the ratio of CH_4 and CO_2 produced. In line with Acharya (1935b), Tsutsuki and Ponnamperuma (1987) reported that much less CH_4 than CO_2 was generated in straw-amended rice soils at 20 °C. Raising the temperature to 35 °C increased the formation of both gases but stimulated especially CH_4 production which sometimes equalled the CO_2 production. For a more detailed description and review of the biogeochemistry of methanogens and their substrate requirements we refer to Oremland (1988). The addition of organic matter to a wetland rice field will enhance CH_4 emissions by fuelling Eq. (1) and Eq. (2). This has indeed been observed in field experiments in Italy (Schütz et al., 1989a), Japan (Yagi and Minami, 1990), the United States (Sass et al., 1991; Cicerone et al., 1992), China (Wassmann et al., 1993a,b) and Philippines (Neue et al., 1993). However, the magnitude of the CH_4 fluxes induced by organic matter addition may vary widely across locations. This may be caused by differences in soil types, water regime, and climatic factors (e.g., temperature and solar radiation) among locations which may limit microbial productivity in general or, as outlined above, influence the ratio of CH_4 and CO_2 produced.

The objective of this paper was to gather baseline CH_4 emission data from a flooded rice field in the tropics (Philippines) and to assess the impact of green manure application on CH_4 emission. Green manure can be produced by growing nitrogen (N_2) fixing plants like Sesbania or cowpeas between rice crops, simultaneous cultivation of Azolla with the rice crop, or by collecting cuttings of annual or perennial plants or trees grown elsewhere. The application of green manure adds and recycles nitrogen and other nutrients, increases soil organic matter, and improves the soils physical and biological properties. (Singh, 1984; Ventura and Watanabe, 1993). Green manuring is an old and common practice in important rice growing countries like India and China (Singh, 1984). Data on organic amendments of rice soils per country are scant, but in general, green manuring decreases as a result of increasing cropping intensity and the decreasing cost and improved availability of fertilizers. The area planted to green manure in China increased from 2 million ha in 1950 to 10 million ha in the middle 1970s but steadily decreased thereafter to 4 million ha in 1987 (Stone, 1990). However, the growing concern about declining soil fertility and sustainability of agricultural systems has increased the interest in N_2-fixing green manure and other organic amendments.

Materials and methods

Field preparation

Field measurements of CH_4 emission were performed during the 1992 dry season (January-May) and 1992 wet season (July-November) in a wetland rice field of the International Rice Research Institute (IRRI), Los Baños, Philippines. The soil at the field site is an Aquandic Epiaqualf (Soil Survey Staff, 1992) consisting in the topsoil of 66% clay, 28% silt, and 6% sand. It contains 1.97% organic carbon, 0.166% total nitrogen, and has a *p*H H_2O of 5.9.

In both the dry and following wet season, rice variety IR72 was planted at a plant spacing of 20x20 cm. The field was flooded, ploughed, and puddled 2 weeks before transplanting. The green manure (*Sesbania rostrata*), grown on neighbouring plots, was harvested, chopped and incorporated without standing water 1 week before transplanting. Basal urea was incorporated without standing water at final harrowing on the day of transplanting. Application rates of urea and green manure (GM) are given in Table 5.1. The GM added one week before panicle initiation was chopped, placed between the rows of rice plants, and pushed into the soil. The topsoil (about 0.2 m) from the plots that received GM in the 1992 dry season was replaced with unamended soil from the same block of the research farm before the wet season to avoid residual effects.

Experimental apparatus

Methane emission rates were monitored with an automatic measurement system based on the closed chamber technique as developed by Schütz et al. (1989a). The

Table 5.1 Number of field plots, chambers installed per plot, fertilizer application, straw yield and total seasonal CH_4 emission from Philippine rice fields on the same soil type in 1992.

Treatment	Number of plots, chambers per plot in parentheses	GM[a] applied ($t\ ha^{-1}$)	N[b] application ($kg\ N\ ha^{-1}$)				Straw yield ($t.ha^{-1}$)		Seasonal CH_4 emission		
			Basic	PI[c]	Flowering	Total	out[d]	in[d]	($g\ m^{-2}$)	sd[e] (%)	6 WAT[f] (%)
					Dry season 1992						
Urea	4 (1)	-	86	30	30	146	6.18	5.84	17.2	9	31[g]
Green manure II	1 (2)	20	100[h]	30	30	160	7.81	7.05	87.1	13	59
					Wet season 1992						
Urea	4 (1)	-	55	30	30	115	5.48	7.69	7.9	18	12
Green manure I	4 (1)	11	55[h]	30	30	115	4.64	8.25	20.6	30	43
Green manure II	1 (2)	20	100[h]	30	30	160	7.75	11.14	44.3	7	65
Green manure III	1 (2)	20 + 11	100[h]	55[h,i]		155	7.30	8.29	38.9	26	72

[a] GM = fresh green manure, ploughed in 7 days before transplanting; 1 t GM provides 5 kg N.
[b] If not specified the N source is urea.
[c] PI = panicle initiation.
[d] out = outside the gas collector chamber, in = inside the gas collector chamber.
[e] sd = standard deviation.
[f] CH_4 emitted during the first 6 weeks after transplanting as percentage of total seasonal emission.
[g] Assuming that the CH_4 emission trend was similar to the urea fertilized plot in the wet season.
[h] as GM
[i] applied one week before panicle initiation (35 days after transplanting).

system allows 24-hour semicontinuous determination of CH_4 emission rates. Measurements were performed in 2-hour cycles, providing 12 flux measurements per day for the entire growing season. Such intensive monitoring is necessary, because the diurnal and seasonal changes in CH_4 fluxes from rice fields are high (Schütz et al., 1989a). The chambers were made of smooth colorless plexiglass and equipped with lids that are opened and closed by time-controlled pneumatic cylinders. Two electrical fans (12 or 24 V DC) were mounted inside the boxes to ensure rapid mixing of the air within the chamber when closed during sampling and with the ambient air when the cover was open. Air samples from the individual closed chambers were analyzed for CH_4 with a gas chromatograph (GC) equipped with a 6-port valve, sample loop, and flame ionization detector (FID). The large number of samples made it necessary to install one GC with two channels and an extra GC with one channel. Further details of the measurement system are given by Schütz et al. (1989a) and International Atomic Energy Agency (IAEA) (1992). Modifications of the system used in this study were (1) the closing time of the chambers during sampling was 24 min to reduce plant stress, and (2) the supply of calibration gas from a separate container, resembling the chambers in the field rather than directly from a gas cylinder, to ensure equal pressure in the gas flow system during sampling and calibration of the system.

The methane emission rate was calculated from the slope of a linear regression of the CH_4 concentration against time over the sampling interval. Four samples were taken per interval. This regression had almost always $r^2 > 0.95$. An extra check on the raw data was performed if r^2 is < 0.9, because this often indicated technical problems with gas sampling or injection; such data were discarded. Daily CH_4 emission rates were calculated from the 12 flux measurements in 24 hours. The chambers could only be placed in the field immediately after transplanting, and reliable flux data were obtained after some days of fine tuning the system. No data are available for the period from flooding the field to transplanting.

Potential CH_4 production in soil columns

Duplicate soil cores of about 10-cm length were taken from each treatment between the rows (10 cm from a hill), using 4.4-cm inner diameter acrylic core tubes with a length of 25 cm. Soil cores were collected at 26, 52, and 94 days after transplanting, corresponding to three growth stages of the rice plant, tillering, panicle initiation, and ripening, respectively. The cores were sliced into 2.5-cm thick segments resulting in four different depth intervals; 0 to 2.5 cm, 2.5 to 5 cm, 5 to 7.5 cm, and 7.5 to 10 cm. Each segment was mixed with 30 mL of demineralized water and transferred to a 125-mL erlemeyer flask of a known total volume. The flasks were sealed with suba-seals, flushed with N_2, and placed in a waterbath shaker (T = 30°C) for preincubation overnight. The following day the flasks were purged with N_2. Six headspace gas samples were taken with intervals of about 1 hour and analyzed for CH_4. After each sampling, the headspace volume was readjusted by injecting a sample volume of N_2 in to the erlemeyer flask. CH_4 production rates were calculated, after correction for dilution, from the increase over time of CH_4 in the headspace.

Field design

The field design for the urea and 11 t ha^{-1} green manure (GM I) treatment was laid out according to a randomized block design with four replicate plots (5x5 m) and one flux chamber (1x1x1.2 m) per plot (Table 5.1). For financial and logistic reasons, such a field design was not possible for all treatments. The highest green manure treatments (GM II and III) were set up parallel to the main experiment (5-m distance) but consisted of one plot (3x5 m) per treatment with two flux chambers (0.6x0.6x1.2 m) for replicate flux measurements. The standard deviations in CH_4 emission from the GM II and GM III treatments were in the same range as observed for the urea and GM I treatments in the randomized block designed experiment (10-30%, Table 5.1). This indicates that the spatial variation in CH_4 emission within plots of the size used here is similar to the variation in CH_4 emission from different plots with the same treatment.

Results and discussion

Total methane emission and standard deviation for the treatments in each season are given in Table 5.1. CH_4 emission was strongly stimulated by green manure application. Extrapolating CH_4 fluxes inside the chamber to respective open fields is only reliable, if the crop biomass inside and outside the chamber is the same (Sass et al., 1990). Straw yield can be used as an indicator for total crop biomass (Table 5.1). In the dry season, straw yields inside and outside the gas collector chambers were not significantly different. The straw yield for the 1992 wet season inside the gas collector chambers was higher than outside the chambers, because the plants growing inside where protected against a typhoon which damaged the plants outside. Since higher biomass is expected to cause greater CH_4 formation (e.g., more roots and root exudates) and transport through the plant, the wet season measurements may slightly overestimate CH_4 emissions from the surrounding field. This is especially true for the GM II plot which had a remarkable high straw yield inside the chambers.

Methane emissions from similar treatments in the dry season are higher than in the wet season (Table 5.1). In both seasons the fields were irrigated and water shortage did not limit CH_4 production or plant growth. In the dry season, solar radiation is higher, but daily mean temperature is lower at transplanting and only higher during the reproductive stage. The relationships of these climate factors to crop growth and CH_4 production/emission are complicated and not well understood. Grain yields are mostly higher in the dry season but straw yields may be similar. Tiller development is different. In the wet season, more unproductive (late) tillers develop. The younger the tillers the less they contribute to CH_4 emission (Kimura, 1992). A fully mechanistic understanding of the causes for interseasonal variation of CH_4 emission is still lacking. Sass et al. (1991) presented a quantitative relationship between solar radiation and CH_4 emission as well as crop yield which, if applied to our fields, would result in higher emissions during the dry season. This is in line with our results for 1992. However, long-term data are required to derive a general relationship between wet season and dry season emissions. In the mean time, both the dry and wet season have to be monitored for a reliable annual CH_4 emission estimate.

Diel CH_4 emissions around 20, 60, and 85 days after transplanting for the urea and GM fertilized plots in the 1992 wet season are shown in Figures 5.1a through 5.1f. Peak emissions are measured between 1100 and 1500 LT. Nighttime emissions are lower, presumably because lower soil temperatures at night cause lower CH_4 production rates, and possibly because higher ambient CO_2 concentrations in the canopy at night can reduce transport through the plant. However, the higher ambient CO_2 concentrations in the canopy at night can only cause small variations in CH_4 emissions of maxium 5-10%, because plant-mediated CH_4 transport is driven by diffusion and mass flow of CO_2 has only a minor reducing impact on CH_4 emission (Denier van der Gon and van Breemen, 1993). Higher CO_2 concentrations in the canopy will also result in stomatal closing, but CH_4 emission is independent of stomatal closing (Seiler et al., 1984; Nouchi et al., 1990).

The original 2-hour CH_4 flux rates were summed to daily fluxes. The average daily CH_4 fluxes in the 1992 dry season and wet season are shown in Figure 5.2. The average daily CH_4 fluxes in the first 2 weeks of the 1992 wet season are plotted separately in Figure 5.3 because the CH_4 emission level was much higher at this early stage, and the seasonal pattern would become less clear if the data were plotted in the same figure. The urea-fertilized plots are characterized by a slow but steady increase in CH_4 flux reaching highest emission levels toward the end of the growing season. This may be caused by the expanding root system of the growing plants which (a) creates a more efficient gas transport system from soil to atmosphere; (b) stimulates methanogens through the release of exudates and litter, as was also suggested by Schütz et al. (1989b) to explain observations in Italian rice paddies.

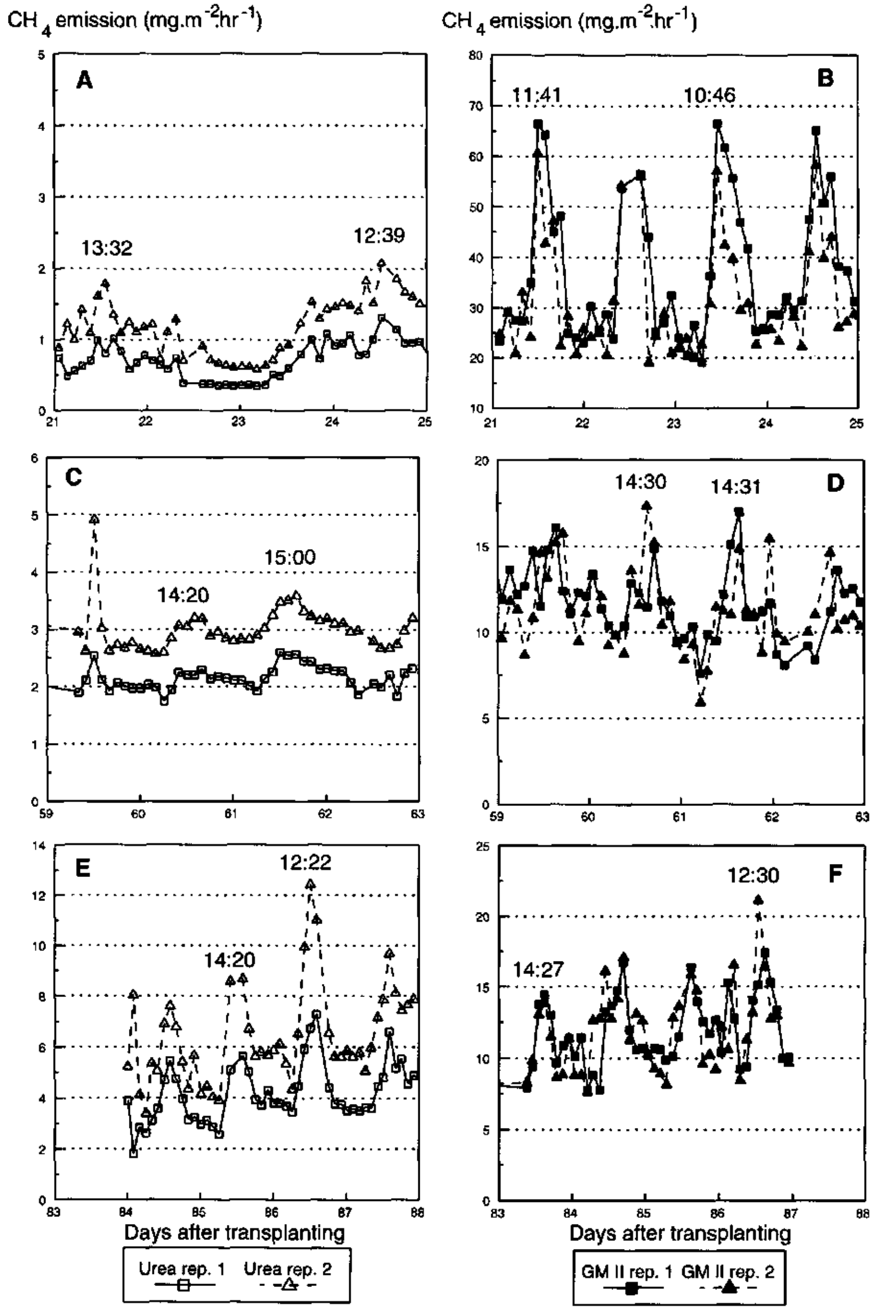

Figure 5.1 Diel methane emissions from a Philippine rice field fertilized with urea (5.1a, 5.1c, and 5.1e) or green manure (5.1b, 5.1d, and 5.1f), at three different stages in the 1992 wet season (note the differences in Y-axis scaling).

The seasonal CH_4 emission pattern is different in the green manure treatment. High CH_4 emission levels occurred within four weeks of transplanting (Figures 5.2 and 5.3). Increasing the green manure application from 11 to 20 t ha^{-1} increased CH_4 emissions, but a further increase to 31 t ha^{-1} did not further increase emission. By contrast, CH_4 emissions from GM III were consistently lower than from GM II with the exception of the peak caused by the additional input of green manure (shaded part III, Figure 5.2b). The GM II and GM III treatments were the same until 1 week before panicle initiation (35 days after transplanting) when the extra green manure was added to the GM III plot (indicated by the arrow in Figure 5.2b). In this early stage the CH_4 emission from GM II was already higher, indicating that the lower emissions from plot GM III where not related to the extra green manure added later in the season. The difference is probably related to the higher straw yield inside the chambers of the GM II plot (Table 5.1).

Cicerone and Shetter (1981) found that more than 90% of the total CH_4 emission in rice fields over a growing season was due to plant-mediated transport. In Italy, ebullition contributed only 4-9% to total CH_4 emission, and CH_4 emission by diffusion through the floodwater amounted to less than 1% of the total seasonal emission (Schütz et al., 1989b). There was little CH_4 emission early in the season in these studies. By contrast, in our green manure plots, early season CH_4 emission is very important, and the first 6 weeks following transplanting was the most important period of CH_4 emission if more than 11 t ha^{-1} green manure was applied (Table 5.1). Schütz et al. (1989b) reported that during the very early growth stage of rice plants, ebullition caused all of the CH_4 emission to the atmosphere because the root system of the rice plants was not well established by then. Up to 20% of the total seasonal emission in the high green manure treatments (GM II) occurred within 2 weeks after transplanting. The corresponding emissions in the urea-fertilized plots were only 1-2% of the total seasonal emission. Applying the seasonal distribution of CH_4 transport mechanisms found by Schütz et al. (1989b), ebullition contributes up to 30% to total CH_4 emission in the green manure treated plots but less than 5% in our urea-fertilized plots.

CH_4 emission from incorporated green manure started 2 to 3 weeks after incorporation, as seen from the effect of the additional 11 tons fresh green manure applied 35 days after transplanting (Figure 5.2b). The effect of the additional green manure was comparable to the the peak observed immediately after transplanting in the GM I plot (compare shaded part I and III, Figure 5.2b) which received the same amount of green manure 1 week before transplanting.

From 6 weeks after transplanting onward, the pattern of CH_4 emission from the

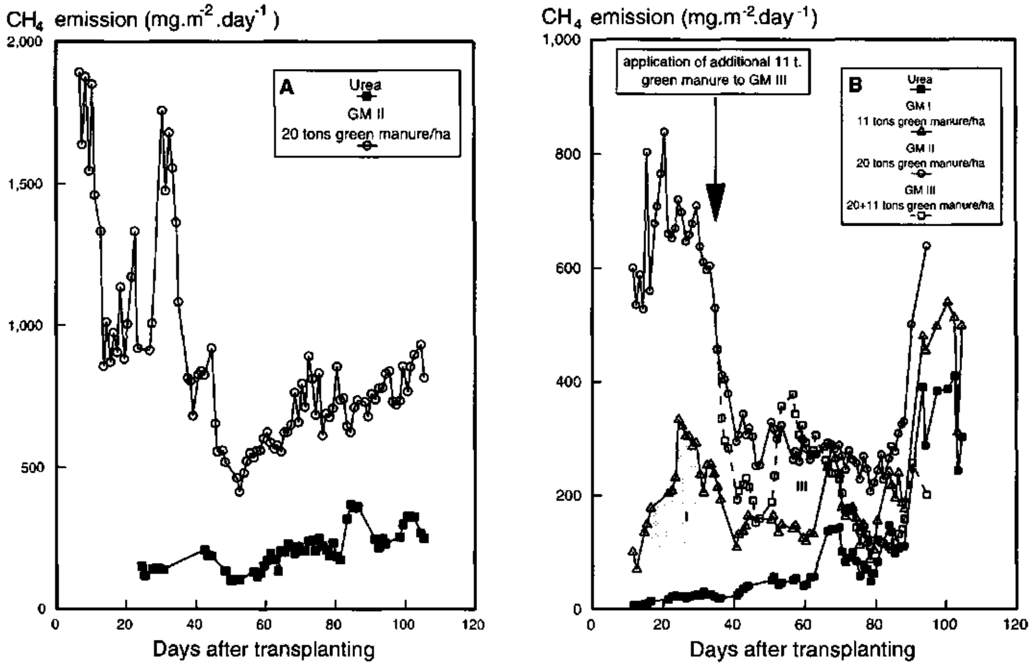

Figure 5.2 Methane emission from a Philippine rice field fertilized with urea or green manure (a) in the dry season and (b) in the wet season of 1992. Shaded areas indicate the initial flush of CH_4 from easily decomposable organic matter after input of 11 t ha^{-1} green manure.

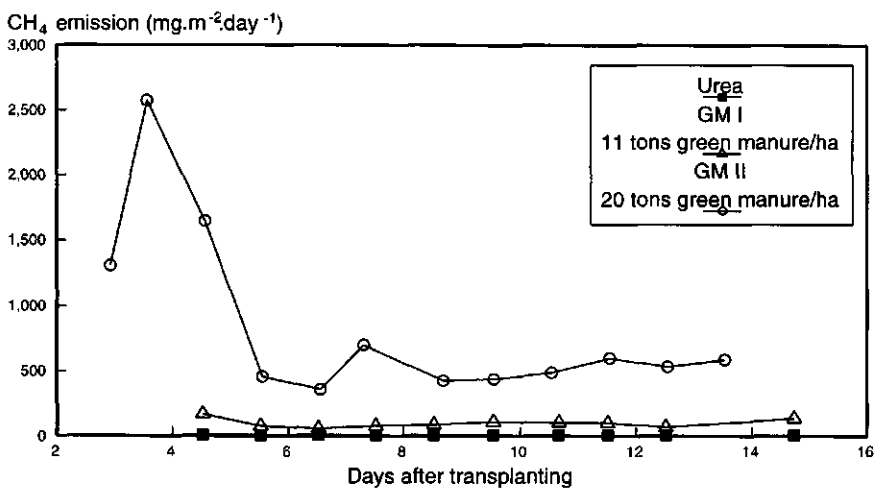

Figure 5.3 Methane emission from a Philippine rice field in the first 2 weeks after transplanting in the wet season of 1992.

GM plots was similar to that from the urea-fertilized plots, although the emission level remained higher. The emission pattern of plot GM III was different because of the additional input of fresh green manure 35 days after transplanting.

Interpretation of the observed diel CH_4 emission patterns

The contribution of ebullition as a major CH_4 transport mechanism early in the growing season, followed by plant-mediated transport later in the season allows the interpretation of observed differences in diel CH_4 emission (Figures 5.1a to 5.1f). A diel fluctuation in CH_4 emission was observed in all studies on CH_4 emission from rice fields and is highly correlated with soil temperature (Sass et al., 1991). The diel emission pattern in our study varied (a) over the season, and (b) with the treatment. The urea-treated plot was characterized by low emissions early in the season. The first weeks after transplanting, the emission pattern was more erratic (Figure 5.1a) than later in the season (Figures 5.1c and 5.1e). Presumably, because ebullition as a transport mechanism is of a more erratic nature than diffusional plant-mediated transport. The diel fluctuation in CH_4 emission in the urea-treated plot becomes important only at the end of the growing season (Figure 5.1e) when nighttime emissions were doubled or tripled in early afternoon. At the end of the season the rice plants release more root exudates and litter, thus stimulating CH_4 production (Schütz et al., 1989b). The increased availability of substrates may result in an enhanced response of methanogenic activity to higher day-time temperatures.

Diel fluctuation in CH_4 emissions in the green manure-treated plots (Figures 5.1b, 5.1d, and 5.1f) was important throughout the season. At the end of the season a similar pattern as in the urea-fertilized plot can be observed (Figures 5.1e and 5.1f), suggesting the same mechanism is at work. By contrast, in the first weeks following transplanting diel fluctuation is large in the green manured plots but of no significance in urea-fertilized plots (Figures 5.1a and 5.1b). Although ebullition was probably the main CH_4 transport mechanism, it did not result in an erratic release of CH_4 from the green manure plots (r-squared of flux measurements > 0.9). Although ebullition itself is a discontinuous process it may result in an apparently continuous increase of CH_4 concentration in a closed chamber if the area covered by the chamber is large (0.36 and 1 m^2 in our study), the closing time of the chamber is long enough (24 min in our study), and the CH_4 production in the soil is high.

Later in the season, when the rice plants are well established, plant-mediated transport is the main CH_4 transport mechanism. Comparison of the diel fluctuation early in the season (Figure 5.1b), with the diel fluctuation later in the season (Figures 5.1d and 5.1f) suggests that ebullition as a transport mechanism is more sensitive to diel

Table 5.2 Average potential production of CH_4 at various depths in soil cores from urea fertilized or green manure (GM), fertilized rice fields in the wet season of 1992.

Growth Stage	Depth (cm)	Potential CH_4 Production (mg m^{-2} h^{-1})		
		Urea	GM I	GM II
Tillering (26 DAT[a])	0-2.5	0.85	17.76	18.42
	2.5-5	0.30	4.88	4.18
	5-7.5	0.05	3.36	2.47
	7.5-10	0.23	3.21	5.55
Cumulative (mg m^{-2} d^{-1})		34.2	701	735
Fraction emitted, %[b]		58.6	44.2	87.1
Panicle initiation (52 DAT[a])	0-2.5	2.69	6.31	13.58
	2.5-5	0.66	5.35	10.89
	5-7.5	0.35	4.12	5.74
	7.5-10	0.80	7.48	4.47
Cumulative (mg m^{-2} d^{-1})		108	558	832
Fraction emitted, %[b]		42.6	25.1	36.0
Ripening (94 DAT[a])	0-2.5	4.92	9.10	10.73
	2.5-5	2.96	6.27	9.71
	5-7.5	2.96	5.09	4.24
	7.5-10	2.37	4.76	5.32
Cumulative (mg m^{-2} d^{-1})		317	605	720
Fraction emitted, %[b]		94.6	76.0	69.4

[a]DAT = days after transplanting.
[b](Field emission / cumulative production) x 100%.

temperature fluctuations than plant-mediated transport. A soil-temperature rise during the day time will not only stimulate CH_4 production, but also gas expansion which will enhance ebullition. This may also explain why the diel emission peaks in Figure 5.1b appear earlier (1100 LT) than in Figures 5.1c and 5.1f (1400 LT), where the diel emission peak is more likely a reaction to enhanced CH_4 production only.

Potential CH_4 production in soil columns

The average potential production of CH_4 at various depths is presented in Table 5.2. Our incubation method involves shaking of the samples which may enhance the substrate availability, and the potential CH_4 production reported here may overestimate in situ CH_4 production. Although the absolute figures may be subject to discussion, a comparison between treatments and different growth stages is possible. The highest CH_4 production occurred in the top layer, as was also found by Sass et al. (1990). This is the layer with the highest biological activity and the turnover of algae, etc. may stimulate CH_4 production. The potential CH_4 production in the green manure plots is higher than in the urea-fertilized plots due to the input of fresh organic matter. Because the green manure was incorporated, CH_4 production in the deeper layers (2.5 to 10 cm) of the green manure plots is an important contribution to the total CH_4 production. In the urea-fertilized plots, CH_4 production in the deeper layers becomes important towards the end of the season. Over time, the incorporated green manure is decomposed and root exudates and root littering from rice plants probably become the most important source of substrate for methanogens. Therefore the difference between urea and green manure treated plots becomes less pronounced toward the end of the season.

The cumulative potential CH_4 production for each treatment was calculated to allow a comparison with the CH_4 emissions as measured in the field. The cumulative potential CH_4 production may be underestimated because the top 10 cm is taken into account only. Although CH_4 production in our fields decreased with depth, deeper layers will contribute to total CH_4 production as well. It is therefore better to look for trends in the data than at absolute values. The potential CH_4 production in the urea-fertilized plot increases with time and resembles the trend in CH_4 emission from the field. This is not the case for the green manure plots where the CH_4 production is fairly stable throughout the season, but the CH_4 emission shows a seasonal pattern with peaks early in the season and at the end of the season (Figure 5.2b). This indicates that CH_4 emission is not simply a fixed proportion of CH_4 produced. Calculation of the percentage of the cumulative potential CH_4 production that is emitted (Table 5.2) reveals that at panicle initiation, a relatively small fraction of the methane produced is emitted, whereas at tillering and especially at ripening, much larger fractions of the produced CH_4 are emitted. CH_4 oxidation is the main sink for CH_4 produced in a rice field (Schütz et al. 1989b). Therefore the lower percentages emitted around panicle initiation suggest a high CH_4 oxidation rate at this growth stage. Seasonal variation in CH_4 oxidation rates may be a clue to explain seasonal patterns in CH_4 emission. However, additional experiments with direct measurements of CH_4 oxidation are

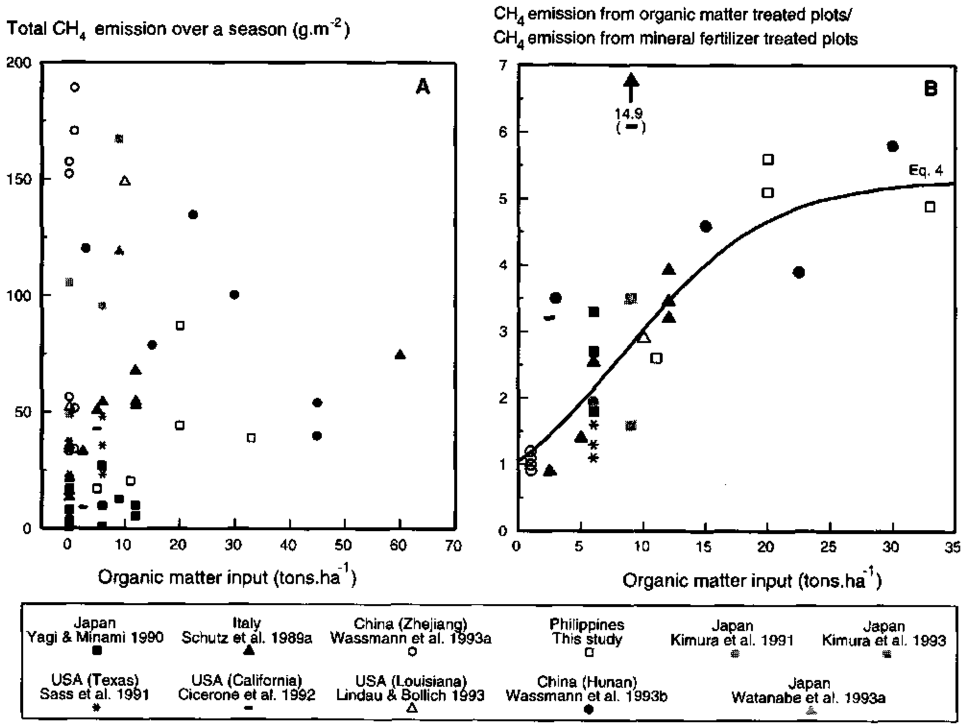

Figure 5.4 Seasonal CH_4 emission from rice fields of various locations of the world (a) as a function of organic matter incorporation and (b) increase of seasonal CH_4 emission upon organic matter incorporation relative to seasonal CH_4 emission from mineral N-fertilized rice fields of the same locations.

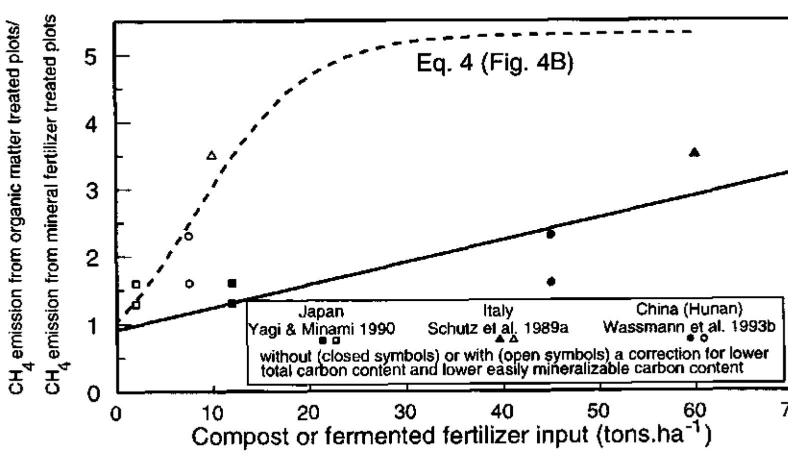

Figure 5.5 Effect of incorporation of fermented residues of biogas pits or compost on seasonal CH_4 emission from rice fields at various locations relative to the seasonal CH_4 emission from mineral N-fertilized rice fields at the same locations.

necessary to confirm this hypothesis. Preliminary experiments with a specific inhibitor for CH_4 oxidation in our laboratory indicated a relation between CH_4 oxidation and the growth stage of the rice plant.

Dose response relationship of CH_4 emission to organic matter input

We broadened our data set by combining it with field data from Schütz et al. (1989a), Yagi and Minami (1990), Sass et al. (1991), Cicerone et al. (1992), Lindau and Bollich (1993), and Wassmann et al. (1993a,b) so as to establish a quantitative relationship between CH_4 emission rates of various organically amended rice fields. We comprised data from experiments that had both organic and mineral fertilizer amendments in the same location, growing season, and year, because CH_4 emissions may differ dramatically between seasons (Table 5.1) and years (Wassmann et al., 1993a). We excluded data from unfertilized treatments and straw treatments without compensatory nitrogen (e.g., urea) addition. Unfertilized control plots are, in any case, not representative for farmer practice and may show residual effects that are not documented. Straw application without additional N application causes various degrees of N immobilization (Nagarajah et al., 1989), which can reduce crop biomass and may effect CH_4 emission rates. The selected data comprise rice fields treated with straw and mineral fertilizer (or urea), green manure, compost, fermented residues from biogas pits, rape seed cake, and mineral fertilizer (or urea). Data from pot experiments by Kimura et al. (1991, 1993) and Watanabe et al. (1993a) are included for comparison (shaded symbols Figure 5.4) but not used to establish a quantitative relationship because our objective was to explain field results.

No clear relationship was found between the amount of organic inputs from these different sources and CH_4 emission (Figure 5.4a). A next step is to look at an added or incremental increase in emissions with added manure. First, different types of manure are distinguished because compost and fermented sludge contain lower amounts of easily decomposable carbon on a weight basis compared to straw or green manure (Inoko, 1984). However, the incremental increase in CH_4 emission with added manure, excluding compost and fermented sludge treatments, is not consistent across locations (graph not shown). This indicates that the increase in CH_4 emission is not dependent on substrate availability only, but other site-specific parameters play a role as well. For example, temperature regimes in different seasons influence the ratio of CO_2/CH_4 produced in anaerobic decomposition, and a soil type may be more or less favourable to methanogens. To take these differences among locations into account, the CH_4 emission from organic matter treated plots was divided by that from mineral N-fertilized plots of the same location and growing season (Figure 5.4b). The fractional increase in CH_4 emission (y) with organic matter added (x) could be described by a dose response curve

$$y = a + \frac{b}{1 + e^{c(d-x)}} , \tag{3}$$

where a, b, c, and d are coefficients. This equation describes a system in which the response to changes in a limiting variable increases initially but then declines to a point where the variable is no longer limiting. It is therefore appropriate for the effect of carbon supply on CH_4 emission. The equation was fitted by nonlinear regression using Gauss-Newton iteration to minimize the residual sum of squares (Eq. (4), r^2 = 0.79, Figure 5.4b).

$$y = \frac{5.3}{1 + e^{0.17(8.2-x)}} \tag{4}$$

Introducing constant a (Eq. (3)) in the fit procedure did not result in a significant increase of the correlation, and it is therefore omitted. Data from California rice paddies (Cicerone et al., 1992) are not included in the curve fitting, because CH_4 emissions increased by a factor of 14.7 upon incorporation of 5 t ha^{-1} straw, which was extremely high compared to other field experiments (Figure 5.4b), showing that exceptions to Eq. (4) exist. The CH_4 emissions from the urea-fertilized plots in the study of Cicerone et al. (1992) are very low compared to the emission from urea-fertilized plots in other studies and therefore cause a relatively high fractional increase in CH_4 emission upon organic amendment. A possible explanation may be that the Californian soil is lower in easy mineralizable carbon due to long-term mineral fertilizer use, resulting in a much stronger increase in CH_4 production once additional carbon is added.

Since Eq. (4) describes the relative CH_4 emission increase as a result of added organic manure, a boundary condition was that y = 1 for an input of 0 t ha^{-1}. Although a linear regression model (y = 0.16x + 1) would also fit the experimental data (r^2 = 0.71, again excluding Cicerone et al. (1992)), a dose response curve appears to be correct from a theoretical point of view. Increasing organic matter inputs will only stimulate CH_4 emission until a factor other than organic carbon availability becomes limiting. Factors limiting CH_4 emission at high organic carbon inputs include accumulation of organic acids to toxic levels, availability of nutrients other than C and, growth rate of microbes that break down organic matter to simple substrates (H_2, acetic acid; Eq. (1) and Eq. (2)) that can be utilized by methanogens.

The lag phase observed at low organic amendments (Figure 5.4b) is unlikely to be due to a lag in methanogenesis, because laboratory experiments showed that CH_4 production increased in proportion to rice straw addition (Wang et al., 1992). The lag may occur because a threshold concentration of soil-entrapped CH_4 has to be exceeded. Once this threshold is reached, CH_4 ebullition may become an important gas transport mechanism when the rice root system is not yet well developed. Because ebullition is intrinsically a more rapid process than the other gas-escape processes, CH_4 escaping in bubbles is not being oxidized at the soil-floodwater interface or soil-root interface. Ebullition as an important CH_4 transporting process in organic amended rice fields, may (partly) explain the more than proportional increase in the steep part of the curve, because a larger fraction of the CH_4 produced is emitted.

The relative increase of CH_4 emission from rice fields in Texas upon incorporation of 6 t ha^{-1} straw was small, ranging from 1.1 to 1.6 (Sass et al., 1991). However, Sass et al. (1991) incorporated 3.6 t ha^{-1} of native vegetation in autumn while preparing the fields for seeding rice plants the following spring. Residual carbon from this field preparation may have stimulated CH_4 emissions from both organic and mineral fertilized plots, thereby decreasing the relative increase upon straw incorporation. The Japanese pot experiments (Kimura et al., 1991, 1993; Watanabe, 1993a) have high CH_4 emissions compared to the Japanese field experiments (Yagi and Minami, 1990) (Figure 5.4a). Although this may be the difference between pot experiments and field experiments, it may also be caused by differences in the soil types or climatic factors. However, after scaling the CH_4 emissions as described earlier, the fractional increase in CH_4 emission from all Japanese experiments are quite similar (Figure 5.4b).

Tsutsuki and Ponnamperuma (1987) have shown in laboratory incubation experiments that incorporation of compost in rice soils had a minor effect on CH_4 emission compared with rice straw or green manure. The amount of acetic acid, an important precursor for CH_4, formed upon incorporation of compost as opposed to straw or green manure is small (Tsutsuki and Ponnamperuma, 1987), suggesting that substrate availability to methanogens limits CH_4 emission rates in compost-amended fields. Aerobic composting results in the degradation of easily decomposable carbon sources to CO_2, reduction of total C, narrowing the C/N ratio, and a relative increase of more resistant organic matter residues (Inoko, 1984). As a result, 1 t compost contains about three times less organic C than 1 t straw or green manure (Tsutsuki and Ponnamperuma, 1987). Fermentation in biogas generators similarly reduces easily decomposable organic matter and increases more resistant residues. Delwiche and

Cicerone (1993) and Watanabe et al. (1993b) have shown that different organic components in rice straw vary considerably in their effectiveness as a precursor for CH_4. If we allow for these differences by considering the effective organic matter content of added compost or fermented residues to be 1/6th of its true C content, the emission data agreed with Eq. (4) for straw and green manure (Figure 5.5, open symbols). This suggests that the amount of substrate for methanogens generated by compost incorporation is approximately 6 times less than that generated by incorporation of equal amounts of straw or green manure. More data are required to verify that higher rates of compost will result in a levelling off of CH_4 emission.

To mitigate CH_4 from rice fields, organic amendments should be minimized. But such a move has to consider also soil fertility aspects. Suzuki et al. (1990) studied the effects of organic and inorganic fertilizers on soil fertility and rice yields in a 60-year long-term field experiment in Japan. The yields in the organic fertilizer plot were clearly lower in the first 10 years, then reached the same level and eventually, after 30 years, became higher than the yields from the inorganic fertilizer plot. These findings are confirmed by other long-term experiments on the effects of organic matter on rice yield (IRRI, 1984). This indicates that to sustain or increase soil fertility and rice yields, moderate organic amendments will be essential. However, the beneficial effects of moderate organic amendments can be obtained by using compost (e.g., composted rice straw) instead of fresh straw or green manure.

Conclusions

Total seasonal methane emission was strongly enhanced by incorporation of green manure. Previous studies indicated that more than 90% of the total CH_4 emission over a season was due to plant-mediated transport, ebullition accounting for less than 10% (Cicerone and Shetter, 1981; Holzapfel-Pschorn et al., 1986; Schütz et al., 1989b). This figure agreed with the results from our urea-fertilized plots but in green manure plots the contribution of ebullition to total CH_4 transport appears to be higher.

CH_4 production in urea-fertilized plots increases strongly over the growing season, but in green manure plots, CH_4 production is constant. For all treatments the fraction of methane produced, which is emitted to the atmosphere, was low around panicle initiation when compared to the tillering stage or ripening stage. This suggests a seasonal pattern in CH_4 oxidation, because it is the most important sink for CH_4 produced in rice fields. Experiments that focus on CH_4 oxidation efficiency throughout the growing season are highly desired.

When CH_4 emission from organically amended plots was expressed relative to emissions from mineral fertilizer-treated plots, the impact of organic amendments on

CH_4 emission can be described by a dose response curve. A single curve accounted for data from locations with different climates, soil types, and field managements. However, the curve fit could not explain all individual data implying that other factors may have to be included. A correction factor is needed for composted and fermented organic matter to account for the lower percentage of easy decomposable carbon. To reduce CH_4 emission from rice fields, organic amendments should be minimized. However, this may conflict with soil fertility aspects as well as with the local availability of fertilizers. Compost has only a slightly stimulating effect on CH_4 emissions as opposed to straw or green manure amendments which greatly enhance CH_4 emissions. Therefore stimulation of composting appears to be a promising mitigation option.

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References

Acharya, C.N., Studies on the anaerobic decomposition of plant materials, I, The anaerobic decomposition of rice straw (*Oryza sativa*), Biochem. J., 29, 578-541, 1935a.

Acharya, C.N., Studies on the anaerobic decomposition of plant materials, II, Some factors influencing the anaerobic decomposition of rice straw (*Oryza sativa*), Biochem. J., 29, 953-960, 1935b.

Blake, D.R., and F.S. Rowland, Continuing worldwide increase in tropospheric methane, Science, 239, 1129-1131, 1988.

Cicerone, R.J., and J.D. Shetter, Sources of atmospheric methane: Measurements in rice paddies and a discussion, J. Geophys. Res., 86, 7203-7209, 1981.

Cicerone, R.J., C.C. Delwiche, S.C. Tyler, and P.R. Zimmerman, Methane emissions from California rice paddies with varied treatments, Global Biogeochem. Cycles, 6, 233-248, 1992.

Delwiche, C.C., and R.J. Cicerone, Factors affecting methane production under rice, Global Biogeochem. Cycles, 7, 143-155, 1993.

Denier van der Gon, H.A.C., and N. van Breemen, Diffusion-controlled transport of methane from soil to atmosphere as mediated by rice plants, Biogeochemistry, 21, 177-190, 1993.

Dlugokencky, E.J., K.A. Masarie, P.M. Lang, P.P. Tans, L.P. Steele, and E.G. Nisbet, A dramatic decrease in the growth rate of atmospheric methane in the northern hemisphere during 1992, Geophys. Res. Lett., 21, 45-48, 1994.

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

International Atomic Energy Agency (IAEA), Manual on measurement of methane and nitrous oxide emissions from agriculture, IAEA-TECDOC-674, Int. At. Energ. Agency, Vienna, Austria, 1992.

Inoko, A., Compost as a source of plant nutrients, in Organic Matter and Rice, pp. 137-145, International Rice Research Institute, Los Baños, Philippines, 1984.

Intergovernmental Panel on Climate Change (IPCC), Climate Change 1992, The supplementary report to the IPCC scientific assessment, 200 pp, Cambridge University Press, New York, 1992.

International Rice Research Institute (IRRI), Organic Matter and Rice, International Rice Research Institute, Los Baños, Philippines, 1984.

Khalil, M.A.K., R.A. Rasmussen, and M.J. Shearer, Trends of atmospheric methane during the 1960s and 1970s, J. Geophys. Res., 94, 18279-18288, 1989.

Kimura, M., Y. Miura, A. Watanabe, T. Katoh, and H. Haraguchi, Methane emission from paddy field, part 1, Effect of fertilization, growth stage and midsummer drainage: Pot experiment, Environ. Sci., 4, 265-271, 1991.

Kimura, M., T. Minoda, and J. Murase, Water-soluble organic materials in paddy soil ecosystem, 2, Effects of temperature on contents of total organic materials, organic acids, and methane in leachate from submerged paddy soils amended with rice straw, Soil Sci. Plant Nutr., 39, 713-724, 1993.

Kimura, M., Methane emission from paddy soils in Japan and Thailand, in World Inventory of Soil Emission Potentials, Proceedings of an International Workshop, edited by N.H. Batjes and E.M. Bridges, pp. 43-80, International Soil Reference and Information Centre, Wageningen, Netherlands, 1992.

Lelieveld, J., P.J. Crutzen, and C. Brühl, Climate effects of atmospheric methane, Chemosphere, 26, 739-768, 1993.

Lindau, C.W., and P.K. Bollich, Methane emissions from Louisiana 1st and ratoon crop rice, Soil Sci., 156, 42-48, 1993.

Nagarajah, S., H.U. Neue, and M.C.R. Alberto, Effect of Sesbania, Azolla, and rice straw incorporation on the kinetics of NH_4, K, Fe, Mn, Zn and P in some flooded rice soils, Plant Soil, 116, 37-48, 1989.

Neue, H.U., and H.-W. Scharpenseel, Gaseous products of the decomposition of organic matter in submerged soils, in Organic Matter and Rice, pp. 311-328, International Rice Research Institute, Los Baños, Philippines, 1984.

Neue, H.U., R.S. Lantin, R. Wassmann, J.B. Aduna, M.C.R. Alberto, and M.J.F. Andales, Methane emission from rice soils of the Philippines, in CH_4 and N_2O, Global emissions and controls from rice fields and other agricultural and industrial sources, edited by K. Minami, A. Mosier, and R. Sass, pp. 55-64, National Institute of Agro-Environmental Sciences, Yokendo Publishers, Tokyo, Japan, 1994.

Nouchi, I., S. Mariko, and K. Aoki, Mechanism of methane transport from the rhizosphere to the atmosphere through rice plants, Plant Physiol., 94, 59-66, 1990.

Oremland, R.S., Biogeochemistry of methanogenic bacteria, in Biology of anaerobic microorganisms, edited by A.J.B. Zehnder, pp. 641-705, John Wiley, New York, 1988.

Sass, R.L., F.M. Fisher, P.A. Harcombe, and F.T. Turner, Methane production and emission in a Texas rice field, Global Biogeochem. Cycles, 4, 47-68, 1990.

Sass, R.L., F.M. Fisher, F.T. Turner, and M.F. Fund, Methane emission from rice fields as influenced by solar radiation, temperature, and straw incorporation, Global Biogeochem. Cycles, 5, 335-350, 1991.

Schütz, H., A. Holzapfel-Pschorn, R. Conrad, H. Rennenberg, and W. Seiler, A 3-year continuous record on the influence of daytime, season, and fertilizer treatment on methane emission rates from an Italian rice paddy, J. Geophys. Res., 94, 16,405-16,416, 1989a.

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

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

Singh, N.T., Green manures as sources of nutrients in rice production, in Organic Matter and Rice, pp. 217-228, International Rice Research Institute, Los Baños, Philippines, 1984.

Soil Survey Staff, Keys to Soil Taxonomy, 5th Ed., SMSS Tech. Monogr., vol. 19, Blacksburg, Virginia, Pocahontas Press Inc., 556 pp., 1992.

Stone, B., Evolution and diffusion of agricultural technology in China, in Sharing innovation global perspectives on food agricultural and rural development, edited by N.G. Kotler, International Rice Research Institute, Los Baños, Philippines, 1990.

Suzuki, M., K. Kamekawa, S. Sekiya, and H. Shiga, Effect of continuous application of organic or inorganic fertilizer for sixty years on soil fertility and rice yield in paddy field, 14th Int. Congr. of Soil Sci. IV, pp. 14-19, Kyoto, Japan, 1990.

Takai, Y., The mechanism of methane fermentation in flooded paddy soil, Soil Sci. Plant Nutr., 16, 238-244, 1970.

Tsutsuki, K., and F.N. Ponnamperuma, Behaviour of anaerobic decomposition products in submerged soils, Effects of organic material amendment, soil properties and temperature, Soil Sci. Plant Nutr., 33, 13-33, 1987

Ventura, W., and I. Watanabe, Green manure production of *Azolla microphylla* and *Sesbania rostrata* and their long-term effects on rice yields and soil fertility, Biol. Fert. Soils, 15, 241-248, 1993.

Wang, Z.P., R.D. Delaune, C.W. Lindau, and W.H. Patrick Jr., Methane production from anaerobic soil amended with rice straw and nitrogen fertilizers, Fert. Res., 33, 115-121, 1992.

Wassmann, R., H. Schütz, H. Papen, H. Rennenberg, W. Seiler, A.G. Dai, R.X. Shen, X.J. Shangguan, and M.X. Wang, Quantification of methane emissions from chinese rice fields (Zhejiang Province), Biogeochemistry 20, 83-101, 1993a.

Wassmann, R., M.X. Wang, X.J. Shangguan, X.L Xie, R.X. Shen, Y.S Wang, H. Papen, H. Rennenberg, and W. Seiler, First records of a field experiment on fertilizer effects on methane emission from rice fields in Hunan Province (PR-China), Geophys. Res. Lett., 20, 2071-2074, 1993b.

Watanabe, A., K. Katoh, and M. Kimura, Effect of rice straw application of CH_4 emission from paddy fields, 1, Effect of weathering of rice straw in the field during off-crop season, Soil Sci. Plant Nutr., 39, 701-706, 1993a.

Watanabe, A., K. Katoh, and M. Kimura, Effect of rice straw application on CH_4 emission from paddy fields, 2, Contribution of organic constituents in rice straw, Soil Sci. Plant Nutr., 39, 707-712, 1993b.

Yagi, K., and K. Minami, Effect of organic matter application on methane emission from some Japanese paddy fields, Soil Sci. Plant Nutr.,36, 599-610, 1990.

Chapter 6

Release of Entrapped Methane from Wetland Rice Fields upon Soil Drying

H.A.C. Denier van der Gon, N. van Breemen, H.-U. Neue,
R.S. Lantin, J.B. Aduna, M.C.R. Alberto, and R. Wassmann

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Release of entrapped methane from wetland rice fields upon soil drying

Abstract

Methane emissions from Philippine rice paddies, fertilized with either urea or green manure, were monitored for several weeks after harvesting the dry and the wet season crops of 1992. The fields were still flooded during harvest but irrigation was stopped after harvest and the fields were allowed to evaporatively dry while CH_4 emissions were monitored with a closed chamber technique. In all plots we observed a sudden, strong increase of CH_4 emissions to the atmosphere for 2 to 4 days just after the soil fell dry. As soil drying continued, the soils began to crack and CH_4 emissions decreased to nil. The release of CH_4 during soil drying was observed for fields on three different soil types and both for urea or organically manured rice fields in both seasons. The absolute amounts of CH_4 emitted during soil drying differed greatly depending on fertilizer treatment. However, the ratio between the amount of CH_4 released upon soil drying and CH_4 emitted during the growing season was quite constant (0.10 ± 0.04). This suggests that about 10% of the CH_4 emitted during a full rice crop cycle is released during drying of the fields and thus needs to be included in estimates of the total CH_4 emission from rice agriculture.

Introduction

Methane (CH_4) is one of the most important greenhouse gases. Wetland rice fields emit CH_4 and are important contributors to the increasing atmospheric methane concentrations (Cicerone and Shetter, 1981; Schütz et al., 1989a). CH_4 emissions from wetland rice fields are often measured with the so-called closed chamber technique (e.g., Schütz et al., 1989a). Although the same technique is used in many studies, the method (e.g., manually versus automatic operation of the flux chambers) and frequency of sampling vary widely. Calculated seasonal CH_4 emissions from rice fields have to include both daily and seasonal variation in CH_4 emission. If CH_4 emissions are monitored continuously this is achieved by summing the individual flux measurements. If CH_4 emissions from rice fields are monitored at a low time resolution, for example, once every week, total seasonal CH_4 emission estimate is obtained by assuming that each measurement point is representative for a certain time window. However, low nighttime CH_4 emissions and/or peak emissions around noon or early afternoon may be missed when sampling at low time resolution. Therefore when monitoring at a low time resolution, intensive 24-hour measurement campaigns should be included. The obtained diel emission pattern can be extrapolated to other measurement points because the diel emission pattern is rather stable on a timescale of a few weeks (Schütz et al., 1989a; Denier van der Gon and Neue, 1995). In addition to the diel fluctuation in CH_4 emissions, agricultural practices, like weeding and post-harvest drainage, may also cause highly variable CH_4 emissions in relatively short periods (Denier van der Gon et al., 1992; Wassmann et al., 1994). In this paper we present data that illustrate the dynamics of CH_4 release upon soil drying and discuss its importance for the total CH_4 emission during a complete rice crop cycle.

Materials and methods

Measuring system

Methane emission was monitored automatically with a closed chamber technique as described by Schütz et al. (1989a). The system allows 24-hour semicontinuous determination of CH_4 emission rates from different gas collector chambers. Measurements are performed in 2-hour cycles, allowing 12 flux measurements per day of each chamber. All chambers were made of smooth colorless Plexiglas and equipped with a Plexiglas cover which could be opened and closed by a time-controlled pneumatic cylinder. The dimensions of the chambers were 1 m x 1 m basal area and 1.2 m height or 0.6 m x 0.6 m basal area and 1.2 m height. To stabilize the chambers, each corner of a chamber has a 20-cm aluminum extension which is placed in the soil. The lower sides of the chambers were submerged, providing a gastight seal between inner and outer atmosphere. During receding floodwater and soil drying, the flux chambers were pushed 10 cm into the soil when the fields were still flooded with about 10 cm of water. After harvest of the 1992 wet season crop, water status, soil drying, reflooding, and soil cracking were recorded on a daily basis for each individual flux chamber. Air samples from the individual closed chambers were analyzed for CH_4 on a gas chromatograph equipped with a 6-port valve, sample loop, and a flame ionization detector (FID). For a schematic overview and technical details of the measurement system we refer to Schütz et al. (1989a). The methane emission rate from a chamber is calculated with linear regression from the temporal increase of the CH_4 concentration in the chamber. Each emission rate is based on four measurements. The r^2 of the linear regression of the CH_4 concentration against time is typically > 0.95. CH_4 emissions from all plots were measured in duplicate.

Soil types

Three soils were used in this study (Table 6.1). Maahas is the soil originally present at the IRRI research farm. Luisiana and Pila are soils from neighbouring districts. The 0- to 20-cm topsoil from farmers fields in Luisiana and Pila was collected and transported to the IRRI research farm. The original 0- to 20-cm topsoil from 3 x 5 m plots was removed and replaced by Luisiana or Pila soil. The newly placed soils were

Table 6.1 Some characteristics of the three soils used in the field experiment.

	Pila	Louisiana	Maahas
pH 1:1 H_2O	7.8	4.5	5.9
CEC (meq/100 g)	27.2	24.9	40.2
Organic Carbon (%)	1.47	1.84	1.97
Total N (%)	0.182	0.180	0.166
Clay (%)	21	56	66
Silt (%)	40	40	28
Sand (%)	39	4	6

separated from the original subsoil by a plastic sheet. Field preparations and other agricultural practices were the same for all three soils. Luisiana and Maahas are clay soils, whereas Pila is a calcareous sandy loam. The rice fields were fertilized with urea or green manure (Table 6.2 and 6.3). An additional treatment in the 1992 wet season was an addition of gypsum to a plot with Maahas clay.

Soil-entrapped CH_4

In the 1992 dry season, the amount of CH_4 entrapped in the soil was measured in each treatment just before harvest, 98 days after transplanting. Triplicate soil cores of 10 cm length were collected from each treatment using 4.4-cm inner diameter acrylic core tubes with a length of 25 cm. The top of the tube is sealed with a rubber stopper with a septum. During sampling a gas collector bag is connected to the headspace of the tube via the septum to collect excess gases which may contain CH_4 released during sampling. Next, the tube is sealed at the bottom with a rubber stopper, the gas collector bag is disconnected, and the tube is vigorously shaken for 2 hours. The headspace of the tube and the gas in the gas collector bag were analyzed for CH_4 on a gas chromatograph with FID. The concentrations were recalculated to micrograms CH_4 using the known volumes and summed to give an estimate of the amount CH_4 entrapped in the soil.

Results

Cutting the plants during harvest did not affect CH_4 emission (Figure 6.1). Pushing the flux chambers into the soil disturbed CH_4 emission by releasing entrapped CH_4 via ebullition. However, after 1 to 2 days the CH_4 emission pattern was the same as before inserting the boxes. In the 1992 dry season the level of the floodwater above

Table 6.2 Soil, fertilizer type, and CH_4 emission during the growing season, soil drying, and post-harvest in the 1992 dry season.

Soil	Fertilizer	Growing season CH_4 emission[a] ($g\ m^{-2}$)	Soil-entrapped CH_4 before harvest[b] ($\mu g\ g^{-1}$)	CH_4 emitted during soil drying ($g\ m^{-2}$)	Ratio CH_4 emission during soil drying to growing season CH_4 emission	Post-harvest CH_4 emission[d] ($g\ m^{-2}$)
Maahas	urea	17.2	18.5 (7.3)	1.7	0.10	2.9
Maahas	GM[c]	87.1	32.4 (2.3)	5.9	0.07	9.4
Luisiana	urea	23.6	21.0 (3.3)	2.9	0.12	5.1
Pila	urea	30.5	12.5 (3.0)	1.6	0.05	5.6

[a] CH_4 emitted in the period from transplanting up to harvest.
[b] Average of three samples collected 98 days after transplanting, standard deviation in parentheses.
[c] GM is green manure; *Sesbania rostrata.*
[d] In the 1992 dry season post-harvest emission equals emission during fallow period because CH_4 emission from the fields had stopped completely 2 weeks after harvest.

Table 6.3 Soil, fertilizer type and CH_4 emission during the growing season, soil drying, and fallow period in the 1992 wet season.

Soil	Fertilizer	Growing season CH_4 emission[a] ($g\ m^{-2}$)	CH_4 emitted during soil drying ($g\ m^{-2}$)	Ratio CH_4 emission during soil drying to growing season CH_4 emission	Fallow period CH_4 emission[d] ($g\ m^{-2}$)
Maahas A[c]	GM[b]	47.1	4.6	0.10	8.5
Maahas B[c]	GM	42.0	3.6	0.09	6.4
Maahas + gypsum	GM	12.1	2.4	0.20	5.0
Pila	GM	42.3	3.8	0.09	9.4

[a] CH_4 emitted in the period from transplanting up to harvest.
[b] GM is green manure; *Sesbania rostrata.*
[c] Plots presented separately because of the different drying pattern (see Figures 6.4a and 6.4c).
[d] Includes post-harvest CH_4 emission and CH_4 emission during soil drying.

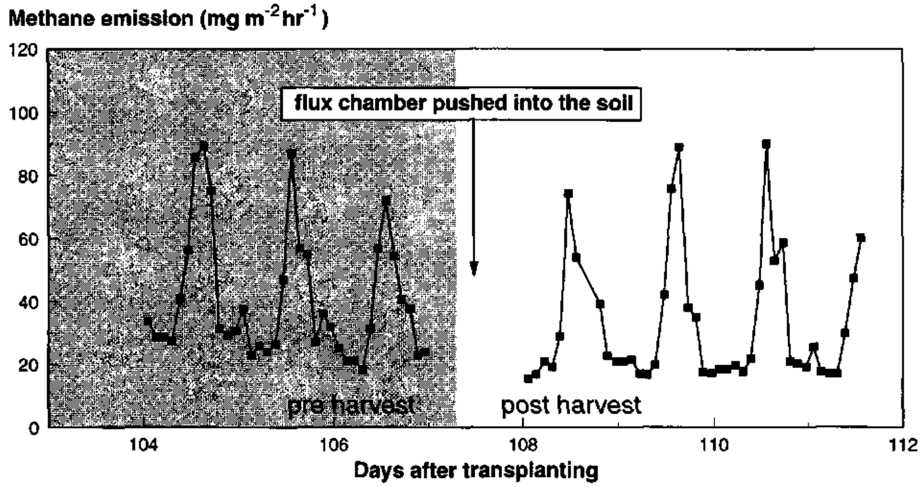

Figure 6.1 Methane emissions from a continuously flooded rice field as measured with a closed chamber before and after harvest in the 1992 dry season.

the soil surface in the plots with Maahas and Luisiana soil dropped from 10 to 0 cm in about 6 days after irrigation was stopped. In the Pila plot, drying took somewhat longer because the floodwater layer was about 15 cm when irrigation was stopped. Percolation was negligible in all three soils because of a plastic sheet below the Pila and Luisiana soils and an impermeable traffic pan at about 18 cm depth in Maahas soil. So, drying of the soils was mainly by evaporation. The normal diurnal pattern of CH_4 emission continued until floodwater had receded completely. Next, the macropores of the soils became air-filled (but the soils had not cracked yet) and a large flush of CH_4 was measured from the soils. CH_4 emission stopped only after the soil was fully aerated (Figure 6.2a, 6.2b, 6.2c, and 6.2d). Interruptions of the curves in Figure 6.2 indicate periods when technical problems prohibited data collection. Table 6.2 lists the amounts of CH_4 released during the growing season, the amount of soil-entrapped CH_4 just before harvest, CH_4 released during soil drying only and total post-harvest CH_4 emission.

In the 1992 wet season, soil drying after ceasing irrigation was slower due to rain (Figure 6.3). Table 6.3 gives the amounts of CH_4 released during soil drying only and the total amounts of CH_4 released from harvest until the CH_4 emission had completely ceased. The CH_4 emissions immediately after harvest showed the same diel pattern and levels as before harvest, as was also observed in the dry season (Figure 6.1).

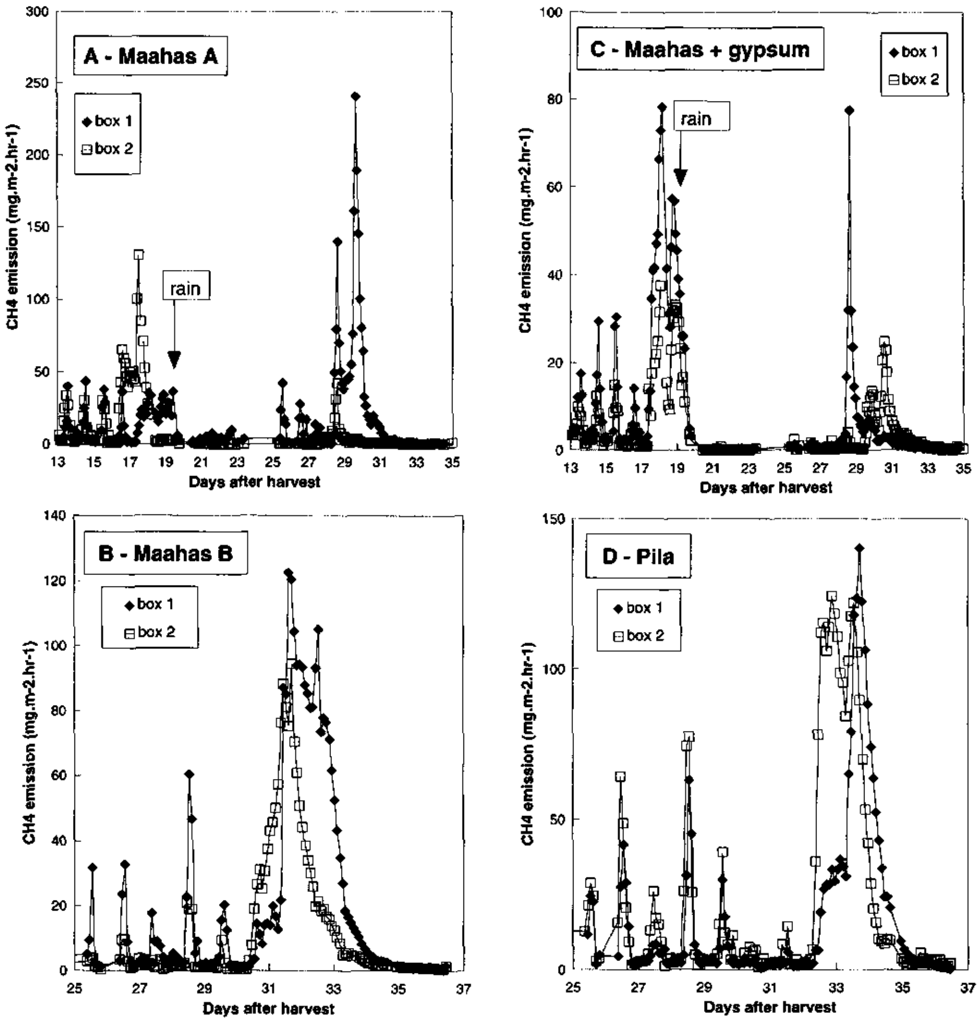

Figure 6.2 Post-harvest methane emissions from rice fields fertilized with urea (6.2a, 6.2c, and 6.2d) or green manure (6.2b) on different soil types; Maahas (6.2a and 6.2b), Luisiana (6.2c), and Pila (6.2d) in the 1992 dry season.

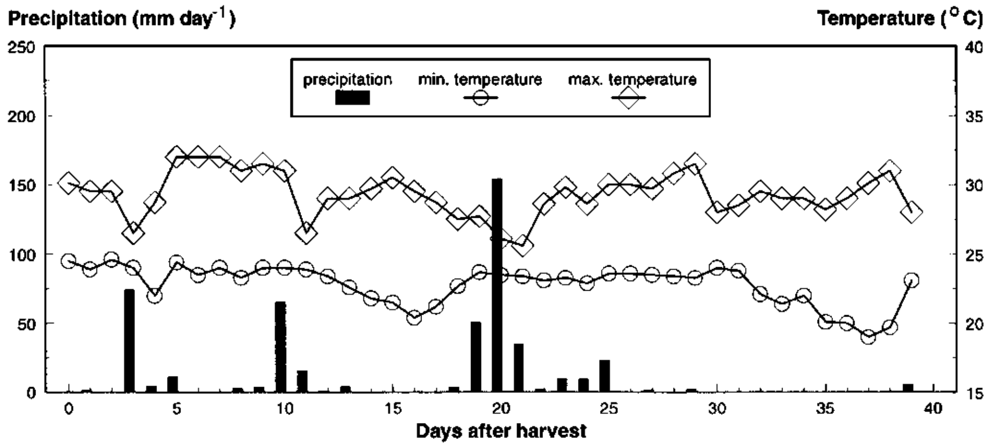

Figure 6.3 Daily precipitation, minimum temperature, and maximum temperature at the IRRI research farm for the first 40 days after harvest in the 1992 wet season.

In Figure 6.4 these periods with a constant diel emission pattern (up to 14 days after harvest in Figures 6.4a and 6.4c, up to 26 days after harvest in Figures 6.4b and 6.4d) are omitted to allow more detailed graphical representation of the periods with drastic changes in CH_4 emission. At 16 days after harvest, the soil surface in box 2 of the Maahas plot A (Figure 6.4a) fell dry and CH_4 emission peaked, apparently due to release of soil-entrapped CH_4. One day later, high CH_4 emissions were also observed from the other box in Maahas plot A (Figure 6.4a) and the gypsum-amended Maahas soil (Figure 6.4c). Heavy rain on day 19-21 after harvest interrupted soil drying and caused reflooding of the soils. CH_4 emissions decreased and stopped at 21 days after harvest at the end of the 2-day rain period. (The soil surface of all but one chamber (box 2 of Maahas plot A) showed no cracks yet.) CH_4 emissions from the reflooded plots did not return to the previous diel emission pattern and were negligible with the exception of box 1 of Maahas plot A where the diel emission pattern observed before soil drying returned after 1 week. At 27 days after harvest the soil surface in box 1 and 2 of Maahas plot A and box 1 of the gypsum-amended plot fell dry again, release of entrapped CH_4 resumed 1-2 days later. The largest CH_4 release was observed from box 1 of Maahas plot A which had emitted relatively little CH_4 during the first period of drying. The soil surface of box 2 of the gypsum-amended plot fell dry on 29 days after harvest, and release of entrapped CH_4 started 1 day later. The soils of Maahas plot A and Maahas plus gypsum started to crack at 31 and 32 days after harvest, respectively. However, the release of CH_4 from the soils had more or less stopped by then.

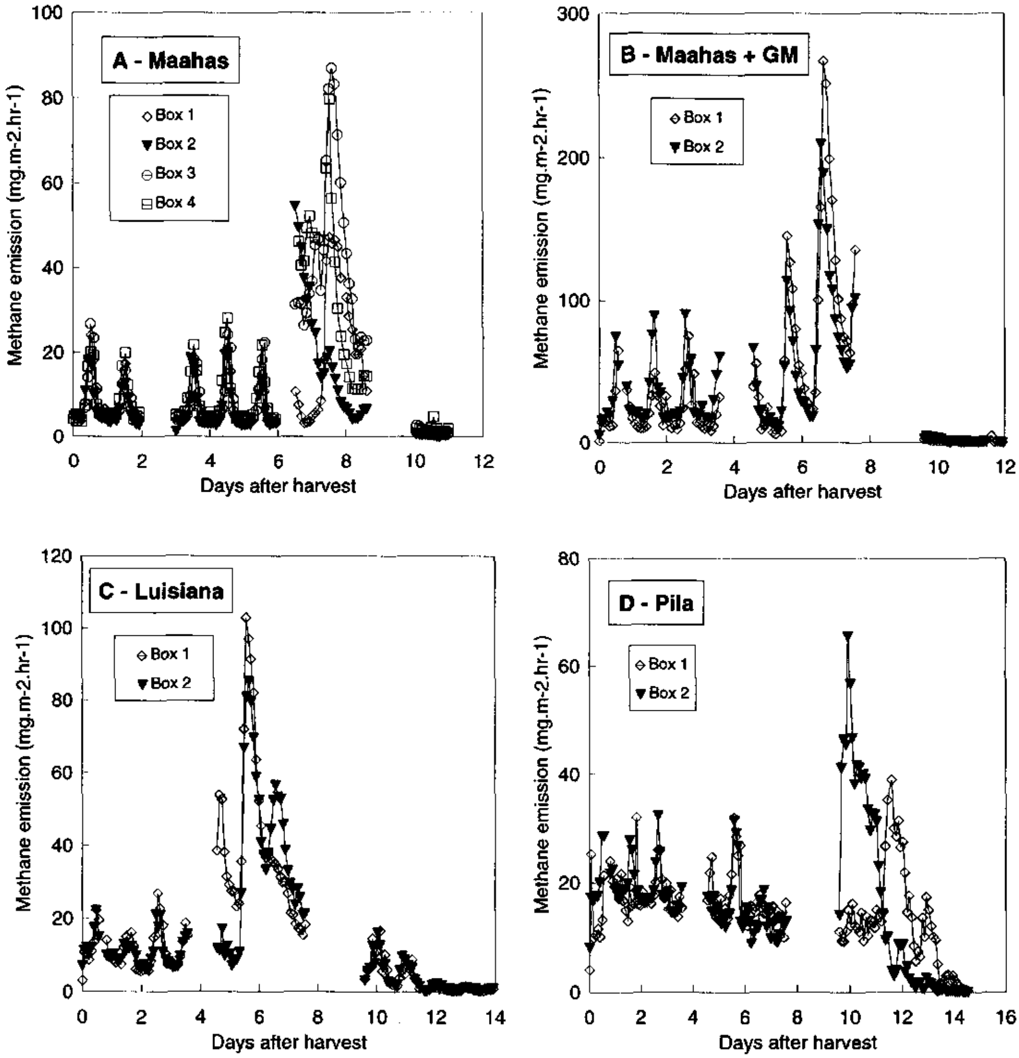

Figure 6.4 Methane emissions after harvest (fallow period) from rice fields fertilized with green manure before and during soil drying on different soil types; Maahas plot A (6.4a), Maahas plot B (6.4b), Maahas with gypsum (6.4c), and Pila (6.4d) in the 1992 wet season.

Maahas plot B and the Pila plot were continuously flooded the first month after harvest and showed the normal diel emission pattern in this period (data not shown). The soil surface of Maahas plot B and Pila fell dry 29 and 31 days after harvest, respectively, and large amounts of CH_4 were released to the atmosphere 1-2 days later (Figures 6.4b and 6.4d). Soil cracking in Maahas plot B and Pila started 34 and 35 days after harvest, respectively.

Discussion

CH_4 emissions did not change after harvest because the plants were cut above the floodwater layer and thus remained a good conduit for CH_4 transport. Owing to spatial heterogeneity within the plots, the timing of drying differed among individual chambers. Therefore emission patterns should be considered for each chamber separately. To facilitate the discussion, we propose the following terminology: (1) "emission during the growing season" covers the period from transplanting up to harvest, (2) "post-harvest emission" is reserved for emission during the initial 2 weeks after harvest, (3) total emission after harvest (including post-harvest emission) is referred to as "fallow emission", and (4) "emission upon/during soil drying" covers the period of drastic changes in CH_4 emission when the soil falls dry (this may happen more than once during a fallow period).

The sharp increase in CH_4 emission during soil drying is a very dynamic process. We observed that the release of entrapped CH_4 starts 1-2 days after the soil surface fell dry but before the soils started to crack. This pattern indicates that soil cracking by itself is not a prerequisite for the release of entrapped CH_4 and that peak emissions upon soil drying may also be expected from soils that do not or only slightly crack (sandy soils, e.g., Pila soil). Our observations indicate that the critical moment that causes the release of soil-entrapped CH_4, is when the macropores become air-filled. The diffusion of CH_4 through the gas phase is about 4 orders of magnitude faster than through the water phase. So, presence of air-filled macropores in a soil could strongly enhance transport of CH_4 from soil to atmosphere. On the other hand, air in the soil macropores would cause the soil to oxidize, creating a good environment for CH_4 oxidizing bacteria. The amount of CH_4 entrapped in the soil per square meter of rice field after the growing season of the 1992 dry season can be estimated using the soil-entrapped CH_4 data given in Table 6.2. Assuming a bulk density of 900 kg m^{-3} and a puddled layer of 17.5 cm, the amount of CH_4 entrapped in Maahas (urea), Maahas (green manure), Luisiana, and Pila would be 2.9, 5.1, 3.3, and 2.0 CH_4 g m^{-2}, respectively. Comparison with the amount of CH_4 emitted during soil drying (Table 6.2) indicates that on average, about 64% of the CH_4 entrapped in the soil was released to the atmosphere during soil drying (and thus escaped oxidation in the soil).

CH_4 emission throughout the growing season from plots fertilized with green manure was about 4 times higher than from comparable urea-fertilized plots (Table

6.2). Likewise the amount of soil-entrapped CH_4 and the amount of CH_4 released during soil drying from fields with green manure application is higher than from comparable urea-fertilized plots. CH_4 emission from gypsum-amended fields was reduced by 50-72%, probably due to competition between sulfate-reducing bacteria and methanogens (Denier van der Gon and Neue, 1994). Again, a similar reduction is observed when the amount of CH_4 released upon soil drying is compared for fields with and without gypsum amendment (Table 6.3). These results suggest that in soils planted to rice, the amount of soil-entrapped CH_4 and the amount of CH_4 released upon soil drying is mainly controlled by the CH_4 productivity of the soil and is therefore influenced by measures that enhance or depress CH_4 production (e.g., green manure incorporation or gypsum application, respectively). In a recent greenhouse study, Byrnes et al. (1995) found that CH_4 release upon soil drying from pots planted to rice accounted for 7-8.5% of the total seasonal emission for both soil types studied. This is in good agreement with our field observations where CH_4 release upon soil drying accounted for about 10% of the total emission (Tables 6.2 and 6.3).

A laboratory study with 16 unplanted, flooded rice soils showed that a higher clay content resulted in a higher percentage soil-entrapped CH_4 and a lower percentage CH_4 emitted to the atmosphere (Wang et al., 1993). Wang et al. (1993) suggested that physical characteristics associated with high clay contents help to reduce CH_4 emissions to the atmosphere. However, it is doubtful whether the amount of CH_4 emitted from rice soils is really depressed by a clayey texture because (1) plant-mediated gas transport is the main transport mechanism for CH_4 from paddy fields to the atmosphere, not ebullition (Cicerone and Shetter, 1981; Schütz et al., 1989b) and, (2) our results show that at least part of the entrapped CH_4 is released to the atmosphere upon soil drying. Furthermore, we did not observe a significant difference between the amount of CH_4 released from clayey soils or a sandier soil. However, Sass and Fisher (1994) reported an inverse relation between CH_4 emission from Texan rice fields and clay content. Clearly, the influence of soil texture on CH_4 emission from rice fields and the mechanism potentially causing this influence deserve further study.

At 20 days after harvest, the high CH_4 emissions of the Maahas plot A and Maahas plus gypsum (Figures 6.4a and 6.4c) were interupted because rain reflooded the soils. Considerable amounts of CH_4 were still present in the soils, indicated by the release of CH_4 during the final soil drying event around 30 days after harvest. In between the two soil drying events, CH_4 emissions did not return to levels observed before soil drying, or only after about a week as in box 1 of Maahas plot A (Figure 6.4a). Why CH_4 emissions do not return to predrying values (or somewhat lower values) but are negligible, although CH_4 was still present in the soil, is not fully understood. Possibly the (short) presence of O_2 poisoned the methanogens and a build-up of CH_4 in the soil to levels that support continuous emission is prohibited. The short drying period at 20 days after harvest in Maahas plot A and Mahaas plus gypsum significantly affected the CH_4 emissions from the rice field and suggests drainage and reflooding before the rice plants suffer from drought stress as a possible mitigation option if water supply is sufficient. Indeed, Sass et al. (1992) showed that floodwater management is an effective instrument in mitigating CH_4 emission from rice fields. Sass et al. (1992) obtained the lowest seasonal total CH_4 emission by applying a multiple aeration treatment. However, when evaluating the efficiency of floodwater management as a means of reducing CH_4 emissions from rice fields, the amount of CH_4 emitted during soil drying has to be taken into account. High-frequency monitoring of CH_4 emissions from rice fields during soil drying events is essential because the full process of release of the soil-entrapped CH_4 lasts only for a few days and can easily be missed if sampling is done at low time resolution. Because appreciable amounts of CH_4 are emitted just after the fields fell dry, the chambers used for monitoring CH_4 emissions during this period need to have a gastight seal between the chamber bottom and the soil, extending to about 10 cm depth to prevent leakage via cracks.

Conclusions

In all plots, both in the wet season and the dry season, we observed very high emissions of CH_4 to the atmosphere during the early phase of soil drying. Cicerone et al. (1992) also reported significant release of CH_4 during soil drying but did not quantify this release. Sass et al. (1991; 1992) observed no significant CH_4 release after drainage. Whether this is due to the drainage method or (partly) due to low time resolution sampling at the time of the drainage event cannot be concluded from the available data. The absolute amount of CH_4 emitted upon soil drying in our fields depended on the fertilizer and/or soil amendment. However, the ratio between the amount of CH_4 released during soil drying and CH_4 emitted during the growing season from our paddy fields was rather constant (0.10 ± 0.04), irrespective of the absolute amount of CH_4 emitted. Therefore CH_4 escaping to the atmosphere upon soil drying is a significant part of the total amount of CH_4 emitted from a rice field. In studies on CH_4 emission from wetland rice fields where CH_4 emission during drying of the fields was not included, the total CH_4 emission during a rice crop cycle may be underestimated by about 10 %.

In the 1992 wet season, drying of the rice fields was prevented by rain and CH_4 emissions continued well in to the fallow period at a similar level as before harvest.

This indicates that considerable production and emission of CH_4 may occur in/from rice fields during a wet fallow period as was also found in a greenhouse study (Trolldenier, 1995). To minimize production and emission of CH_4, a dry fallow period is recommended. However, a wet, or partially wet, fallow period cannot always be prevented, for example, when frequent rains do not allow soil drying.

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References

Byrnes, B.H., E.R. Austin, and B.K. Tays, Methane emissions from flooded rice soils and plants under controlled conditions, Soil Biol. Biochem., 27, 331-339, 1995.

Cicerone, R.J., and J.D. Shetter, Sources of atmospheric methane: Measurements in rice paddies and a discussion, J. Geophys. Res., 86, 7203-7209, 1981.

Cicerone, R.J., C.C. Delwiche, S.C. Tyler, and P.R. Zimmerman, Methane emissions from California rice paddies with varied treatments, Global Biogeochem. Cycles, 6, 233-248, 1992.

Denier van der Gon, H.A.C., H.-U. Neue, R.S. Lantin, R. Wassman, M.C.R Alberto, J.B. Aduna, and M.J.P. Tan, Controlling factors of methane emissions from rice fields, in World Inventory of Soil Emission Potentials, Proceedings of an International Workshop, edited by N.H. Batjes and E.M. Bridges, pp. 81-92, ISRIC, Wageningen, The Netherlands, 1992.

Denier van der Gon, H.A.C., and H.-U. Neue, Impact of gypsum application on the methane emission from a wetland rice field, Global Biogeochem. Cycles., 8, 127-134, 1994.

Denier van der Gon, H.A.C., and H.-U. Neue, Influence of organic matter incorporation on the methane emission from a wetland rice field, Global Biogeochem. Cycles., 9, 11-22, 1995.

Sass, R.L., F.M. Fisher, P.A. Harcombe, and F.T. Turner, Mitigation of methane emissions from rice fields: Possible adverse effects of incorporated rice straw, Global Biogeochem. Cycles., 5, 275-287, 1991.

Sass, R.L., F.M. Fisher, Y.B. Wang, F.T. Turner, and M.F. Jund, Methane emissions from rice fields: The effect of floodwater management, Global Biogeochem. Cycles., 6, 249-262, 1992.

Sass, R.L., and F.M. Fisher, CH_4 emission from paddy fields in the United States Gulf Coast area, in CH_4 and N_2O: Global Emissions and Controls From Rice Fields and Other Agricultural and Industrial Sources, edited by K.Minami et al., pp. 65-77, Nat. Inst. of Agro-Environ. Sci., Tsukuba, Japan, 1994.

Schütz, H., A. Holzapfel-Pschorn, R. Conrad, H. Rennenberg, and W. Seiler, A 3-year continuous record on the influence of daytime, season, and fertilizer treatment on methane emission rates from an Italian rice paddy, J. Geophys. Res., 94, 16,405-16,416, 1989a.

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

Trolldenier, G., Methanogenesis during rice growth as related to the water regime between crop seasons, Biol. Fertil. Soils, 19, 84-86 , 1995.

Wang, Z.P., C.W. Lindau, R.D. Delaune, and W.H. Patrick, Methane emission and entrapment in flooded rice soils as affected by soil properties, Biol. Fertil. Soils, 16, 163-168, 1993 .

Wassmann, R., H.U. Neue, R.S. Lantin, J.B. Aduna, M.C.R. Alberto, M.J. Andales, M.J. Tan, H.A.C. Denier van der Gon, H. Hoffmann, and H. Papen, Temporal patterns of methane emissions from wetland rice fields treated by different modes of N-application, J. Geophys. Res., 99, 16,457-16,462, 1994.

Chapter 7

Diffusion-Controlled Transport of Methane from Soil to Atmosphere as Mediated by Rice Plants

H.A.C. Denier van der Gon and N. van Breemen

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Diffusion-controlled transport of methane from soil to atmosphere as mediated by rice plants

Abstract

Methane emission from rice grown in flooded soil was measured in pot experiments using headspaces with different gas composition. The emission rates varied with the atmospheric composition. Based on the kinetic theory of gases the binary diffusion coefficients for methane in various gases were calculated. The ratios of the measured emissions under a certain atmosphere relative to that in air were similar to the ratios of the binary diffusion coefficients showing that plant-mediated CH_4 transport is driven by diffusion. Small deviations from the theoretical ratios of emissions support the hypothesis that mass flow of gas to the submerged parts of the rice plant may depress the upward diffusive CH_4 flux. The results in combination with data from the literature suggest that the rate limiting step in plant-mediated methane transport is diffusion of CH_4 across the root/shoot junction.

Introduction

Methane (CH_4) is an important greenhouse gas that traps part of the thermal radiation from the earth's surface and plays an active role in the atmospheric chemistry (Wang et al., 1976; Bouwman, 1990). Methane, produced by strict anaerobes in waterlogged soils, is transported to the atmosphere by diffusion, ebullition or plant-mediated transport. Wetland rice fields are considered a globally important source of methane (Cicerone and Oremland, 1988; Bouwman, 1990). In rice fields 80-90% of the CH_4 emission is due to plant-mediated transport (de Bont et al., 1978; Holzapfel-Pschorn and Seiler, 1986; Holzapfel-Pschorn et al., 1986). Rice can grow in anoxic soil because it possesses a well-developed system of air spaces (aerenchyma) which supplies atmospheric O_2 to the roots for respiration. At the same time this system is an effective vent for the release of CH_4 from the soil to the atmosphere. The transport of oxygen from the atmosphere to the roots depends on diffusion and/or mass flow (Jensen et al., 1967; Armstrong, 1979; Raskin and Kende, 1985). Transport of O_2 in rice plants may differ from that of CH_4 in several respects. 1) Methane is transported in the opposite direction; 2) respiration of roots and microorganisms form an active sink for O_2 along its way to the soil and 3) diffusive transport will be influenced by the difference in molecular weight between O_2 and CH_4. Because there is a downward mass flow of gas in rice plants (Raskin and Kende, 1985), it is unlikely that the upward transport of CH_4 occurs by mass flow. Therefore, CH_4 transport is probably by diffusion, driven by the concentration gradient between the soil (source) and the atmosphere, which acts as an infinite sink due to the low concentration of CH_4 in ambient air. The rate of transport of ethylene through rice plants from the rooting medium to the atmosphere, however, was not proportional to the partial pressure of ethylene around the roots (Lee et al., 1981). This indicates that processes other than diffusion may play a role too.

Clearly, the mechanisms and limitations of plant-mediated CH_4 transport are not fully understood. A proper understanding of the CH_4 transport through the plant is essential for mechanistic modelling of CH_4 emission on a field scale. The aim of the experiments described here is to further elucidate the mechanisms of CH_4 transport through rice plants. Based on the kinetic theory of gases an experiment is designed to test the hypothesis that plant-mediated CH_4 transport is driven by diffusion.

Theory

For the diffusion of a trace gas *i* through any gas mixture the Fickian diffusion coefficient D_{Fi} is independent of the mole fraction of *i* and of the diffusional fluxes of other gases (Jaynes and Rogowski, 1983). In this case the D_{Fi} equals the binary diffusion coefficient D_{ij} of gas *i* in gas *j* (Hirschfelder et al., 1964).

$$D_{ij} = c\frac{[T^3(M_i + M_j)/(2M_iM_j)]^{1/2}}{p\sigma_{ij}^2\Omega_{ij}} \quad \textbf{(1)}$$

where
- D_{ij} = binary diffusion coefficient of species *i* in *j* ($m^2.s^{-1}$)
- c = constant; 8.42 x 10^{-24} ($J^3.K^{-3}.mol^{-1}$) (Leffelaar, 1987)
- T = temperature (K)
- M_i = molecular weight of species *i*
- p = pressure (Pa)
- σ_{ij} = arithmic mean of the collision diameters for species *i* and *j* (m)
- Ω_{ij} = collision integral for species *i* and *j*

Eq. (1) shows that a change of the molecular weight of the bulk gas in the atmosphere would influence diffusion of a trace gas from soil to atmosphere. This offers the possibility to test if diffusion controls the emission rate by studying the effect of atmospheric composition on trace gas emission. The dimensionless collision integral (Ω_{ij}) has been tabulated by Hirschfelder et al. (1964) as a function of reduced temperature T_{ij} (= $\kappa T/\varepsilon_{ij}$). Both the arithmic mean of the collision diameters for species *i* and *j* (σ_{ij}) and ε_{ij}/κ are obtained from empirical combining laws (Eq. (2) and (3), Leffelaar, 1987).

$$\sigma_{ij} = \frac{(\sigma_{ii} + \sigma_{jj})}{2} \tag{2}$$

$$\frac{\epsilon_{ij}}{\kappa} = [(\frac{\epsilon_{ii}}{\kappa})(\frac{\epsilon_{jj}}{\kappa})]^{1/2} \tag{3}$$

where ε_{ii}, = Lennard-Jones potential parameter; maximum energy of attraction occurring between molecules of component *i* (J)
κ = Boltzmann constant; 1.3805×10^{-23} ($J.K^{-1}$)

Table 7.1 gives the force constants necessary for calculating the binary diffusion coefficient for CH_4 in several other gasses. Using Eq. (1) through (3) and the data from Table 7.1 the binary diffusion coefficients for CH_4 in air, N_2, O_2, CO_2 and He are calculated (Table 7.2).

When applied to CH_4 transport via the rice aerenchyma the binary diffusion coefficients have to be used with caution. If its concentration inside the plant or root aerenchyma would be high, CH_4 would no longer qualify as a trace gas. In that case the Fickian diffusion coefficient D_{FCH4} no longer equals the binary diffusion coefficient D_{CH4j}, but would also depend on the gas mole fraction of CH_4 in the aerenchyma, Y_{CH4}, and on the gas flux ratio f_{jCH4} (Jaynes and Rogowski, 1983):

$$D_{F_{CH_4}} = \frac{D_{CH_4j}}{1-(1-f_{jCH_4})Y_{CH_4}} \tag{4}$$

However, up to partial pressures of 10% CH_4 in the aerenchyma (Y_{CH4}= 0.1) and with $0 \leq f_{jCH4} \leq 2$ the deviation of the diffusion coefficient for CH_4 D_{FCH4}, is within 10% of trace gas values ($0.91 D_{CH4j} \leq D_{FCH4} \leq 1.11 D_{CH4j}$).

Table 7.1 Force constants for calculating binary diffusion coefficients for CH_4 in other gasses according to Eq. (1) through (3) derived from tables in Hirschfelder et al. (1964).

Gas	CH_4	Air	N_2	O_2	CO_2	He
σ_{ii} ($\times 10^{10}$ m)	3.822	3.617	3.681	3.433	3.966	2.567
ε_{ii}/κ (K)	137	97	91.5	113	190	10.22
$\Omega_{CH4}j$ (T=30 °C)	–	0.986	0.978	1.008	1.10	0.77

Table 7.2 Binary diffusion coefficients for CH_4 calculated with Eq. (1) through (3) and the experimental CH_4 fluxes relative to the flux under air derived from Figure 7.4.

Gas pair	Binary diffusion coefficient ($D_{CH4\,j}$ x 10^5 $m^2.s^{-1}$)	$D_{CH4\,j}/D_{CH4\,air}$ (x 100%)	Experimental CH_4 flux relative to air (Figure 7.4)
CH_4-Air	2.27	100	99
CH_4-N_2	2.26	99	120
CH_4-O_2	2.29	101	ND
CH_4-CO_2	1.72	76	76
CH_4-He	7.04	310	302

Furthermore the ratios of the binary diffusion coefficients will all be influenced by Y_{CH4} in the same way. Therefore, by comparing the ratios of the experimental results for two different headspaces, interference of Y_{CH4} can be avoided. So, the hypothesis that the plant-mediated CH_4 flux is driven by diffusion can be tested by comparing the ratio of CH_4 fluxes at different bulk gas compositions with the ratio of the respective relevant binary diffusion coefficients.

Materials and methods

Maahas clay soil from the IRRI research farm (Block C) in The Philippines was air-dried and sieved. Plastic 5 liter pots were filled with 2.5 kg of soil mixed with 0.27 g urea, equivalent to 100 kg $N.ha^{-1}$. Half of the pots received 6.25 g chopped straw per pot, equivalent to 5 $tons.ha^{-1}$. The soil in the pots was mixed and puddled. The next day, two seedlings (11 days old, variety IR 72) were transplanted into each pot. After transplanting the pots were placed in the greenhouse and a constant floodwater layer of 5 cm was maintained. Approximately 65 days after transplanting the stems of the rice plants were cut approx. 5 cm above the floodwater. Cutting the plants presumably does not influence plant-mediated CH_4 emission (Seiler et al., 1984), but has several advantages; 1) The covers can be smaller making the experimental set-up simpler and the CH_4 detection limit lower because of volume reduction. 2) Photosynthesis is strongly reduced or stopped and does not influence the gas composition of the headspace. 3) The total distance from atmosphere via the leafs, stems and roots to the rhizosphere is reduced, creating a quicker response to headspace composition changes. The assumption that cutting the plants does not influence emission was tested in a separate pilot experiment prior to the main experiment. In the pilot experiment methane emission of rice plants before and approx. 1 hour after cutting the stems above the floodwater was measured.

After cutting, the pots used in the main experiment were moved to a building next to the greenhouse with dim light and with relatively small diurnal temperature variations. A part of the floodwater was removed and a styrofoam disk (⌀ = inner diameter of the pot) with holes for the stems was placed over the plants and pushed into the pot. The space between stems or rim of the pot and the styrofoam was sealed off with vacuum grease, so that gas transport between soil and atmosphere could take place only via the stems and roots of the rice plants.

The emitted CH_4 was trapped under a cover resting on a water-filled support ring that formed a gas-tight seal separating the inner atmosphere from the outside. The cover was equipped with a small 12 V DC fan to ensure good mixing of the gas phase, and with two septa for sampling or flushing the headspace (Figure 7.1). With a 5 ml disposable syringe 3 ml gas samples were taken from the headspace. The samples were injected immediately into a 2 ml sample loop connected to a gaschromatograph equipped with a Flame Ionization Detector (FID, N_2 as carrier gas, column oven temperature 45 °C). The CH_4 flux was calculated with linear regression from the increase of the CH_4 concentration in the headspace over time. For each flux calculation the headspace was sampled 5 times with an interval of 5-10 minutes. The r^2 of the linear regressions is typically > 0.95.

The CH_4 flux was measured at 9:00 on the six days following cutting of the stems. On day 1 and 5 the CH_4 flux was measured every 2 or 3 hours. The pots where temporarily moved on day 5 to a different part of the building where diurnal temperature fluctuations are higher to check for temperature effects on CH_4 emission.

On day 2, 3, 4 and 6, immediately after the flux measurement at 9:00, the headspace composition was changed from air to He, next to CO_2, to N_2 and again to He. The gases were flushed in through septum 1, while a needle through septum 2 connected to a tubing hanging into a beaker with a small layer of water acted as an outlet. To test the efficiency of gas renewal in the system, the headspace was spiked with a high concentration of CH_4. After 45 minutes more than 98.5% of the CH_4 originally present in the headspace was removed. During the main experiments flushing was continued for 1.5 hours before the CH_4 flux was measured at the new headspace composition. The measurements on days 1,2,3,4 and 6 were performed under the same conditions in terms of temperature and light intensity.

The change from air to N_2, CO_2 or He includes a change from an aerobic to an anaerobic system, which might affect the CH_4 source strength by depressing oxidation of CH_4 in the rhizosphere. Therefore a separate experiment was performed consisting

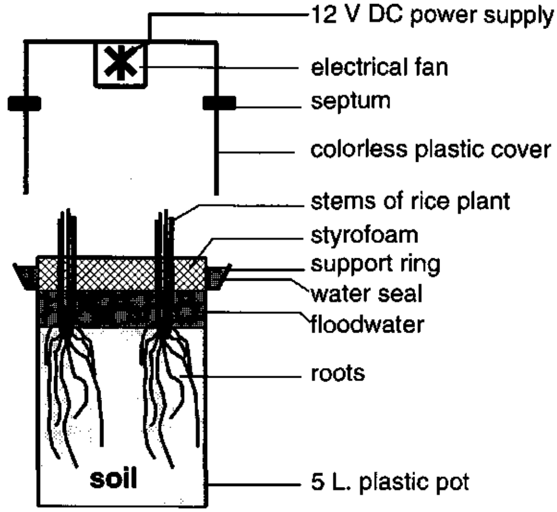

Figure 7.1 Experimental set-up for measuring methane emissions.

of a CH_4 flux measurement at the end of a 15 hour pre-incubation with an N_2 headspace followed by CH_4 flux measurement after flushing with CO_2 for 1.5 and 5 hours.

Results and Discussion

The pilot experiment revealed no significant differences in the amount of CH_4 emitted by cut and intact plants, both at high and low levels of emission (Table 7.3). This confirms the results by Seiler et al. (1984) and shows that cut plants are useful proxis for intact plants in studying factors that determine CH_4 emissions from rice fields. Emission of CH_4 is not influenced by cutting the stems above the floodwater because plant-mediated gas transport between soil and atmosphere is independent of transpiration rate or stomatal opening (Lee et al., 1981; Seiler et al., 1984) and takes place mostly via micropores in the leaf sheaths (Nouchi et al., 1990). All further results refer to measurements on cut plants.

Figure 7.2 shows that the CH_4 emission from cut plants gradually decreased with time over six consecutive days to about 70 % of the initial value. To compare the effect of changes in headspace composition on CH_4 emission over a prolonged period, this gradual decrease has to be taken into account. Therefore, the CH_4 emissions fluxes into a headspace with a specific gaseous composition, that were measured

Table 7.3 Methane emission before and after cutting the stems above the floodwater for 6 pots planted with rice plants, 1 month after transplanting.

Pot nr.	Straw addition (g)	CH_4 emission[b] ($nmol.s^{-1}.plant^{-1}$)	
		Intact	Cut
1-3	0	0.243	0.228
4-6	6.25[a]	1.840	2.495

[a]chopped straw, equivalent to 5 $tons.ha^{-1}$.
[b]A one sided *t*-test indicated no significant difference at the 95% level between CH_4 emission of intact versus cut plants.

on a certain day at 11:00 a.m., will always be expressed as a percentage of the CH_4 emission into the same headspace with air, measured at 9:00 a.m. of the same day. This approach carries the risk that emission differences caused by other factors are included. For instance, CH_4 emissions from cut plants into a headspace of constant composition, show a distinct diurnal pattern, with highest emissions around 14:00 (Figure 7.3). Similar fluctuations have been observed with intact plants (Schütz et al., 1989; Schütz et al., 1990). Because (1) the diurnal pattern in CH_4 emission parallels that in temperature, and (2) the greatest amplitudes in both CH_4 emission and temperature were observed in the same day (viz. on day 5, Figure 7.3), temperature is probably the factor driving the diurnal fluctuation in CH_4 emission. Because the experiments were not thermostated, potential effects of temperature will have to be considered when comparing CH_4 fluxes measured at different times during the day.

Figure 7.4 shows that replacing air in the headspace by He tripled the CH_4 flux. The effect of He on the relative increase in CH_4 emission was the same on day 2 as on day 6, even though absolute fluxes were lower (by about 30 %) on day 6 (Figure 7.2). Replacing air by N_2 increased the CH_4 flux by 20 %, while replacement of air by CO_2 decreased that flux by 24 %. Because the difference in temperature between 9:00 (emission into air) and 11:00 (emission into headspace with variant composition) was too small to markedly affect the CH_4 emission (see Figure 7.3, left panel), no attempt will be made to correct for temperature effects in this experiment.

The ratios of the CH_4 fluxes into He or CO_2 relative to those into air are very close to the ratios of the corresponding diffusion coefficients (Table 7.2).

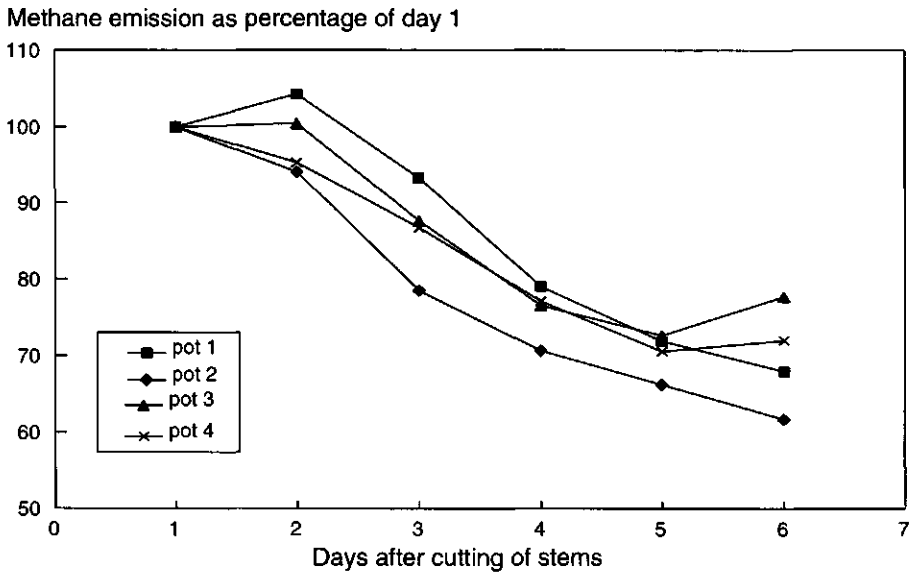

Figure 7.2 Plant-mediated methane emission from planted pots measured at 9:00.

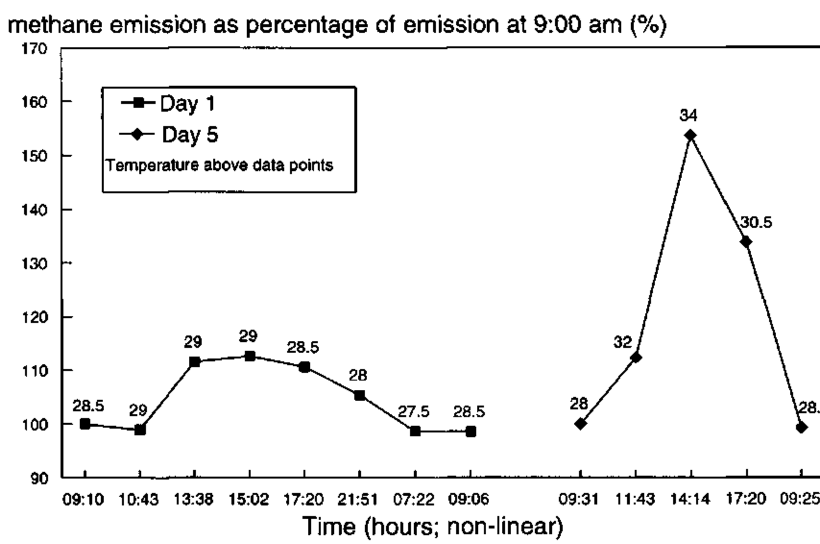

Figure 7.3 Diurnal emision pattern from pots with cut plants (Average of 4 pots, air temperature above data point).

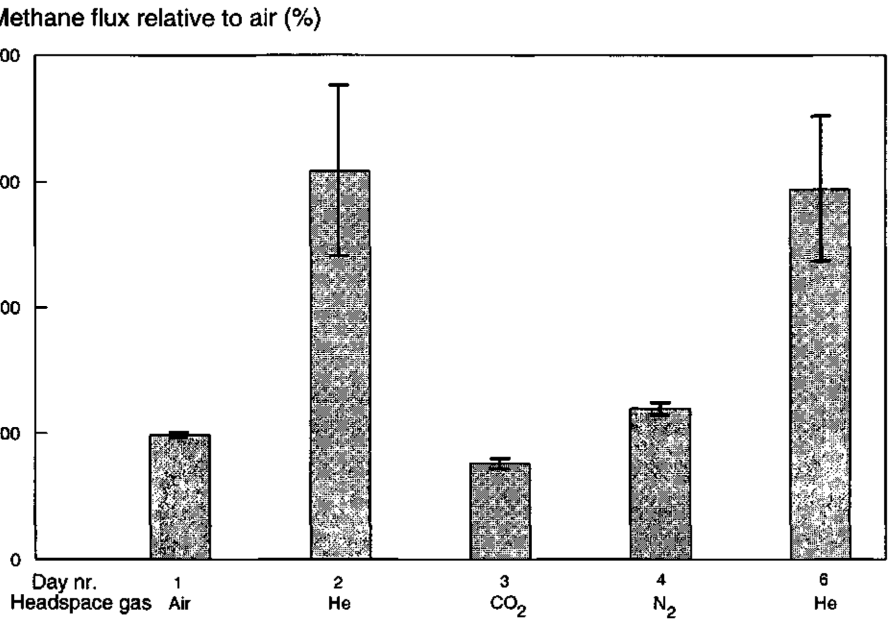

Figure 7.4 Mean methane flux from 4 pots with cut plants at 11:00 on successive days. Flux expressed as percentage of flux under air headspace at 9:00 of each day. Error bars indicate positive and negative standard deviation.

This strongly suggests that, on the time scale of the experiments, CH_4 transport is driven mainly by molecular diffusion. However, CH_4 fluxes into an N_2 atmosphere, were about 20 % higher than expected on the basis of diffusion only, indicating that additional factors are involved.

Two processes in addition to diffusion should be considered. First, by changing the headspace composition from air to any of the other gases considered, the supply of O_2 to the rhizosphere is stopped. Due to respiration of roots and microorganisms the rhizosphere would then become anaerobic. This would suppress CH_4 oxidation by the large number of methane oxidizing bacteria normally present in the rhizosphere (de Bont et al., 1978) and possibly stimulate methanogenic activity in the immediate surroundings of the former oxic rhizosphere. Thus the CH_4 source strength would increase. Methane emission from rice cultures increased by more than 242% after incubation under N_2 for 15-24 hours (Holzapfel-Pschorn et al., 1986) illustrating that a shift from aerobic to anaerobic condition increases CH_4 emission. The 20% higher CH_4 flux after 2 hours of N_2 relative to air may be explained by O_2 depletion, depressing CH_4 oxidation and/or stimulating CH_4 production in the rhizosphere.

Table 7.4 Average CH_4 flux from six planted pots in CO_2 relative to the flux in N_2 headspace composition, after correction for diurnal variation.

Exposure to CO_2 (hr)	T (°C)	Correction factor[a]	Average CH_4 flux (%)[b]
1.5	32	1.20	58 (8)
5	30	1.15	54 (6)

[a] correction factor based on temperature and Figure 7.3.
[b]Relative flux is first calculated per pot than averaged, standard deviation in brackets.

The relatively low increase in CH_4 emission is probably due to the short duration of the N_2 incubation.

Second, changing the gas composition would lead to a shift in equilibrium between gaseous and dissolved gases in the rhizosphere. Increased dissolution of a gas in the soil solution around the rhizosphere would cause mass flow of that gas from the headspace into the plant. Downward mass flow would, in turn, suppress emission of CH_4. This effect should be particularly important in case of the soluble gas CO_2 (1.713 $l.l^{-1}$ H_2O, Weast (1974)): the partial pressure of CO_2 would increase from 0.05-0.2 bar (Ponnamperuma, 1972) to almost 1 bar, and much less so for N_2 (shift from about 0.8 to almost 1 bar and low solubility in water; 0.0233 $l.l^{-1}$ H_2O, Weast (1974)). The relative increase in partial pressure would be largest for He but, in view of its low solubility in water (0.0105 $l.l^{-1}$ H_2O, Weast (1974)), the associated mass flow and its depression effect on CH_4 emission would be small. The expected difference between the effects of CO_2 and N_2 on CH_4 emission was confirmed by a second experiment where a change of headspace composition is not accompanied by a change in aerobic/anaerobic status of the system. To compare the different emission levels the flux for each pot was expressed relative to its flux under N_2 and then averaged for all pots (Table 7.4). Although emission levels varied among the pots the response to a change from N_2 to CO_2 headspace composition was similar. The CH_4 flux measured at 13:05 and 16:00 under CO_2 headspace is influenced by the diurnal variation in the CH_4 emission (as in Figure 7.3). Based on the temperature variation of 2 °C and Figure 7.3 it was estimated that, under otherwise unchanged conditions, the flux at 13:05 and 16:00 would be respectively 120% and 115% of the flux at 9:40. This estimate is used for correcting the measured fluxes (Table 7.4). The change from N_2 to CO_2 resulted in a quick reduction of the CH_4 flux by 35-40%. The flux did not significantly change if the exposure to CO_2 was continued. This reduction is 10-15 % lower than expected on the basis of diffusion alone. The additional reduction can be explained by downward mass flow of CO_2. Mass flow of air to the submerged parts of rice plants driven by solubilization of CO_2 was previously observed by following changes in headspace volume of a leaf chamber (Raskin and Kende, 1985). Mass flow can also be induced by temperature or barometric fluctuations but it is unlikely that this will be of any great significance in the overall plant-mediated gas transport process (Armstrong, 1979). Mass flow of gas to the submerged parts of the plants would be especially important for O_2 transport to the roots but may also play a role by reducing the upward diffusive CH_4 flux. In such a case CH_4 has to diffuse against the downward flow of gas.

That a change from air to CO_2 headspace composition did not show the additional flux reduction due to downward mass flow (Table 7.2) can be explained if the flux reduction due to mass flow was balanced by the enhanced CH_4 flux resulting from a shift from aerobic to anaerobic conditions. Indeed, the decrease in CH_4 flux due to downward mass flow of CO_2 is in the same order of magnitude as the increase in CH_4 flux from changing air to N_2. Figure 7.5 presents a schematic overview of the processes influencing the plant-mediated CH_4 emission as a function of the change in headspace gas explaining all our observations and which is in accordance with the findings of Jensen et al. (1967); Lee et al. (1981) and Raskin and Kende (1985).

The quick reaction of the CH_4 emission to a change of headspace (at least within 1.5 hours) indicates a limiting step for diffusive transport close to the atmosphere. A possible source of internal diffusive resistance is the root/shoot junction. Experiments assessing total pore space resistance prior and after excision of the root/shoot junction indicated that the effective porosity across the junction is low compared to that in roots, stems or leaves (Armstrong, 1979). That the root/shoot junction acts as a barrier for gas transport is further supported by; 1) Cutting the stems did not influence the emission rate proving that the rate limiting step in plant-mediated CH_4 transport is not located in the cut-off part of the plants. 2) The observation that the transport rate of ethylene from the rooting medium via the rice plant to the atmosphere was not proportional to the partial pressure of ethylene in the rooting medium (Lee et al., 1981). Lee et al.'s (1981) finding appears to be in conflict with diffusive transport since diffusion is driven by a concentration gradient. However, the concentration in the root aerenchyma of the dissolved gases present in the rooting medium may become so high that changes in partial pressure outside the roots do not significantly influence the concentration in the root aerenchyma. Then the concentration gradient across the root/shoot junction is no longer influenced by increasing partial pressures in the rooting medium and diffusive transport across the junction would not increase.

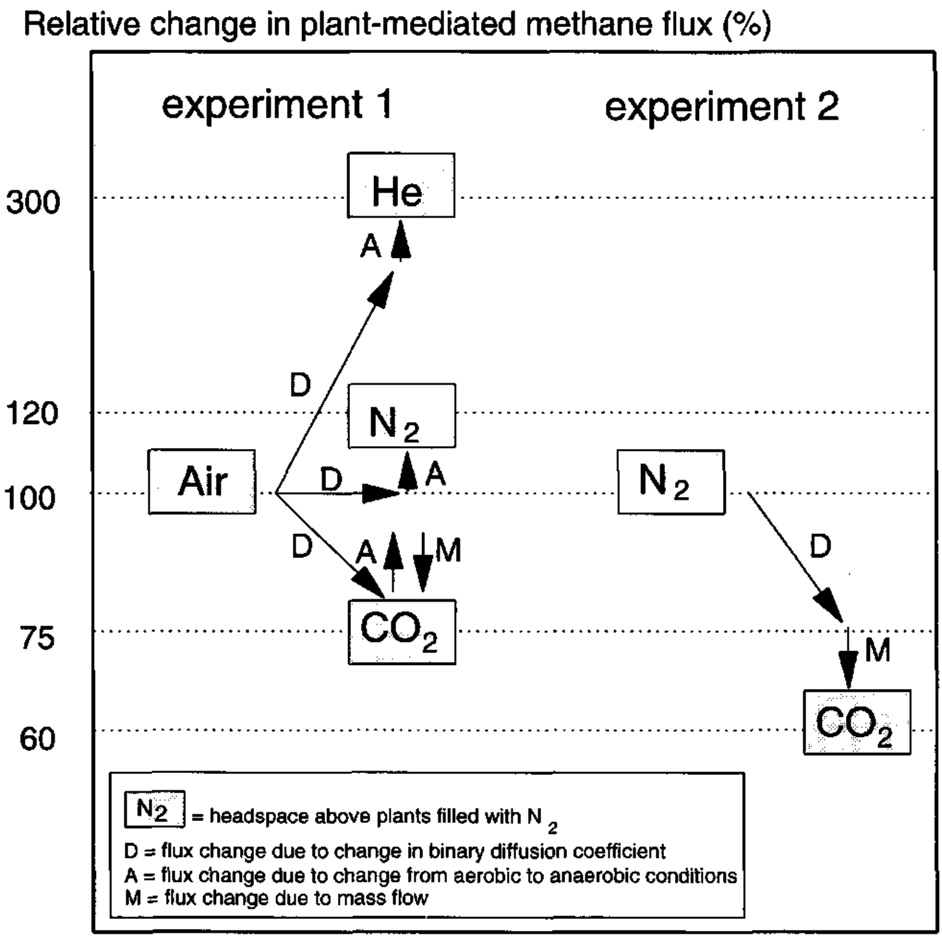

Figure 7.5 Schematic model indicating the changes in plant-mediated methane flux induced by various processes, when changing the headspace gas from air to He, N_2 or CO_2 (experiment 1), or from N_2 to CO_2 (experiment 2).

Diurnal variation patterns of methane emissions from rice fields differ substantially among locations e.g. Italy (Schütz et al., 1989) and China (Wang et al., 1990). The combination of mass flow and diffusion in rice plants is part of the processes necessary to come to a mechanistic understanding of methane emissions from rice fields.

Conclusions

The response of the plant-mediated CH_4 flux to a headspace with a variable gas composition corresponds with the change in binary diffusion coefficients of CH_4 in these headspace compositions. Deviations from this pattern can be explained qualitatively by increased CH_4 emission due to decreased CH_4 oxidation and/or enhanced CH_4 production in the rhizosphere when replacing air by an anaerobic gas, and by downward mass flow of the bulk gas if that would dissolve to an appreciable extent in the soil solution (CO_2). The results indicate that diffusion is the rate limiting step in plant-mediated CH_4 transport to the atmosphere. Therefore in a field situation factors that enhance diffusion rates will enhance CH_4 emission (e.g. temperature increase, concentration gradient). The results in combination with literature data suggest that, as soon as the partial pressure of CH_4 in the rhizosphere reaches a threshold value, diffusion across the root/shoot junction becomes the rate limiting step in plant-mediated CH_4 transport.

Acknowledgments The experiments were performed during a stay of the first author as research fellow at the International Rice Research Institute (IRRI). We would like to thank dr. H.-U. Neue, R.S. Lantin and M.C.R. Alberto of the dept. of Soil and Water Sciences (IRRI) for supplying facilities and indispensable support. 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.

References

Armstrong, W., Aeration in higher plants, in: Adv. Bot. Res. vol. 7, edited by H.W. Woolhouse, pp 225-332, Academic Press, London, 1979.

Bont, J.A.M. de, K.K. Lee, and D.F. Bouldin, Bacterial oxidation of methane in a rice paddy, in: Environmental role of nitrogen-fixing blue-green algae and asymbiotic bacteria, Ecological Bulletin, Stockholm, 26, pp. 91-96 , 1978.

Bouwman, A.F. (Editor), Soils and the greenhouse effect, Wiley, Chichester, U.K , 1990.

Cicerone, R.J., and R.S. Oremland, Biogeochemical aspects of atmospheric methane, Global Biogeochem. Cycles, 2, 299-327, 1988.

Hirschfelder, J.O., C.F. Curtiss, and R.B. Bird, Molecular theory of gases and liquids, Wiley, New York, 1964.

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

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

Jaynes, D.B., and A.S. Rogowski, Applicability of Fick's law to gas diffusion, Soil Sci. Soc. Am. J., 47, 425-430, 1983.

Jensen, C.R., L.H. Stolzy, and J. Letey, Tracer studies of oxygen diffusion through roots of barley, corn and rice, Soil Sci., 103, 23-29, 1967.

Lee, K.K., R.W. Holst, I. Watanabe, and A. App, Gas Transport through Rice. Soil Sci. Plant Nutr, 27, 151-158, 1981.

Leffelaar, P.A., Dynamic simulation of multinary diffusion problems related to soils, Soil Sci., 143, 43-55, 1987.

Nouchi, I, S. Mariko, and K. Aoki, Mechanism of Methane Transport from the Rhizosphere to the Atmosphere through Rice Plants, Plant Physiol., 94, 59-66, 1990.

Ponnamperuma, F.N., The chemistry of submerged soils, Adv. Agr., 24, 29-96, 1972.

Raskin, I., and H. Kende, Mechanism of Aeration in Rice, Science, 228, 327-329, 1985.

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

Schütz, H., W. Seiler, and R. Conrad, Influence of soil temperature on methane emissions from rice paddy fields, Biogeochemistry, 11, 77-95, 1990.

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

Wang, M.-X., A. Dai, R.-X. Shen, H.-B. Wu, H. Schütz, H. Rennenberg, and W. Seiler, CH_4 emission from a Chinese rice paddy field, Acta Meteorologica Sinica, 4, 265-275, 1990.

Wang, W.C., Y.L. Yung, A.A. Lacis, T. Mo, and J.E. Hansen, Greenhouse effects due to man-made perturbations of trace gases, Science, 194, 685-690, 1976.

Weast, R.C. (Editor), Handbook of Chemistry and Physics, 55th edition, CRC press, Cleveland, Ohio, 1974.

Chapter 8

Oxidation of Methane in the Rhizosphere of Rice Plants

H.A.C. Denier van der Gon and H.-U. Neue

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Oxidation of methane in the rhizosphere of rice plants

Abstract

Oxidation of CH_4 in the rhizosphere of rice plants was quantified using (1) methyl fluoride, a specific inhibitor of CH_4 oxidation, and (2) measuring changes in plant-mediated CH_4 emission after incubation under air, N_2, or 40% O_2. No significant rhizospheric CH_4 oxidation was observed from rice plants in the ripening stage. CH_4 emission from rice plants 1 week before panicle initiation increased by 40% if CH_4 oxidation in the rhizosphere was blocked. The growth stage of the rice plant is an important factor determining the rhizospheric CH_4 oxidation. Fluctuation of rhizospheric CH_4 oxidation during the growing season may help to explain the observed seasonal CH_4 emission patterns in field studies. Measurements from four rice varieties showed that one variety, Pokkali, had higher rhizospheric CH_4 oxidation. This was probably because Pokkali was in an earlier growth stage than the other three varieties. Both in the early *and in the late growth stages, incubation under N_2 caused a much stronger CH_4 flux than* inhibition of CH_4 oxidation alone. Apparently, N_2 incubation not only blocked CH_4 oxidation but also stimulated methanogenesis in the rhizosphere. Incubation under a higher O_2 atmosphere (40% O_2) than ambient air decreased the CH_4 flux, suggesting that increasing the oxidation of the rice rhizosphere may help in reducing CH_4 fluxes from rice agriculture. The O_2 pressure in the rhizosphere is an important factor that reduces the plant-mediated CH_4 flux. However, inhibition of methanogenesis in the rhizosphere may contribute more to CH_4 flux reduction than rhizospheric CH_4 oxidation.

Introduction

CH_4 is an important greenhouse gas and a key factor in tropospheric and stratospheric chemistry (Wang et al., 1976; IPCC, 1992). Wetland rice fields are an important source of CH_4, accounting for approximately 20% of the global anthropogenic methane emission (IPCC, 1992). CH_4 is produced by strictly anaerobic bacteria that are common in anoxic soils such as wetland rice fields (Cicerone and Oremland, 1988). CH_4 emission from a rice field is the net effect of CH_4 production (methanogenesis) and CH_4 oxidation (methanotrophy). Methanotrophs are obligate aerobes because the enzyme monooxygenase, responsible for the oxidation of CH_4 to CH_3OH, requires molecular O_2 (Bedard and Knowles, 1989; King, 1992; Knowles, 1993). Therefore, methanotrophs occur and are active close to oxic-anoxic interfaces where the concentration gradients of CH_4 and O_2 overlap.

In rice fields oxic-anoxic interfaces are found at the floodwater-soil interface and in the rice rhizosphere. The rice plant relies on aerobic respiration for growth and transports atmospheric O_2 to its roots to survive in the anaerobic environment (Armstrong, 1978). Oxidation of the rice rhizosphere is caused partly by enzymatic oxidation but mostly by radial O_2 loss through the root wall (Ando et al., 1983). Hereby a very thin oxidized layer forms around the rice roots, creating a habitat for aerobic a very thin oxidized layer forms around the rice roots, creating a habitat for aerobic microorganisms, like methanotrophs, in an otherwise anoxic soil environment. Methanotrophy can be an important sink for CH_4 produced in anaerobic soils (King, 1992). Unfortunately, investigations of methanotrophy in ecosystems have been hampered by the lack of a specific inhibitor that inhibits CH_4 oxidation only and has no inhibitory effect on other processes such as methanogenesis (Bedard and Knowles, 1989). Therefore, CH_4 oxidation was often estimated as CH_4 production minus CH_4 emission (Schütz et al., 1989; Sass et al., 1990; Conrad and Rothfuss, 1991; Denier van der Gon and Neue, 1995b).

A large number of CH_4-oxidizing bacteria is present in the rhizosphere, indicating a high potential for CH_4 oxidation (de Bont et al., 1978). But C_2H_2 (an inhibitor of CH_4 oxidation) did not increase plant-mediated emission of CH_4, suggesting little or no CH_4 oxidation in the rhizosphere (de Bont et al., 1978). However, C_2H_2 inhibits not only oxidation (de Bont and Mulder, 1976), but also the production of CH_4, at least at higher concentrations (Oremland and Taylor, 1975; Sprott et al., 1982). Recently, Oremland and Culbertson (1992a, b) reported that CH_3F and dimethyl ether are specific inhibitors of methanotrophs, although dimethyl ether was a less effective inhibitor than CH_3F. The use of CH_3F as a specific inhibitor allows a direct quantification of methanotrophy in ecological systems and the ambiguities in indirect assessments of methane oxidation can be avoided. Using CH_3F, Oremland and Culbertson (1992a) showed that methanotrophs at the soil-water interface can consume more than 90% of the potentially available CH_4. This confirmed estimates for CH_4 oxidation, obtained by indirect assessments, at the soil-water interface of wetlands (King, 1990; King et al., 1990) and rice fields (Conrad and Rothfuss, 1991; Denier van der Gon and Neue, 1995b).

Preliminary experiments with rice plants, using CH_3F, showed that between 10 and 47% of the potential CH_4 flux was oxidized in the rhizosphere (Epp and Chanton, 1993). Increasing CH_4 oxidation in the rhizosphere could be a potential mitigation option that may reduce the CH_4 source strength of paddy fields without affecting rice yields. The objective of the present work was to investigate the significance of CH_4-oxidizing activity in the rice rhizosphere by using CH_3F as a specific inhibitor of CH_4 oxidation. To investigate whether the CH_4-oxidizing activity in the rhizosphere is limited by O_2 availability, CH_4 emission was measured from plants incubated under variable O_2 concentrations.

Materials and methods

Maahas clay soil from the International Rice Research Institute (IRRI) research farm with 2.5 kg air-dried, ground soil mixed thoroughly with 0.27 g urea, equivalent to 100 kg N ha^{-1}. The pots were flooded and puddled by hand. The next day, two 2-week-old seedlings, rice variety IR 72 unless otherwise stated, were transplanted in each pot. IR 72 was also used in several studies that monitored CH_4 emission from rice fields (Denier van der Gon and Neue, 1994; Wassmann et al., 1994; Denier van der Gon and Neue , 1995a, b). The pots were placed in the greenhouse and a floodwater layer of about 5 cm was maintained.

CH_4 emission rates from the planted pots were measured with closed chambers as described by Denier van der Gon and van Breemen (1993). Before a CH_4 flux measurement, the stems of the rice plants were cut 5 cm above the floodwater. Earlier experiments revealed no significant differences in the CH_4 emitted by cut and intact plants, both at high and low levels of emission (Denier van der Gon and van Breemen, 1993). The CH_4 flux into a headspace with normal air was measured. Next, the pots were separated into different batches, each batch with a different headspace composition. The headspace compositions studied comprised: air, air with 1.5% CH_3F, air with 3% CH_3F, 100% N_2, and air with 40% O_2. Throughout each experiment, the batch with air in the headspace served as the control treatment. At the end of each experiment the tiller number, root length, dry weight of panicles, aboveground biomass, and belowground biomass were measured for each pot.

CH_4 flux measurements

After an incubation, five headspace samples were collected with 5-10 min intervals. The gas samples were injected immediately into a 2-ml sample loop connected to a gas chromatograph equipped with a flame ionization detector, N_2 as carrier gas, and a column oven temperature of 45 °C. The CH_4 flux was calculated by a linear regression from the increase in the CH_4 concentration in the headspace over time. The r^2 of the linear regressions is typically > 0.95. Each flux measurement was repeated at least once. Modification of the system used in this study, compared to the set-up described by Denier van der Gon and van Breemen (1993), was that the floodwater layer was not separated from the headspace. The plant-mediated CH_4 flux was differentiated from the flux through the floodwater layer by additional measurements with a 140-ml glass beaker placed upside down over the stems of the rice-plant hill with the rim of the beaker submerged in the floodwater. Thus emission via the stems of the rice plant into the headspace was blocked and only CH_4 emission via the floodwater was measured.

Methyl fluoride treatments

Epp and Chanton (1993) reported that for measurements on rhizospheric CH_4 oxidation, one 16 to 18-h incubation period with a 1.5% CH_3F chamber headspace concentration was sufficient to inhibit CH_4 oxidation, without significantly affecting methanogenesis. In the present work we adopted their methodology. After measuring the CH_4 flux under air, the headspace of the closed chambers was spiked with 80 or 160 ml pure (99+%) CH_3F (Scott Specialty Gases) to obtain about 1.5 or 3% (vol/vol) CH_3F in the headspace, respectively. After incubation the CH_3F concentration in the headspace was measured to check whether it remained constant. CH_3F was measured on the same gas chromatograph with a flame ionization detector as CH_4. Standards of CH_3F in air were made by injecting pure CH_3F into glass bottles with a known volume to obtain 0, 1, and 5% (vol/vol) CH_3F. After 15 h of incubation, the average CH_3F concentration in the headspace above the planted pots was 1.4% (± 0.1) and 2.9% (± 0.2) CH_3F for the 1.5 or 3% CH_3F treatment, respectively. This indicates that the closed chambers were gastight and that the CH_3F concentration remained high enough for inhibition of methanotrophy throughout the incubation period. After an incubation of 16 h the closed chambers were removed and the pots were allowed to equilibrate for 1-3 h. Next, the CH_4 flux was measured as described above. We did not observe a significant difference in CH_4 flux after incubation with 1.5 or 3% CH_3F (data not shown), in line with Oremland and Culbertson (1992b) and Epp and Chanton (1993). Therefore, all other experiments with CH_3F treatments reported in this paper were performed with 1.5% (vol/vol) CH_3F.

N_2 and 40% O_2 treatments

The headspace of the closed chambers was flushed for about 1.5 h with either N_2 or 40% O_2 (balance 60% N_2) at a high rate. Earlier experiments had shown that flushing for 1.5 h is sufficient to change the headspace composition for > 99% (Denier van der Gon and van Breemen, 1993). The atmosphere inside the cover was kept at a small over-pressure throughout the incubation period, causing a slow continuous escape of bubbles from the water seal separating inner and outer atmosphere, to ensure a fixed headspace composition. After 15 h the flushing rate was increased for 1 h to remove any accumulated CH_4. Next, the flushing was stopped and the CH_4 flux was measured as described below. One hour later the headspace was flushed again with 100% N_2 or 40% O_2 to remove trapped CH_4 and refresh the headspace gas composition, and a second CH_4 flux was measured.

A number of experiments were performed using the techniques described above.

Experiment 1: CH_4 oxidation in the rice rhizosphere at ripening stage
Seventeen pots prepared as described above were planted with IR 72. Because a limited number of closed chambers was available the seventeen pots were divided in to a group of eleven pots and a group of six pots. The plants from the eleven pots were cut 65 days after transplanting (ripening stage). The CH_4 fluxes from each pot were measured, 0, 18, 24, and 47 h after cutting, under an air headspace. Next, three of the pots were incubated under N_2, four pots under 40% O_2,and four pots under air. The CH_4 fluxes were measured after 19 and 26 h of incubation. In between, after 23 h of incubation, CH_4 emission via the floodwater only was measured. The plants of the remaining six pots were cut 5 days later and CH_4 fluxes were measured 0, 4, and 6 h after cutting the plants. Next, half the pots were incubated under air, the other half under 1.5% CH_3F. CH_4 fluxes were measured after incubation as described above.

Experiment 2: Measurements in the field
CH_4 emissions from rice fields have a distinct diurnal pattern (Schütz et al., 1989; Denier van der Gon and Neue, 1994; 1995a) which complicates any interpretation of the impact of headspace incubations on CH_4 emissions. To reduce the influence of diurnal variation in CH_4 emission, fluxes measured at a particular time of day are compared only with fluxes measured at exactly the same time the next day. Six hills of IR 72 were cut at harvest stage, about 100 days after transplanting. A closed chamber as used to measure the CH_4 flux from planted pots (Denier van der Gon and van Breemen, 1993) was placed over each hill. CH_4 fluxes were measured at 1130 and 1500 h. Next, three hills were incubated under air with 1.5% CH_3F, while the remaining three were incubated under air. The incubation was stopped after 16 h and the chambers were removed. After 3 h of equilibration, the CH_4 fluxes were measured at 1130 and 1500 h.

Experiment 3: Varietal differences
Three pots each, prepared as described above, were planted with rice variety IR 72, IR 65597, Pokkali, or Dular. The stems of the rice plants were cut 65 days after transplanting. The CH_4 flux from the pots was measured 0, 3 and 5 h after cutting. Next, the pots were incubated under air with 1.5% CH_3F and the CH_4 fluxes were measured the next day (see above). After two flux measurements, the pots were incubated under N_2 (as described under N_2 treatments) for 20 h and the CH_4 flux was measured twice.

Experiment 4: CH_4 oxidation in the rice rhizosphere before panicle initiation
About 30 days after transplanting (1-2 weeks before panicle initiation) 12 rice plants (IR 72) were collected in the field by using a 5-liter pot with a cut-out bottom and a sharpened edge as a corer. The soil core with the rice plant was immediately transferred to a pot and placed in the greenhouse. After 1 week the plants were cut, and the CH_4 fluxes were measured 0 and 4 h after cutting under an air atmosphere. In between, 2 h after cutting, CH_4 emitted through the floodwater only was measured by excluding plant-mediated CH_4 emission. Next, four pots each were incubated under 40% O_2, 1.5% CH_3F, and air for 16-18 h. After equilibration for 2 h, two CH_4 fluxes (each based on five headspace samples over time) were measured. Next, the pots that had been incubated under CH_3F were now incubated for 20 h under 100% N_2 while the remaining eight pots were incubated under air, and two CH_4 fluxes (each based on five headspace samples over time) were measured after the incubation.

Results

Plant-mediated CH_4 emission
CH_4 transport directly through the floodwater layer, either diffusive or by ebullition, contributed less than 10% to the total CH_4 flux, irrespective of the incubation gas or age of the rice plants (data not shown). So, plant-mediated transport consistently contributed over 90% (average 95%) to the total CH_4 emission from the pots. Therefore, changes in CH_4 emission upon incubation with different gases can be attributed to changes in the plant-mediated CH_4 emission. Keeping a control set of plants under air headspace throughout the experiment proved a useful approach which facilitated interpretation.

Experiment 1: CH_4 oxidation in the rhizosphere of IR 72 in ripening stage
Although all pots were prepared in the same manner, the CH_4 emissions from the pots differed by a factor of 3-4 (Table 8.1). No correlation between the number of tillers or plant biomass and the rate of CH_4 emission was found. The variation shows how variable CH_4 emission may be, even under apparently similar conditions. With this large variation in CH_4 fluxes it was not possible to compare the mean CH_4 emissions per treatment and attribute different flux rates to different treatments. However, the CH_4 emission level per pot varied little with time, as can be seen from the standard deviation in Table 8.1. For comparison, CH_4 fluxes of each pot are scaled by setting the first measured CH_4 flux under air for each pot at 100%. CH_4 emissions of seven pots from Table 8.1 are plotted relative to the first measurement under air for each pot

Table 8.1 Experiment 1: CH_4 flux into air from planted pots measured 0, 18, 25, and 47 h after cutting and some plant parameters. CH_4 flux is expressed as means (SD) and biomass as dry weight.

Pot	CH_4 flux ($\mu g\ CH_4.pot^{-1}.hr^{-1}$)	Tillers	Above ground biomass (g)	Below ground biomass (g)	Root length (cm)
1	72.2 (6.1)	29	90.5	20.3	42.0
2	169.7 (19.5)	28	88.1	23.7	51.5
3	151.0 (9.4)	27	88.6	17.5	42.3
4	234.2 (27.2)	25	85.4	14.4	34.1
5	199.9 (47.8)	27	90.7	16.2	46.5
6	78.8 (3.6)	27	90.4	16.0	35.4
7	209.5 (51.6)	28	85.5	21.1	33.1
8	310.3 (34.3)	26	88.5	11.6	37.3
9	252.5 (27.3)	30	89.6	19.3	44.2
10	82.6 (5.2)	29	101.2	19.2	44.4
11	148.6 (22.0)	26	95.2	14.5	38.6

on the right half of Figure 8.1. After incubation under N_2 for 19 h, the CH_4 emission was strongly stimulated, to about 210% of the first flux measurement (Figure 8.1a). The relative effect of N_2 was the same despite the large differences in absolute emission levels, indicating that the scaling procedure is useful. The CH_4 emission from the control pots under air increased over time to about 125% (Figure 8.1b). The flux increase after N_2 incubation has to be corrected for this "baseline drift" to give the impact of N_2 incubation only. Figure 8.2 shows the impact of incubation under various gases scaled to the CH_4 flux measurement under air and corrected for a drift in the CH_4 flux over time as derived from the control measurement under air. The standard deviation for each treatment, represented by the error bars, indicates the uniformity of the relative fluxes of different pots with the same headspace composition. Adding 1.5% CH_3F did not alter the CH_4 flux. Incubation under N_2 or 40% O_2 resulted in a CH_4 flux of about 190 or 80% of the CH_4 flux under air, respectively.

Experiment 2: Measurements in the field

For comparison, the CH_4 fluxes were scaled in the same way as in Figure 8.2. The CH_4 emission from rice plants at harvest stage in the field did not significantly increase upon incubation under 1.5% CH_3F (Figure 8.3). This suggests little or no CH_4 oxidation in the rhizosphere, confirming the result of the pot experiment (experiment 1).

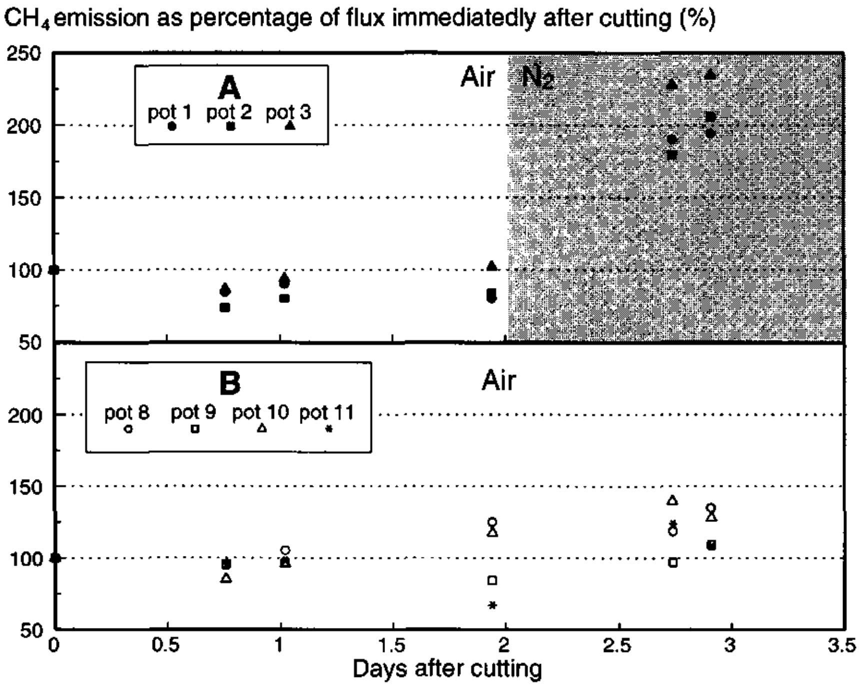

Figure 8.1 Experiment 1: CH_4 flux from pots with rice plants (ripening stage) in the first 3 days after cutting the stems, expressed as a percentage of the initial CH_4 flux under air. Pot numbers refer to those given in Table 8.1. Pots 1-3 were under air and N_2 (a) and pots 8-11 under air as the control (b).

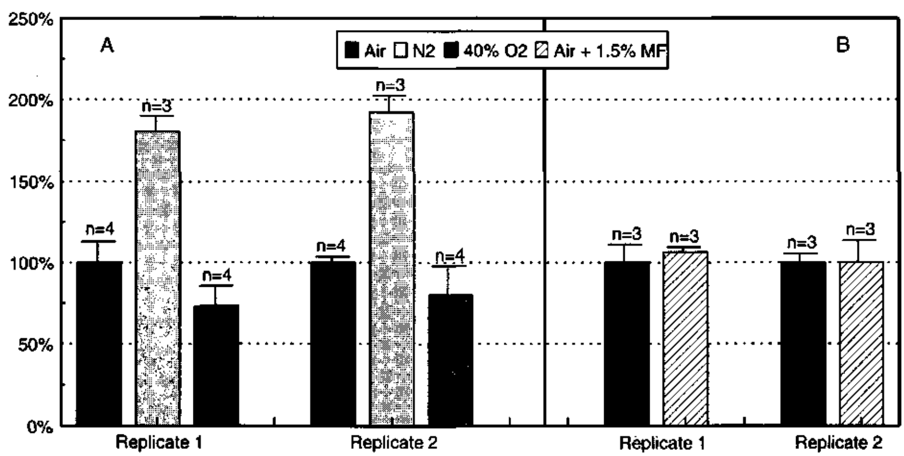

Figure 8.2 Experiment 1: CH_4 flux from pots with rice plants (ripening stage) under air, N_2, 40% O_2, or 1.5% CH_3F (*MF*) relative to the previous CH_4 flux under air, corrected for changes in emissions from the control measurements. *Error bars* indicate standard deviation.

Experiment 3: Varietal differences

CH_4 emission 65 days after transplanting was much higher from IR 72 and IR 65597 than from Pokkali or Dular (Table 8.2). Other differences included the high tiller number of IR 72, the high biomass of Pokkali, and the long roots of Dular plants. Furthermore, Pokkali had not yet flowered whereas the other three varieties had already panicles. The results cannot be scaled as in Figures 8.2 and 8.3, because the number of closed chambers available did not allow control measurements under air headspace. The CH_4 flux from Pokkali increased by 37% under 1.5% CH_3F, whereas fluxes from the other varieties did not change significantly (Table 8.3). The results for IR 72 under 1.5% CH_3F were in line with the observations in the previous experiments, where a control measurement under air was available. Therefore, we assume that the 37% flux increase from Pokkali plants is representative for the amount of CH_4 consumed by CH_4 oxidation in the rhizosphere of Pokkali. Under N_2, the flux from Pokkali increased by 50% and the flux from IR 72, IR 65597 and Dular increased by about 10%. This 10% flux increase after incubation under N_2 was small compared to the twofold flux increase observed in the previous experiment. However, since control flux measurements under air were not available we cannot exclude the possibility that other factors influenced the CH_4 emission as well.

Table 8.2 Experiment 3: Average CH_4 emission, tiller number, panicle weight, biomass, and root length per pot of pots planted with two seedlings each, about 70 days after transplanting. Values are expressed as means (SD), n = 3. Panicle weight and biomass represent dry weights. Aboveground biomass includes panicle weight. No panicles had developed for the Pokkali variety and those for the IR varieties were not fully developed.

Rice variety	CH_4 emission ($\mu g.pot^{-1}.hr^{-1}$)	Tiller nr.	Panicle weight ($g.pot^{-1}$)	Above ground biomass ($g.pot^{-1}$)	Below ground biomass ($g.pot^{-1}$)	Root length (cm)
IR 72	483 (45)	33 (2)	17 (2)	89 (2)	19 (2)	37 (1)
IR 65597	375 (35)	19 (2)	8 (0.2)	61 (2)	20 (4)	36 (1)
Pokkali	84 (45)	19 (1)	-	107 (9)	31 (1)	37 (3)
Dular	44 (17)	20 (3)	21 (2)	97 (4)	19 (3)	46 (1)

Table 8.3 Experiment 3: Relative change (SD) in CH_4 flux for four rice varieties upon incubation under 1.5% CH_3F or N_2 compared to previous measurements under air.

Variety	Relative change in CH_4 flux (%)		CH_4 flux relative to IR 72 (%)	
	1.5% CH_3F	N_2	1.5% CH_3F	N_2
IR 72	-1 (1)	+9 (3)	100	100
IR 65597	-2 (2)	+9 (3)	99	100
Pokkali	+37 (5)	+50 (8)	134	134
Dular	+4 (1)	+11 (7)	101	99

Experiment 4: CH_4 oxidation in the rice rhizosphere before panicle initiation

The variation in CH_4 emission levels of IR 72 about 1 week before panicle initiation was similar to that of plants in the ripening stage. Again, CH_4 emission from various pots differed by a factor of about 4, but the emission level of each individual pot varied little with time (data not shown). The observed CH_4 fluxes from the planted pots after different incubations were scaled in the same way as those shown in Figures 8.2 and 8.3. CH_4 emission from rice plants under 1.5% CH_3F increased to 140% of the CH_4 flux under air (Figure 8.4, left). Next, the plants previously treated with 1.5% CH_3F were incubated under N_2. The CH_4 flux increased from 140 to about 190% of the flux under air (Figure 8.4, right). So, on top of the 40% flux increase due to blocking of CH_4 oxidation, the CH_4 flux increased by another 50% due to stimulation of methanogenesis. The flux reduction under 40% O_2 (Figure 8.4, 100% → 77%) was similar to that observed for plants in the ripening stage (Figure 8.2). On the second day, when the plants previously incubated under 40% O_2 were incubated again under air, the CH_4 flux fully recovered to about 100%.

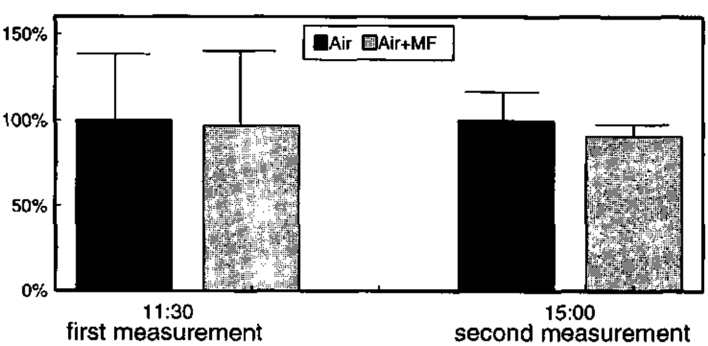

Figure 8.3 Experiment 2: CH_4 flux from plants in the field under air or 1.5% CH_3F (*MF*) relative to the previous CH_4 flux under air, corrected for changes in emissions from the control measurements under air. *Error bars* indicate standard deviation (*n*=3).

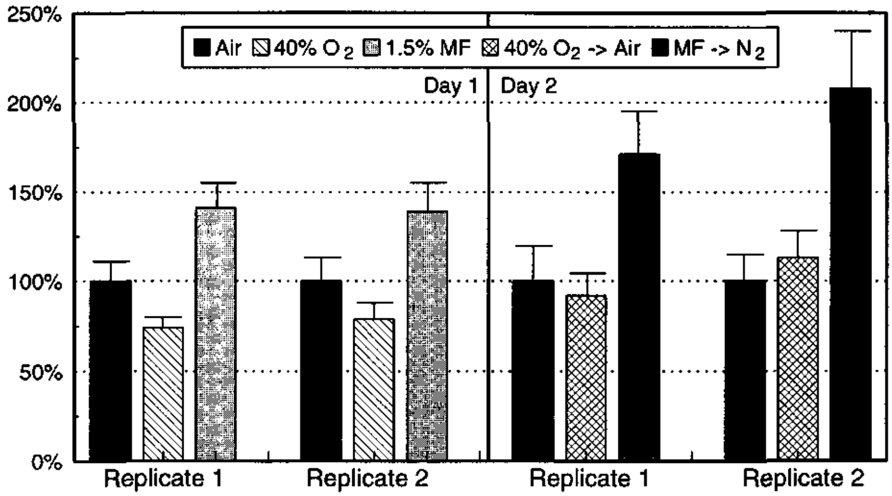

Figure 8.4 Experiment 4: CH_4 flux from pots with rice plants about 1 week before panicle initiation, under air, 40% O_2, or 1.5% CH_3F (*MF*) (*day 1*) and under air or N_2 (*day 2*) relative to the previous CH_4 flux under air, corrected for changes in emissions from the control measurements under air. *Error bars* indicate standard deviation (n=4).

Discussion

Emission of CH_4 is not influenced by cutting the stems above the floodwater because plant-mediated gas transport between soil and atmosphere is independent of the transpiration rate or stomatal opening (Lee et al., 1981; Seiler et al., 1984) and takes place mostly via micropores in the leaf sheaths (Nouchi et al., 1990). Cutting the plants has several advantages: (1) the covers can be smaller, making the experimental set-up simpler and the CH_4 detection limit lower because of volume reduction; (2) photosynthesis is strongly reduced or stopped, and does not influence the gas composition of the headspace; and (3) the total distance from the atmosphere via the leaves, stems, and roots to the rhizosphere is reduced, creating a quicker response to headspace composition changes. A more detailed discussion on measurements with cut plants compared to intact plants has been presented previously (Denier van der Gon and van Breemen, 1993). CH_4 transport from the soil to the atmosphere through rice plants is driven by diffusion (Denier van der Gon and van Breemen, 1993). The headspace compositions used in our experiments do not alter the rate of CH_4 diffusion. Therefore, changes in plant-mediated CH_4 emission rates can only be invoked by changes in the concentration gradient between rhizosphere and atmosphere. If the CH_4 concentration in the rhizosphere increases because CH_4 oxidation is inhibited or methanogenesis is stimulated, the CH_4 flux from rhizosphere to atmosphere will increase.

The doubling of the CH_4 flux under N_2 (Figure 8.2; Experiment 1) cannot be attributed to decreased or blocked methanotrophy because the 1.5% CH_3F incubation indicated that no significant CH_4 oxidation occurred. So, the increased CH_4 flux from plants in the ripening phase under N_2 must be due to increased methanogenesis. Indeed, Kimura et al. (1991) showed that CH_4 was produced from substances released by rice roots. This suggests that methanogenesis close to the oxic-anoxic rhizosphere interface is an important component of total plant-mediated CH_4 emission and that if CH_4 production is measured by incubating rhizosphere soil samples under N_2 this could lead to an overestimate because the inhibition of methanogenesis in the oxidized parts of the rhizosphere is no longer present.

Rhizospheric CH_4 oxidation in rice plants appears to be less effective than in some other wetland plants such as *S. lancifolia* and *P. cordata* (Epp and Chanton, 1993). In IR 72 rhizospheric CH_4 oxidation was of minor importance at the end of the growing season (Experiments 1 and 2). This is in line with de Bont et al. (1978) who found that C_2H_2 had no effect of acetylene on the rate of CH_4 emission from rice plants in the ripening stage. Epp and Chanton (1993) reported that the CH_4 oxidation in the rhizosphere of 3-month-old rice plants was 14-52% of the potential CH_4 flux, or (recalculated) 116-208% of the original flux under air. Although Epp and Chanton's (1993) results are not fully comparable with our results and those by de Bont et al. (1978) because they did not have a control set of plants under air they indicate that at the end of the growing season rhizospheric CH_4 oxidation is not always negligible.

Blocking rhizospheric CH_4 oxidation increased the plant-mediated CH_4 flux by 40% in IR 72 just before panicle initiation (Experiment 4) or in Pokkali before flowering (Experiment 3). Rhizospheric CH_4 oxidation apparently varies with the growth stage of the rice plant. This may be related to the observation that oxidizing activity of rice roots varies with the growth stage (Armstrong, 1969). Growth stage dependence of rhizospheric CH_4 oxidation may help explain why at tillering and especially at ripening larger fractions of the produced CH_4 were emitted from rice fields than at panicle initiation (Denier van der Gon and Neue, 1995a). Clearly, the relationship between the growth stage of rice and the CH_4 oxidation in its rhizosphere should be the subject of further study.

Schütz et al. (1989), using CH_4 production minus CH_4 emission to estimate CH_4 oxidation, reported that at the end of the growing season only 6% of the total produced CH_4 was emitted and over 90% of the total produced CH_4 was oxidized (implying that the CH_4 flux should increase ~17-fold after incubation with CH_3F). Similar high oxidation rates were reported in other studies that assessed CH_4 oxidation indirectly (Holzapfel-Pschorn et al., 1986; Frenzel et al., 1992). Rhizospheric CH_4 oxidation quantified with the "CH_4 production minus CH_4 emission" approach may be overestimated because *in-situ* methanogenesis is probably overestimated by the anaerobic incubation of soil samples in the laboratory. This can be illustrated by re-evaluating the results of Holzapfel-Pschorn et al. (1986). These authors measured the CH_4 flux from a microcosm with rice plants incubated under air, air with 5% C_2H_2, and N_2. The CH_4 flux under 5% C_2H_2 and N_2 was 136 and 342% of the flux under air, respectively. The flux increase upon N_2 incubation compared reasonably well with their indirect assessment of CH_4 oxidation (CH_4 production minus CH_4 emission) in the field but the 5% C_2H_2 incubation indicated a much lower CH_4 oxidation rate. The large difference between N_2 and 5% C_2H_2 incubation was not discussed by Holzapfel-Pschorn et al. (1986). However, the much larger flux increase under N_2 than under 1.5% CH_3F in our experiments shows that most of the increase under an N_2 atmosphere is due to increased methanogenesis, not to blocked CH_4 oxidation. The CH_4 flux increase observed after incubation with 5% C_2H_2 by Holzapfel-Pschorn et al. (1986) is similar to CH_4 flux increases under 1.5% CH_3F observed in our experiments and by Epp and Chanton (1993). This suggests that in the experiments of Holzapfel-Pschorn et al. (1986) the CH_4 flux increase under 5% C_2H_2 was a better estimate of rhizospheric CH_4 oxidation than the incubation under N_2. The high CH_4 oxidation efficiency reported for intact soil columns from rice fields (Conrad and Rothfuss, 1991; Denier van der Gon and Neue, 1995b) are representative for the soil-water interface but not for the rhizosphere soil. The four varieties screened in Experiment 3 represent different plant types. IR 72 is representative of the successful, high-tillering, high-yielding varieties. IR 65597, the so-called new plant type, is a more recent development in plant breeding, with fewer tillers but more filled panicles. Pokkali is a tall, salt tolerant, long duration variety from India, both Dular and Pokkali are traditional varieties. Dular and Pokkali emitted very little CH_4 compared to both IR varieties. However, a thorough comparison of the amount of CH_4 emitted by different varieties was not possible because (1) the measurements did not cover the full growing season and (2) during the experiment the varieties were in different growth stages. Remarkably, first results with the same varieties in a field experiment, where CH_4 emission was continuously monitored, indicate exactly the opposite trend with higher emissions from Dular and Pokkali (H.-U. Neue, unpublished data, 1995). Possibly the larger root biomass of Pokkali and the deeper rooting of Dular (Table 8.4) result in higher CH_4 fluxes under field conditions because the roots are not confined to the limited amount of soil in a pot. However, no good explanation is available at present and more research on variety-specific CH_4 emission is required.

To compare the varieties, the measurements were scaled with the response of IR 72 upon different incubations as 100% (Table 8.3). IR 72, IR 65597, or Dular responded in the same way to changing headspace compositions. Pokkali behaved differently, with a 34% increasing CH_4 flux under 1.5% CH_3F or N_2. Clearly, CH_4 oxidation was a more important CH_4 sink in the rhizosphere of Pokkali plants than in the rhizosphere of IR 72, IR 65597, and Dular plants. When the impact of blocking CH_4 oxidation with CH_3F was subtracted from the flux increase for Pokkali under N_2, the relative CH_4 flux increase for Pokkali was equal to that of IR 72, IR 65597, and Dular. So, the stimulation of methanogenesis by N_2 was equal for all four varieties. Although the higher CH_4 oxidation in the rhizosphere of Pokkali may be a varietal trait, it is more likely related to the growth stage. All varieties were planted on the same day but at the time of the experiments Pokkali was behind in physiological development and had not flowered (Table 8.4). CH_4 oxidation efficiency in young IR 72 plants (experiment 4, Figure 8.4) was similar to that in the Pokkali plants.

The CH_4 flux decrease after incubation under 40% O_2 indicates that increased oxidation of the rhizosphere may be a promising mitigation option. The recovery of the CH_4 flux to its original value when the plants were incubated under air again shows that the CH_4 flux decrease under 40% O_2 is reversible. The relatively fast recovery suggests that changes in microbial activity rather than death and/or new growth of microbes causes the changes in CH_4 emission. Since the variability in root-oxidizing power among rice cultivars is high (Armstrong, 1969; Ando et al., 1983) it may be possible to breed high-yielding varieties with high root-oxidizing power. The most important mechanism behind CH_4 emission reduction due to a more highly oxidized rhizosphere could well be increased inhibition of methanogenesis in the rhizosphere instead of increased CH_4 oxidation in the rhizosphere.

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References

Ando, T., S. Yoshida, and I. Nishiyama, Nature of oxidizing power of rice plants, Plant and Soil, 72, 57-71, 1983.

Armstrong, W., Rhizosphere oxidation in rice: An analysis of intervarietal differences in oxygen flux from the roots, Physiol. Plan., 22, 296-303, 1969.

Armstrong, W., Root aeration in the wetland condition, in: Plant life in anaerobic environments, edited by D.D. Hook and R.M.M. Crawford, Ann Arbor Science, Ann Arbor, Mich., 1978.

Bedard, C., and R. Knowles, Physiology, biochemistry and specific inhibitors of CH_4, NH_4 and CO oxidation by methanotrophs and nitrifiers, Microbial. Rev., 53, 68-84, 1989.

de Bont, J.A.M., and E.G. Mulder, Invalidity of the acetylene reduction assay in alkane-utilizing, nitrogen-fixing bacteria, Appl. Environ. Microbiol., 31, 640-647, 1976.

de Bont, J.A.M., K.K. Lee, and D.F. Bouldin, Bacterial oxidation of methane in a rice paddy, Ecol. Bull., Stockholm, 26, 91-96, 1978.

Cicerone, R.J., and R.S. Oremland, Biogeochemical aspects of atmospheric methane, Global Biogeochem. Cycles, 2, 299-327, 1988.

Cicerone, R.J., and J.D. Shetter, Sources of atmospheric methane: Measurements in rice paddies and a discussion, J. Geophys. Res., 86, 7203-7209, 1981.

Conrad, R., and F. Rothfuss, Methane oxidation in the soil surface layer of a flooded rice field and the effect of ammonium, Biol. Fertil. Soils, 12, 28-32, 1991.

Denier van der Gon, H.A.C., and N. van Breemen, Diffusion-controlled transport of methane from soil to atmosphere as mediated by rice plants, Biogeochemistry, 21, 177-190, 1993.

Denier van der Gon, H.A.C., and H.U. Neue, Impact of gypsum application on the methane emission from a wetland rice field, Global Biogeochem. Cycles, 8, 127-134, 1994.

Denier van der Gon, H.A.C., and H.U. Neue, Influence of organic matter incorporation on the methane emission from a wetland rice field, Global Biogeochem. Cycles, 9, 11-22, 1995a.

Denier van der Gon, H.A.C., and H.U. Neue, Methane emission from a wetland rice field as affected by salinity, Plant and Soil, 170, 307-313, 1995b.

Epp, M.A., and J.P. Chanton, Rhizospheric methane oxidation determined via the methyl fluoride inhibition technique, J. Geophys. Res., 98, 18413-18422, 1993.

Frenzel, P., F. Rothfuss, and R. Conrad, Oxygen profiles, methane turnover in a flooded rice microcosm, Biol. Fertil. Soils, 14, 84-89, 1992.

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

IPCC Climat change: Supplementary report to the IPCC scientific assessment, Cambridge University Press, Cambridge, 1992.

Kimura, M., H. Murakami, and H. Wada, CO_2, H_2, and CH_4 production in rice rhizosphere, Soil Sci. Plant Nutr., 37, 55-60, 1991.

King, G.M., Dynamics and controls of methane oxidation in a Danish wetland sediment, FEMS Microbiol. Ecol., 74, 309-324, 1990.

King, G.M., Ecological aspects of methane oxidation, a key determinant of global methane dynamics, Adv. Microbial. Ecol., 12, 431-468, 1992.

King, G.M., P. Roslev, and H. Skovgaard, Distribution and rate of methane oxidation in sediments of the Florida Everglades, Appl. Environ. Microbiol., 56, 2902-2911, 1990.

Knowles, R., Methane:Processes of production and consumption, in: Agricultural ecosystem effects on trace gases and global climate change, Am. Soc. Agron. Spec. Publ., 55, pp 145-155, 1993.

Lee, K.K., R.W. Holst, I. Watanabe, and A. App, Gas transport through rice, Soil Sci. Plant Nutr., 27, 151-158, 1981.

Nouchi, I., S. Mariko, and K. Aoki, Mechanism of methane transport from the rhizosphere to the atmosphere through rice plants, Plant Physiol., 94, 59-66, 1990.

Oremland, R.S., and C.W. Culbertson, Importance of methane-oxidizing bacteria in the methane budget as revealed by the use of a specific inhibitor, Nature, 356, 421-423, 1992a.

Oremland, R.S., and C.W. Culbertson, Evaluation of methyl fluoride and dimethyl ether as inhibitors of aerobic methane oxidation, Appl. Environ. Microbiol., 58, 2983-2992, 1992b.

Oremland, R.S., and B.F. Taylor, Inhibition of methanogenesis in marine sediments by acetylene and ethylene: Validity of the acetylene reduction assay for anaerobic microcosms, Appl. Microbiol., 30, 707-709, 1975.

Sass, R.L., F.M. Fisher, P.A. Harcombe, and F.T. Turner, Methane production and emmision in a Texas rice field, Global Biogeochem. Cycles, 4, 47-68, 1990.

Schütz, H., W. Seiler, and R. Conrad, Processes involved in formation and emission of methane in rice paddies, Biogeochemistry, 7, 33-53, 1989.

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

Sprott, G.D., K.F. Jarrell, K.M. Shaw, and R. Knowles, Acetylene as an inhibitor of methanogenic bacteria, J. Gen. Microbiol., 128, 2453-2462, 1982.

Wang, W.C., Y.L. Yung, A.A. Lacis, T. Mo, and J.E. Hansen, Greenhouse effects due to man-made perturbations of trace gases, Science, 194, 685-690, 1976.

Wassmann, R., H.U. Neue, R.S. Lantin, J.B. Aduna, M.C.R. Alberto , M.J. Andales, M.J. Tan, H.A.C. Denier van der Gon, H. Hoffmann, and H. Papen, Temporal patterns of methane emissions from wetland rice fields treated by different modes of N-application, J. Geophys. Res., 99, 16457-16462, 1994.

Chapter 9

General Discussion

General discussion

Introduction

The first field measurements of methane emission from rice paddies were performed in the 1980s (Cicerone and Shetter, 1981; Cicerone et al., 1983; Seiler et al., 1984; Holzapfel-Pschorn and Seiler, 1986). The rice-soil-water ecosystem was treated as a black box and usually only the net CH_4 flux from the ecosystem to the atmosphere was measured. Estimates of the contribution of rice agriculture to the global methane budget based on these field studies replaced the previous estimates that were based on rice soil incubations by Koyama (1963). The field studies drastically lowered the estimate of the CH_4 source strength of rice paddies from 190-280 $Tg.yr^{-1}$ to about 50-150 $Tg.yr^{-1}$. The difference can be attributed to the fact that in the field part of the CH_4 produced is oxidized, while CH_4 oxidation was ignored by Koyama (1963). Studies on CH_4 flux measurements showed large diurnal, day-to-day, seasonal and annual variations in emissions due to (location specific) variables such as temperature, type of fertilizer, water management. The large variation in seasonal methane emissions from rice fields could not be explained by the available data thus causing a large uncertainty in the global estimates. In general, global estimates were obtained by averaging the observed seasonal emissions and multiplying with the harvested area of rice fields, sometimes including temperature coefficients to account for presumably higher emissions from tropical regions. Clearly, more detailed studies about underlying controlling processes of production and oxidation of CH_4 and variables that influence these processes were necessary. The first of such studies was published by Holzapfel-Pschorn et al. (1986) and Schütz et al. (1989a; 1989b). In the past years various research groups contributed to the fast increasing knowledge about the rice-soil-water ecosystem as a source of CH_4. The research described in this thesis is among the studies providing insight in mechanisms controlling CH_4 emission from rice fields and aims at elucidating the role of soil parameters. The ultimate objectives were (1) to improve the estimate of the global source strength of rice paddies and/or reduce the uncertainty in this estimate and, (2) insight in the mechanisms controlling CH_4 emission from rice paddies is essential to design mitigation strategies leading to reduced emissions. In this chapter factors influencing methane emission from rice fields are discussed, partly based on the work described in the previous chapters of this thesis but supplemented with relevant literature. Currently the CH_4 source strength of rice paddies is estimated at 60 ± 40 $Tg.yr^{-1}$ (IPCC, 1994), indicating that the uncertainty in this estimate still needs to be narrowed.

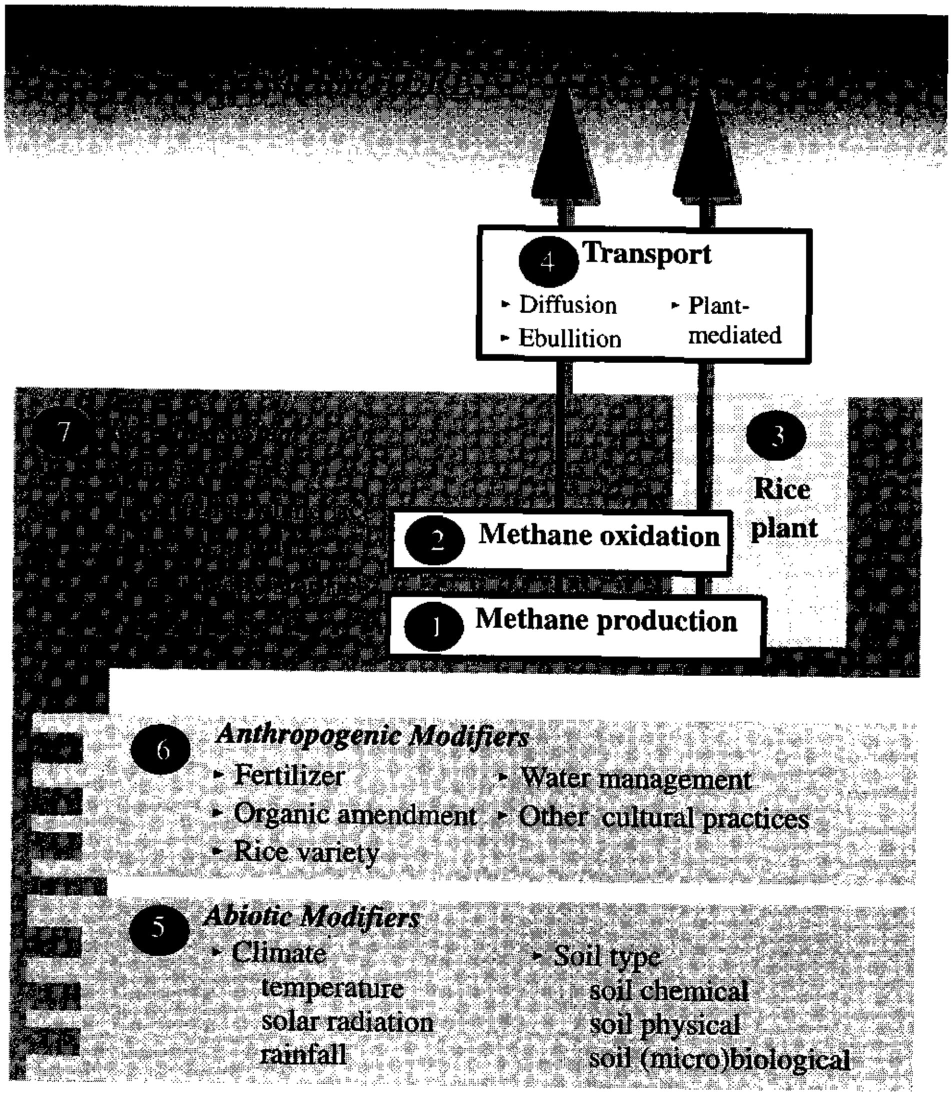

Figure 9.1 A schematic, conceptual representation of the process of methane emission from a wetland rice field and its modifiers.

Factors controlling methane emissions from wetland rice fields
Methane emission from wetland rice fields can be described by the formula "CH_4 Production minus CH_4 Oxidation equals CH_4 Emission", complemented by a transport factor and several process modifiers (Figure 9.1). The modifiers determine the location-specific CH_4 emission and include abiotic and human factors. The various components of the CH_4 emission process as represented by Figure 9.1 will be discussed in this chapter. There are a number of arbitrary choices in Figure 9.1 that require some motivation.

- CH_4 emission from a rice field can be measured and modelled on various time scales (diurnal, seasonal and annual), and at the different time scales different processes may come in to play. The modifier boxes A and B of Figure 9.1 contain variables that influence CH_4 emission throughout the growing season. However, the impact of the rice plant on CH_4 emission changes with its growth stage. To account for this more dynamic, temporal influence on the CH_4 emission process, the rice plant is placed outside the modifier boxes. The choice of a certain rice variety influences the CH_4 emission on each time scale and can therefore be placed in the anthropogenic modifier box.
- Fertilizer application, organic amendments and water management are all cultural practices but of such an overall importance for the actual CH_4 emission that they are represented separately.
- An additional modifier box, rice ecosystem, is added to figure 1 although this is conceptually incorrect because a rice ecosystem is defined by a combination of several abiotic and anthropogenic modifiers. However, information on the type of rice ecosystem is often available whereas it may be difficult to get information on the individual modifiers that define that location as a specific rice ecosystem. Knowledge on the type of rice ecosystem provides a shortcut in the data requirements for estimating CH_4 emission from a certain location and information on the harvested area for each rice ecosystem on a regional or country basis is available (IRRI, 1988; 1995). Thus it makes sense, from a practical point of view, to introduce rice ecosystem as a composed modifier.

1 Methane production (methanogenesis)
Methane is produced by strict anaerobic bacteria (methanogens). Anaerobic conditions occur in wetland rice fields as a result of soil submergence. Water saturation highly limits the transport of O_2 in to the soil and within a few hours after submergence, microbial activity renders a water saturated soil practically devoid of O_2. Next, microorganisms start using alternative electron acceptors in their respiration causing

further soil reduction. The redox potential drops sharply in a sequence predicted by thermodynamics, eventually leading to methanogenesis. The process of soil reduction tends to stabilizes the soil pH near neutral, which is optimal for methanogenesis (Oremland, 1988). The chemistry of flooded rice soils has been extensively reviewed, e.g., Ponnamperuma (1972), Patrick and Reddy (1978) and De Datta (1981). The biogeochemistry of methanogens and their substrate requirements have been reviewed by Oremland (1988). Methanogens can only grow on a limited number of simple compounds (H_2 plus CO_2, formate, acetate, methanol, and methylated amines). Therefore, the production of methanogenic substrates by other groups of microorganisms is an integral part of the process of methanogenesis as the terminal step in organic matter decomposition in a reduced environment. Conrad (1989) presents a general scheme of anaerobic methanogenic degradation which requires the cooperation of four types of bacteria within a substrate food chain: (a) hydrolytic and fermenting bacteria, (b) H^+-reducing bacteria, (c) homoacetogenic bacteria, and (d) methanogenic bacteria. In many studies on CH_4 emission from wetland rice fields the overall effect on net CH_4 emission is measured and usually no further investigations are done on the impact of variables on groups of bacteria participating in the complete substrate food chain. This approach helps to simplify concepts (or models) by bringing the required information on microbial processes back to two major processes, methanogenesis and methanotrophy (such as presented in Figure 9.1). However, one should bear in mind that this simplification, which is also used in this thesis, may in some cases lead to a misjudgment of the controlling process and a misinterpretation of the observed phenomena. Methanogenesis in a rice field is influenced by a number of abiotic and anthropogenic modifiers that will be discussed below in the section dedicated to each modifier. Underlying the impact of these modifiers are certain characteristics of methanogenic bacteria;

- Methanogens are strict anaerobes and very sensitive to low levels of oxygen (e.g., a few ppm), exposure to which causes death (Oremland, 1988).
- Presence (or addition) of alternate electron acceptors (e.g., nitrate, ferric iron, sulfate) inhibits methanogenesis in mixed microbial ecosystems by channelling electron flow to microorganisms that are thermodynamically more efficient than methanogens (Oremland, 1988; Conrad, 1989).
- Methanogens grow over the relatively narrow pH range of about 6-8 (Oremland, 1988).
- Like all microorganisms methanogens are temperature-sensitive.
- Methane production is substrate-limited, provided temperature and pH of the medium are not limiting.

2 Methane oxidation (methanotrophy)

Methanotrophs are obligate aerobes and require molecular O_2 (Bedard and Knowles, 1989; King, 1992; Knowles, 1993). Therefore, methanotrophs occur and are active close to oxic-anoxic interfaces where the concentration gradients of CH_4 and O_2 overlap. In rice fields such oxic-anoxic interfaces are found at the floodwater-soil interface and in the rice rhizosphere (see Chapter 8 for a more detailed description of these interfaces). Methanotrophy within the rice ecosystem is a major factor limiting the CH_4 flux from rice fields to the atmosphere. Methanotrophs at the soil-water interface of irrigated rice fields can consume more than 90% of the potentially available CH_4 (Conrad and Rothfuss, 1991; Denier van der Gon and Neue, 1995b; Chapter 4). An extensive review on the ecological aspects of biological methane oxidation is given by King (1992). Like methanogenesis, methanotrophy in a rice field is influenced by a number of abiotic and anthropogenic modifiers that will be discussed in the respective sections. Characteristics of methanogenic bacteria that may help to assess the influence of each modifier on methanotrophy are;

- Methanotrophs require both O_2 and CH_4 for growth.
- Aerobic microorganisms living in the rhizosphere and oxidizing organic substrates (e.g., root exudates, root litter) or inorganic compounds (e.g., NH_4^+) may compete with methanotrophs for the little O_2 available (Conrad, 1989).
- CH_4 oxidation may be (partly) inhibited by NH_3 and/or NH_4^+ (Dalton, 1977; Conrad and Rothfuss, 1991), elevated pH and/or presence of $CaCO_3$ (King, 1990; King et al., 1990; Chapter 2), and salinity (Denier van der Gon and Neue, 1995b; Chapter 3).

3 The rice plant

Paddy fields planted to rice emit more CH_4 than otherwise comparable unplanted paddy fields (Cicerone and Shetter, 1981; Holzapfel-Pschorn et al., 1986; Schütz et al., 1989a) The enhancement of CH_4 emission by the presence of rice plants is further confirmed by the observations that plots with one-third plant density of the control plot emitted about 25 % less CH_4 (Schütz et al., 1989a) and that spatial variability of methane production coincided with spatial distribution of roots in wetland rice fields (Sass et al., 1991). The rice plant relies on aerobic root respiration for growth. To that end it transports atmospheric O_2 to its roots through a well-developed system of air spaces (aerenchyma) (Armstrong, 1978). At the same time this system is an effective vent for the release of CH_4 from the soil to the atmosphere. However, radial oxygen loss through the root wall oxidizes the rice rhizosphere (Ando et al., 1983), creating a habitat for aerobic microorganisms, like methanotrophs, in an otherwise anoxic soi l environment. Summarizing the role of rice plants in CH_4 emission from rice fields we can say that; (1) rice plants provide substrate for methanogens in the form of exudates, roots, stubbles and remnants of the previous crop, (2) the aerenchyma system allows CH_4 transport from soil to atmosphere, and (3) the O_2 pressure in the rhizosphere is an important factor that reduces the potential plant-mediated CH_4 flux by allowing rhizospheric CH_4 oxidation and inhibiting methanogenesis in the rhizosphere.

The importance of these features of the rice plant depend on the growth stage of the rice plant. In the early growth stage (~ up to tillering) the rice plants and their root system are poorly developed, and plant-mediated gas transport, rhizospheric CH_4 oxidation and methanogenesis from root exudates and root littering are of minor importance. In that period, remnants of the previous crop are the most important substrate for methanogens. Rhizospheric CH_4 oxidation varies with the growth stage of the rice plant (Denier van der Gon and Neue, 1996b; Chapter 8) as does the oxidizing activity of rice roots (Armstrong, 1969). In the intermediate growth stages (tillering up to flowering) rhizospheric CH_4 oxidation appears to be highest. In rice varieties IR 26 and IR 72 rhizospheric CH_4 oxidation was of minor importance at the end of the growing season (de Bont et al., 1978; Denier van der Gon and Neue, 1996b; Chapter 8). In the intermediate (tillering up to flowering) and late growth stages (flowering to harvest), incubation of rice plants under an anoxic headspace (which blocks CH_4 oxidation in the rhizosphere by creating an anoxic rhizosphere) enhanced the CH_4 flux much stronger than blocking of CH_4 oxidation with a specific inhibitor, indicating that methanogenesis in or close to the rhizosphere is an important component of total plant-mediated CH_4 emission (Denier van der Gon and Neue, 1996b; Chapter 8). However, the source of methanogenic substrates may vary with the growth stage. Probably root exudates are an important substrate source in the medium growth stages while root litter is the major source in the late growth stages.

4 Transport of methane from soil to atmosphere

Methane is transported from the reduced zones in a rice field to the atmosphere by diffusion, ebullition or plant-mediated transport. These transport pathways have different characteristics, and their importance varies throughout the growing season (Table 9.1). The different pathways offer different opportunities for methanotrophy and the importance of a transport mechanism in the overall CH_4 transport to the atmosphere may be promoted by several modifiers (as will be discussed in the section on modifiers). The diffusive flux from the soil through the floodwater contributes very little to total CH_4 emission transport (e.g., less than 1% of the total seasonal emission

Table 9.1 Relative contribution of diffusion, ebullition and plant-mediated transport to CH_4 emission in an urea-fertilized Italian paddy field (adapted from Schütz et al., 1989b).

Approximate days after seed dissemination[a)]	Plant height (cm)	CH_4 emission ($ml.m^{-2}.h^{-1}$)	Percentage emitted via		
			Diffusion through soil and floodwater	Ebullition	Plant-mediated transport
25	5-10	11	7	93	0
54	50-60	24	1	51	48
76	60-80	40	< 1	10	90
103	60-80	33	< 1	2	97

[a)] no exact date of dissemination is given by Schütz et al. (1989b)

from an Italian rice paddy (Schütz et al., 1989b)). Ebullition and plant-mediated transport appear to be complementary; as the season progresses the importance of ebullition decreases from >90% to <10% and vice versa for plant-mediated transport (Table 9.1). When the rice plants are well established, plant-mediated transport is the main CH_4 transport mechanism. So, if methane production in the rice field is high early in the season, e.g., in organically amended fields (Denier van der Gon and Neue, 1995a; Chapter 5) the contribution of ebullition to total seasonal emission is significant but if there is little CH_4 production early in the season, ebullition contributes only 4-9% to total CH_4 emission (Schütz et al., 1989b; Denier van der Gon and Neue, 1995a; Chapter 5). Consequently, in unvegetated paddy soils CH_4 is emitted almost exclusively by ebullition (Holzapfel-Pschorn et al., 1986).

- Upward-diffusion of CH_4 from the reduced, flooded soil (high concentration) to the atmosphere (low concentration) is a rather slow process because all diffusion takes place through the water phase (~ 10^4 slower than diffusion through the gas phase). This allows methanotrophs in the soil-water interface to oxidize 70-90% of this diffusive flux of CH_4 to the atmosphere (Chapter 2; Chapter 4; Conrad and Rothfuss, 1991). In general, the contribution of diffusion through soil and floodwater to total CH_4 emission from a vegetated rice field is negligible (Table 9.1). Furthermore, the absolute amount of CH_4 transported by diffusion through soil and floodwater is rather constant throughout the season (Schütz et al., 1989b). Although theoretically the diffusive flux through soil and floodwater is dependent on the concentration gradient, enhanced CH_4 production in the rice paddy mainly results in more CH_4 transported by ebullition or plant-mediated transport and the relative contribution of diffusion through soil and floodwater decreases even further.

- During ebullition, gas bubbles traverse the oxic soil-water interface too rapidly for appreciable methanotrophic oxidation to take place. Therefore, practically all CH_4 produced that is transported by ebullition reaches the atmosphere. Thus an increase in CH_4 production in a part of the season where ebullition is the main transport mechanism causes a proportionally high increase of net CH_4 emission.
- Field experiments in the 1980s indicated that more than 90% of the total CH_4 emission over a season was due to plant-mediated transport, ebullition accounting for less than 10% (Cicerone and Shetter, 1981; Holzapfel-Pschorn et al., 1986; Schütz et al., 1989b). However, as discussed above, this ratio depends on the time of high CH_4 production in the rice paddy (Denier van der Gon and Neue, 1995a; Chapter 5). Plant-mediated CH_4 transport is driven by diffusion, just as the direct diffusive flux through the floodwater layer, (Denier van der Gon and van Breemen, 1993; Chapter 7). However, plant-mediated transport is mainly by diffusion through the gas phase of the aerenchyma system of the rice plant where the diffusion constant is ~10^4 higher than in the water saturated soil. Tracer studies showed that gas transport through the rice plant increased with plant age even after plant height and root weight had reached maximum values (Schütz et al., 1991). CH_4 transported via the plant to the atmosphere has to pass the root-soil interface to enter the aerenchyma system of the rice plant. In the oxidized parts of the rhizosphere CH_4 diffusing into the rice root may be subject to methanotrophy. The significance of CH_4 oxidizing activity in the rice rhizosphere is still under debate, but recent experiments indicate that up to 40% of the potential CH_4 flux can be oxidized in the rhizosphere (Epp and Chanton, 1993; Denier van der Gon and Neue, 1996b; Chapter 8). This is considerably lower than previous estimates based on indirect assessments which suggested that 50-90 % of the CH_4 transported through the rhizosphere in to the aerenchyma system of the rice plant was oxidized (e.g., Holzapfel-Pschorn et al., 1986; Schütz et al., 1989b; Frenzel et al., 1992).

5 Abiotic modifiers

Abiotic conditions like climate and soil type modify the CH_4 emission from rice fields but daily, monthly or seasonal CH_4 emissions at a specific location are rarely well-correlated with these abiotic modifiers. This lack of correlation is due to (1) the growing rice plant, which is the main factor controlling the seasonal emission pattern (Chapter 2), and (2) small seasonal variation in these modifiers (e.g., average daily temperature near the equator, soil type). By contrast, inter-location variation of these abiotic modifiers may be high and very relevant. The need to understand inter-location variation was illustrated by Denier van der Gon and Neue (1995a; Chapter 5) who showed that no clear relationship was found between organic amendments and CH_4 emission if data from various locations were combined although many individual studies had shown that CH_4 emission increased with increasing organic inputs.

Climate

Temperature The temperature of flooded rice soils at the time of planting may range from 15 °C in northern latitudes to 40 °C in equatorial wetlands (Neue and Roger, 1994). The formation of CH_4 and CO_2 in rice soils is positively correlated with temperature and the ratio of both products shifts towards CH_4 as temperature increases (Tsutsuki and Ponnamperuma, 1987). Methanogenic bacteria in rice fields are mesophyllic (temperature optimum 30-40 °C) but they depend on substrate supply by groups of bacteria which often have a lower temperature optimum (Conrad, 1989). Thus, the optimum temperature for CH_4 production in rice fields is a balance between temperature limitation and substrate limitation. Optimum temperature for CH_4 emission from a rice field is influenced by even more factors because CH_4 oxidation and possibly release of exudates by rice plants are also temperature dependent. The diurnal variation of CH_4 emission from rice fields is highly correlated with air and/or soil temperature fluctuation (Chapter 2). Review of temperature and CH_4 production/emission correlation are given by e.g., Conrad (1989), Neue and Roger (1994), and Neue and Sass (1994). Ebullition as a transport mechanism appears to be more sensitive to diurnal temperature fluctuations than plant-mediated transport which is reflected in stronger diurnal fluctuation early in the season than later in the season (Chapter 5).

Rainfall In rainfed rice, flooding of the field is often controlled by rainfall within the watershed. In such a case data on rainfall patterns and quantities may be key-information for predicting CH_4 emission from rice fields. A more detailed discussion is given in the section dealing with rice ecosystems.

Solar radiation Solar radiation is the source of energy for plant growth. It may play an important role in explaining regional variation because larger biomass results in enhanced CH_4 emission by increasing substrate availability and increasing plant-mediated gas transport. Solar radiation and temperature are often highly correlated and to separate their influence on CH_4 emission is difficult. A positive correlation between solar radiation and annual CH_4 emission as well as crop yield was reported for Texan rice fields (Sass et al., 1991; Sass and Fisher, 1994). In tropical regions this relationship appears to be less evident which may be, again, related to the smaller seasonal variations in temperature and solar radiation in the tropics. However, in periods with a climatic event, while other non-climate variables such as plant biomass remained constant a positive correlation between average daily CH_4 emission, maximum daily temperature and solar radiation was observed in Philippine paddy fields (Chapter 2).

Soil type

Soil properties strongly influence the physical and chemical environment in which methanogens, methanotrophs and rice plants alike have to grow. Anaerobic incubation of a range of rice soils revealed high variations in the potential of these soils to produce CH_4 (Denier van der Gon et al., 1992; Wang et al., 1993b). That CH_4 emissions from rice fields on different soil types do differ was observed in Japan (Yagi and Minami, 1990) and the USA (Sass et al., 1990; 1991). Variation in soil type is one of the major causes for variation in CH_4 emission from site to site. Naturally, the soil type on a specific location does not vary within experimental periods making it a somewhat hidden factor in studies focusing on experimental results obtained at one particular site. This complicates quantification of the impact of soil type on CH_4 emission because when CH_4 emissions from different locations are compared, variables other than soil type tend to vary as well (e.g., climate, cultural practices). This problem may be solved by selection of sites relatively close together (Sass et al., 1991; 1992) or artificially changing or transporting soil types to one site (Denier van der Gon and Neue, 1994; 1995b; Chapter 2; 3; 4). The influence of soil type on the process of methane emission from a wetland rice field can be separated in to a soil physical component and a soil chemical component.

Soil chemical factors

Soil chemical factors will influence CH_4 formation in rice fields because soil chemical composition determines the environment in which methanogens have to live but the effect of a certain soil chemical factor may not be significant compared to other variables. The impact of several soil chemical factors is discussed briefly in this section. Attributing the effect of a certain soil type on CH_4 emission to one particular soil chemical factor is difficult because soil chemical factors are often inter-related. For example, acid sulfate soils have both high sulfate contents and a low pH and calcareous soils both contain $CaCO_3$ and have a high pH. Screening of soil chemical factors in microcosm experiments with growing rice plants could yield useful new information.

Sulfate Inhibition studies demonstrated that sulfate reducers (in the presence of sulfate) can outcompete methanogens for substrates (Lovley and Klug, 1983; Oremland, 1988). CH_4 emission from a soil artificially enriched in sulfate was strongly reduced compared to the CH_4 emission from the control field (Denier van der Gon and Neue, 1994; Chapter 3). Methane emissions from Thai soils rich in sulfate were considerably lower than CH_4 emissions from near-by soils low in sulfate (Jermsawatdipong et al., 1994; Yagi et al., 1994), although this may be the combined effect of sulfate availability and low pH. Competition between methanogens and sulfate-reducing bacteria significantly reduces CH_4 emission from soils high in sulfate such as (coastal) saline soils with high sulfate content, acid sulfate soils, and sodic and/or alkaline soils amended with gypsum. Theoretically, a high redox buffer caused by an other electron acceptor than sulfate might have a similar effect on CH_4 emission.

Salinity Salinity accompanied by high sulfate concentrations will reduce CH_4 emissions according to the mechanism described above for soils high in sulfate. Although salinity is often accompanied by high sulfate concentrations, this is not necessarily the case. A rice paddy artificially salinized with non-sulfate salts (mainly NaCL) had 25% lower CH_4 emission than the control plot. This was not unexpected because NaCl inhibits microbial growth and CH_4 production in pure cultures of methanogens, albeit at much higher concentrations (Patel and Roth, 1977). Studies of intact soil cores revealed that production and oxidation of CH_4 were much stronger reduced than the net 25% net reduction in CH_4 emission (Denier van der Gon and Neue, 1995b; Chapter 4). So, the reduction in CH_4 emission is not proportional to the reduction in CH_4 production. CH_4 emissions from wetland rice fields on saline, low-sulfate soils are lower than CH_4 emissions from otherwise comparable non-saline rice fields but the reduction is less dramatic than from (saline) soils high sulfate.

Calcareous soils Elevated pH or free $CaCO_3$ (partly) inhibits CH_4 oxidation but the mechanism behind this phenomenon is not clear. (Chapter 2; King et al., 1990) Furthermore, calcareous soils show rapid formation of CH_4 upon flooding (Neue and Roger, 1994). Therefore we expect higher CH_4 emissions from calcareous soils grown to rice. However, the difference in CH_4 emission between the calcareous and non-calcareous soil disappeared upon the application of organic amendments (Chapter 2). This still leaves several hypotheses about the mechanism behind higher emissions from calcareous soils and why it is no longer significant if organic amendments are used: (1) the formation of organic acids neutralized the pH effect of $CaCO_3$, (2) the quicker, and higher substrate generation in a calcareous soil is not significant compared to the additional substrate supply by organic amendments, and (3) the contribution of ebullition to total CH_4 transport greatly increased upon incorporation of organics, thus by-passing CH_4 oxidation in both soils, and thereby reducing the impact CH_4 oxidation inhibition in the calcareous soil.

pH Incubation experiments with rice soils in microcosms showed that CH_4 production in reduced soils is very sensitive to pH, with an optimum pH of 6.9-7.1 (Wang et al., 1993a). Soils that remain low in pH, even upon flooding, are expected to have considerable lower production and emission of CH_4.

Soil physical factors

Texture and clay content Sass and Fisher (1994) reported a clear inverse relation between seasonal CH_4 emission of Texan rice fields and soil clay content. A similar relation was observed in Philippine rice fields (Chapter 2) although in this study the effects of $CaCO_3$ and texture could not be separated. The inverse relation between seasonal CH_4 emission may be caused by the ability of clay minerals to protect organic matter from breakdown (Jenkinson, 1977; Oades, 1988). Furthermore, higher clay content promoted soil entrapment of CH_4 in laboratory experiments (Wang et al., 1993b). The percolation of a rice field is controlled by soil physical properties but often even more so by agricultural management, and is therefore discussed under anthropogenic modifiers (cultural practices).

Soil incubations, assessing the capacity of soils to produce CH_4, may help explaining inter-location variation in CH_4 emission. However, direct improvement of regional CH_4 emission estimates by combining soil incubations with soil maps is an

Table 9.2 Influence of soil characteristics on production and oxidation of CH_4.

Soil characteristic	CH_4 production	CH_4 oxidation
High sulfate availability	-	
Salinity	-	-
High clay content	-	
High soil organic carbon CaCO3 / high pH	+	
Acidic, pH < 5.5 after submergence	+	-
Low soil fertility[1]	-	
High redox buffer[2]	-	
	-	

[1]composed characteristic, lowers input of methanogenic substrate by limiting plant growth.
[2]high availability of electron acceptors functioning at high Eh, e.g., ferric iron, prevents reaching the critical soil Eh for initiation of CH_4 production (Eh≈ -150 mV)

illusion due to the large influence of the growing rice plants and various climatic and anthropogenic modifiers. An overview of the soil characteristics that influence CH_4 emission from wetland rice fields is presented in Table 9.2.

Soil (micro) biological factors

Methanogens and methanotrophs are an integral part of the soil microbiological community. So, obviously the soil microbiological composition and activity is of great importance for CH_4 emission from rice fields. Methanogens and methanotrophs were discussed above under the respective headings methane production (1) and methane oxidation (2). Furthermore, as was also discussed in the section on methane production (1), methanogens depend on other groups of microorganisms for the production of methanogenic substrates. Soil fauna like tubificids stimulates the degradation and mineralization of organic substrates in flooded rice soils (Neue and Roger, 1994). In general, a high diversity of micro- and macroorganisms will stimulate carbon turnover in rice soils and thus also promote methane production. However, quantification of the effect of soil fauna, and their occurrence in various soil types, on CH_4 emission from rice fields is not possible at present due to a lack of specific research.

6 Anthropogenic modifiers

Fertilizer

Nutrient supply Additional nutrient supply to rice plants by fertilization increases plant biomass. This will generally stimulate CH_4 production indirectly by generation of more methanogenic substrate (root exudates and plant litter). However, there may be other effects of fertilization that overrule the impact of increased substrate supply or the increase of substrate supply may not be significant.

Inhibitory effects on methanogenesis The use of sulfate-containing fertilizers such as ammonium sulfate ($(NH_4)_2SO_4$) could reduce CH_4 emission because sulfate-reducing bacteria can out-compete methane-producing bacteria and thus reduce the amount of CH_4 produced in the rice field. However, normal fertilizer application rates (50-200 $kg.ha^{-1}$ ammonium sulfate) do not contain enough sulfate to guarantee successful outcompetition of methanogens and had contradicting effects on CH_4 emission (Cicerone and Shetter, 1981; Wassmann et al., 1993; Schütz et al., 1989a; Lindau et al., 1993; for detailed discussion see Chapter 3). Nitrogen fertilizer may be amended with a nitrification inhibitor to increase fertilizer-use efficiency. Nitrification inhibitors, e.g., Nitrapyrin or N-serve (Salvas and Taylor, 1980), encapsulated calcium carbide (Bronson and Mosier, 1991), and dicyandiamide (Lindau et al., 1993) also block or reduce CH_4 production in a rice field.

Inhibitory effects on methanotrophy Presence of ammonium in the floodwater, e.g. from urea application, was found to reduce CH_4 oxidation in the soil-water interface (Conrad and Rothfuss, 1991). It is most likely that NH_4^+ in the rhizosphere will have a similar effect on rhizospheric CH_4 oxidation. Quantification of this effect on plant-mediated CH_4 transport requires specific research because the concentration of NH_4^+ in the rhizosphere is determined by a highly dynamic balance due to mineralization, plant uptake and nitrification in the oxidized zones of the rhizosphere. In aerobic soils, N fertilization lead to a long-term decrease of CH_4 oxidizing activity (Steudler et al., 1989; King, 1992), whether this also applies to wetland rice fields requires further research. Methanotrophs are basically sensitive to all nitrification inhibitors (King, 1992).

Mode of application Neither mode of urea application nor the timing of basal N fertilization affected the CH_4 emission from Philippine rice fields (Wassmann et al., 1993). The mode of ammonium sulfate application had a distinct influence on CH_4 emission in an Italian rice paddy (Schütz et al., 1989a). Compared to an urea-fertilized field in the same year, CH_4 emission was reduced by 47% if $(NH_4)_2SO_4$ was incorporated into the soil, but CH_4 emission was enhanced by 58 % if $(NH_4)_2SO_4$ was surface applied. The mechanism behind these observations may be that (1) incorporation of $(NH_4)_2SO_4$ in the soil introduces sulfate in the methanogenic zone causing competition between sulfate-reducers and methanogens (see above), while (2) surface application does not introduce sulfate in the methanogenic zone and surface applied NH_4^+ may inhibit CH_4 oxidation at the soil-water interface (Conrad and Rothfuss, 1991) thereby reducing the internal CH_4 sink in the rice ecosystem. However, it is unlikely that the latter causes an enhancement of 58%, given the contribution of diffusion across the soil-water interface to total CH_4 transport (Table 9.1) and some additional factor must play a role.

Organic amendment

Addition of organic matter such as animal manure, rice straw or green manure to a wetland rice field enhances CH_4 emissions (e.g., Schütz et al., 1989a; Yagi and Minami, 1990; Sass et al., 1991; Cicerone et al., 1992; Wassmann et al., 1993a;

1993b; Neue et al., 1994; Denier van der Gon and Neue, 1995a; Chapter 5). The magnitude of the CH_4 fluxes induced by organic amendments varies widely across locations. However, once the inter-location variability caused by differences in climate, soil type etc. is eliminated, the fractional increase in CH_4 emission with organic matter added at different locations of the world can be described by a single curve. Clearly, the disadvantage of not understanding the inter-location variability is that one can only predict the fractional (or relative) increase of CH_4 emission upon treatments but not the absolute emission level. The content of easily decomposable carbon in organic amendments is positively correlated with CH_4 emissions from the amended field (Yagi and Minami, 1990; Denier van der Gon and Neue, 1995a; Chapter 5). Application of organic amendments leads to more CH_4 emission early in the season. This would suggest that ebullition becomes a more important transport mechanism in organically amended fields. Applying the seasonal distribution of CH_4 transport mechanisms given in Table 9.1, ebullition contributed up to 30% to total CH_4 emission in green manure treated plots but less than 5% in urea-fertilized plots (Denier van der Gon and Neue, 1995a; Chapter 5). Large organic amendments may also have an influence on plant physiological development by causing extremely low soil Eh. Plants grown under severe reducing conditions of -300 mV had much lower root and shoot dry weights and mean root length than plants grown at Eh 200 to -200 (Kludze et al., 1993). However, the stimulation of CH_4 production under these strongly reduced conditions, causing a strong increase in CH_4 emission appears to be far more important than the changes in plant physiological development. Furthermore, it is obvious that organic amendments causing such an extremely reduced soil environment will have adverse effects on rice yields and will not be practised by rice farmers.

Rice variety

Since up to 90% of the methane released from a rice field may be emitted via the rice plant (Cicerone and Shetter, 1981; Schütz et al., 1989a), rice plant characteristics may have a strong impact on CH_4 emission. A comparison over two seasons showed that fields planted to two Italian rice varieties differed significantly in their CH_4 emission. Variety Lido had 24-29 % lower CH_4 emissions than variety Roma (Butterbach-Bahl, 1993). Lido also had a lower gas transport capacity than Roma. In a study with six varieties, semi-dwarf varieties evolved 36 % less CH_4 than tall rice cultivars (Lindau et al., 1995). Modern semidwarf varieties were introduced in the 1960s to increase rice yields mainly by increased resistance to lodging (De Datta, 1981). This suggests that rice farmers, unintentionally, started mitigating CH_4 emissions in the 1960s by growing semidwarf varieties instead of traditional varieties. Rice plant characteristics differ among varieties and influence CH_4 emission through:

- Stimulation of CH_4 production in the rice soil by providing methanogenic substrate (root exudates, root litter, total biomass production and remnants of the previous crop incorporated in the field). These factors differ among varieties because of selective breeding for desired traits and/or specific varietal adaptations to adverse environments (e.g., increased root exudation for nutrient mobilization, minimum plant height to survive in flood prone area's). Total biomass production of good rice crops varies between 10-20 ton.ha^{-1} (Yoshida, 1981).
- The rice plant's aerenchyma transports CH_4 from soil to atmosphere and transports O_2 in the opposite direction thus creating (1) an escape route for CH_4, and (2) a (partly) oxidized rhizosphere. The variability in root-oxidizing power among rice cultivars is high (Ando et al., 1983). Increasing oxidation of the rhizosphere is inversely related to CH_4 emission due to increased inhibition of rhizospheric methanogenesis and enhanced rhizospheric CH_4 oxidation (Denier van der Gon and Neue, 1996; Chapter 8). However, higher gas transport capacity may lead to more CH_4 transported (increasing emission) but also to increased O_2 transport to the root zone (decreasing emission). The net impact of rice varietal characteristics on CH_4 emission is not well understood. Clearly, specific research is needed to unravel the combined influences of rice varietal traits on CH_4 emission.

Cultural practices

The effects of cultural practices other than fertilization, organic amendments and water management on CH_4 emission are not well documented and received little attention up to now. Most rice soils are prepared for the new rice crop by wet tillage. Wet tillage comprises land soaking, ploughing, puddling and harrowing. A detailed description and the advantages of wet tillage are given by De Datta (1981). As soon as the rice soil is flooded and becomes reduced, CH_4 production may start. Disturbance of the flooded paddy soil due to e.g., land preparation, transplanting, weeding, pest control releases (part of the) soil-entrapped CH_4, thus temporarily increasing CH_4 emission from the rice field (Denier van der Gon et al., 1992). The presence of a hard pan (also called plough or traffic pan) caused by land preparation and the destruction of soil structure by puddling greatly reduces percolation rates in rice fields. CH_4 emission is negatively correlated to percolation rates because CH_4 and its precursors are transported to the subsoil allowing more time for oxidation (Kimura et al., 1992). In a Japanese lysimeter paddy field CH_4 emission was almost negligible at a percolation rate of 20 mm.d^{-1} (Minami, 1990). Application of pesticides to the floodwater or soil may have significant effects on CH_4 fluxes by affecting aquatic and soil flora and fauna. Several recently introduced cultural practices are likely to cause less CH_4 emission than their common alternatives, e.g., dry (or direct) seeding versus transplanting and dryland (or zero) tillage versus wet tillage, although actual field conditions will often not allow introduction of such cultural practices (Neue, 1992).

Water management

Water management (irrigation and drainage) is of major importance in rice production and has a major impact on CH_4 emission. Submergence and drainage of the rice fields controls oxygen availability in the rice soil which eventually determines CH_4 emission by controlling methanogenesis, CH_4 oxidation, and regeneration of electron acceptors (e.g., ferric iron, sulfate). The water regime during the growing season, largely controlled by water management, is the main factor by which rice ecosystems are distinguished and is discussed separately below (rice ecosystems). Increased water percolation and/or well-timed, short drainage periods during the growing season were found to reduce CH_4 emission and do not necessarily reduce the rice yield (Sass et al., 1992; Sass and Fisher, 1994). If water supply is sufficient percolation rates may be increased by water management, e.g., a short drainage period which causes irreversible soil cracking, because medium to high percolation rates (8-20 $mm.d^{-1}$) are associated with high rice yields in subtropical East Asia (Neue, 1992). The high percolation rates remove substances toxic to rice plants (organic acids, Fe^{2+}) and will reduce CH_4 emissions from these fields. Complications with quantifying the influence of water management on CH_4 emission are:

- Large amounts of soil-entrapped CH_4 are released to the atmosphere upon soil drying (Denier van der Gon et al., 1996; Chapter 6). This flush of CH_4 in the first stage of soil drying has to be taken into account when calculating the impact of a water management strategy on CH_4 emission.
- Intermittent wetting and drying of the rice soil may cause emissions of N_2O, another potent greenhouse gas
- Planned water management regimes cannot always be accomplished due to water shortage or excess water by severe floods.

7 Rice Ecosystems

Neue (1989) proposed a comprehensive classification of rice ecosystems by hierarchically applying floodwater source and floodwater depth as diagnostic criteria. This classification also discriminates rice ecosystems with respect to their capacity to emit methane because submergence of soils causes methane formation through anaerobic decomposition of organic matter (Neue and Roger, 1994). A slightly simplified version of the classification of rice ecosystems proposed by Neue (1989) is presented in Table 9.3.

Irrigated rice

Irrigated rice has the highest potential for CH_4 emission because flooding, which causes the anaerobic conditions essential for CH_4 production, is assured. The submergence of the soil is not (directly) dependent on rainfall therefore rainfall distribution and drought spells are often not important. Floodwater management that is used in combination with irrigation such as mid-season drainage is crucially important as are periods with lack of irrigation water. Irrigated rice covers 53 % of the total harvested rice area of the world (IRRI, 1995).

Rainfed rice

Rainfed rice has a highly variable potential for CH_4 production since its floodwater regime is controlled primarily by rainfall within the watershed (Neue and Roger, 1994). The subecosystems (Table 9.3) differ considerably in their physical environment and therefore in the type of rice varieties grown and length of growing season. The world's harvested area of deepwater and very deepwater rice is about 8 % of the total harvested rice area (IRRI, 1995). These rice ecosystems are not of major importance in the global methane budget but in specific regions the contribution of deepwater and very deepwater rice will be substantial.

Table 9.3 Classification of rice ecosystems with respect to their capacity for CH_4 emission (adapted from Neue, 1989).

Floodwater source	Irrigation	Pluvial, Phreatic, Surface flow, or Tidal			
Floodwater depth (cm)	1-25	0-50	50-100	>100	<0
Rice ecosystem	Irrigated rice		Rainfed rice		Upland rice
Subecosystem	Irrigated rice[1]	Rainfed lowland rice[1]	Deepwater rice	Very deepwater rice	Upland rice
Land ecosystem		Wetland			Upland

[1] Neue (1989) distinguishes shallow and medium floodwater depth in this subecosystem.

Rainfed lowland rice is similar to irrigated rice except that water supply is not secured and the land often falls dry during the growing season. In the last decades much of the rainfed lowland rice area has been transformed into irrigated rice. At present rainfed lowland rice covers 27 % of the total harvested rice area (IRRI, 1995). Drought periods that cause the soil to dry and become (partially) aerobic have a major impact on the CH_4 production in the rice soil. For estimating or modelling CH_4 emission from rainfed lowland rice, information on the occurrence of such droughts is essential.

Deepwater rice varieties have a similar plant physiological structure and internal gas transport as irrigated rice varieties and rainfed lowland rice varieties but have several additional plant characteristics, e.g., intermediate plant height, submergence tolerance, and ability to elongate if the water level increases (De Datta, 1981). The growing season of deepwater rice is rather long, from 150 days up to 240 days, implying a longer period of CH_4 emission than with irrigated rice. Also the floodwater of deepwater rice fields may become anoxic (Whitton and Rother, 1988) implying that the soil-water interface is no longer a methane oxidizing environment. Due to the large quantity of litter available from the deepwater rice plants, the floodwater itself may even become a source of CH_4 (Neue and Roger, 1994)

Very deepwater rice (often "floating rice") has a maximum floodwater depth of 1-6 m. The rice roots that penetrate the soil mainly function as an anchor. The transport of CH_4 from soil to atmosphere in such rice plants differs from that in other rice ecosystems in that transport through the water column, especially ebullition, will probably be more important than plant-mediated CH_4 transport. In analogy with the observation by Whitton and Rother (1988) that the floodwater layer for deepwater rice fields becomes anoxic during the crop cycle, it can be expected that the main CH_4 producing zone in very deepwater rice fields may be the top soil layer and lower water column. Dead plant material accumulating in the detritus layer on top of the soil may become the main substrate source for methanogens instead of native soil organic matter and/or root exudates. The growing season of very deepwater rice is usually 3-4 months (Bangladesh, Thailand, India) with extremes of up to 10 months (Niger) (Vergara et al., 1976). Naturally, the length of the growing season has an important influence on the annual CH_4 emission from this rice ecosystem.

Upland rice

Upland rice is never flooded for a significant period of time. The anaerobic conditions essential for CH_4 production do not occur and therefore no significant CH_4 emission will occur. Upland rice covers 12 % of the total harvested rice area (IRRI, 1995).

Interaction of various modifiers on CH_4 emission

The impact of the modifiers described above on CH_4 emission from a rice field was mainly determined in studies that focus on one modifier only. However, the impacts of various modifiers on CH_4 emission are inter-dependent, so to predict CH_4 emission under varying conditions the interaction between these modifiers needs to be known. The research described in this thesis provides two examples of such interaction. In Chapter 3, methane emission from plots amended with 6.66 tons.ha^{-1} gypsum was reduced by 55-70% compared to non-amended plots. While input of fresh organic matter strongly enhanced CH_4 emission, relative reduction in CH_4 emission upon gypsum application was independent of organic matter addition. So, here both factors operated more or less independent of each other: organic amendments enhanced CH_4 emission and gypsum application reduced the emission by a fixed percentage. In Chapter 2, a calcareous soil was found to have a higher CH_4 emission than a near-neutral clay soil. However, upon application of organic amendments CH_4 emission from both soils were strongly enhanced and the difference in emission was no longer observed. Apparently the addition of organic amendment "overruled" the influence of calcareous soil on CH_4 emission.

More examples of such interactions may be available and unravelling the various interactions in to basic or single processes requires further research in the coming years.

Future perspectives

Despite the identification of controlling variables the uncertainty in the global CH_4 source strength estimate from rice paddies is still among the highest of all CH_4 sources (IPCC, 1994). To achieve a reliable global CH_4 budget and develop cost-efficient mitigation options to stabilize the atmospheric CH_4 concentration, this uncertainty needs to be narrowed. The large uncertainty in the source strength estimate of rice fields is a scale-related problem. The scale for which we want to have information on CH_4 emissions for global budgets (> 10 km to global) is much larger than the scale of emission measurements (1-100 m), which is again larger than the scale at which production and oxidation of CH_4 occurs (< cm). Reliable estimates and future predictions of the CH_4 source strength of rice paddies at the global scale can only be reached if we bridge the various scales. A first step in connecting the different scales is the construction of process models that link the production and oxidation of CH_4 in the rice soil to emission at the field level. After calibration and validation with field measurements the models can predict CH_4 emission for a range of fields if the relevant input data are available. Geo-reference data acquisition for such regional predictions will be very important in the near future. Aggregation of thus acquired field fluxes yields a regional estimate of CH_4 emission from rice fields and further aggregation will provide the desired larger regional/global estimates with a strongly reduced uncertainty. Although such an approach seems feasible, the accomplishment of these improved CH_4 source strength estimates is currently wishful thinking. Process models are being developed but not operative yet, geo-referenced databases on CH_4 emission controlling factors are not readily available. Furthermore, once regional estimates are obtained some sort of validation is essential, to reduce the uncertainty in the aggregated global estimate. It is obvious that an immediate "jump" from the process level scale to a global scale is not feasible and a gradual approach linking each scale to the scale immediately below and above seems the only solution. A recently developed technique, so-called inverse modelling, estimates global CH_4 sources by obtaining optimal agreement between observed atmospheric mixing ratio's of CH_4, supplemented with isotope ratio's of atmospheric CH_4 and known global distribution of sources and sinks (Hein and Heimann, 1994). Potentially, inverse modelling can provide a validation of regional or global estimates based on up-scaling from the process level and vice versa.

References

Ando, T., S. Yoshida, and I. Nishiyama, Nature of oxidizing power of rice plants, Plant and Soil, 72, 57-71, 1983.

Armstrong, W., Rhizosphere oxidation in rice: An analysis of intervarietal differences in oxygen flux from the roots, Phys. Plant, 22, 296-303, 1969.

Armstrong, W., Root aeration in the wetland condition, in: Plant life in anaerobic environments, edited by D.D. Hook and K. K. Crawford, Ann Arbor Science, Ann Arbor, Mi, 1978.

Bedard, C. and R. Knowles, Physiology, biochemistry and specific inhibitors of CH_4, NH_4 and CO oxidation by methanotrophs and nitrifiers, Microbial Rev., 53, 68-84, 1989.

Bont, J.A.M. de, K.K. Lee, and D.F. Bouldin, Bacterial oxidation of methane in a rice paddy, in: Environmental role of nitrogen-fixing blue-green algea and asymbiotic bacteria, Ecol. Bull., Stockholm, 26, 91-96, 1978.

Bronson, K.F. and A.R. Mosier, Effect of encapsulated calcium carbide on dinitrogen, nitous oxide, methane, and carbon dioxide emissions from flooded rice, Biol. Fertil. Soils, 11, 116-120, 1991.

Butterbach-Bahl, K., Mechanismen der Produktion und Emission von Methan in Reisfeldern, IFU Schriftenreihe Band 14-93, Fraunhofer-Institut für Atmosphärische Umweltforschung, Garmisch-Partenkirchen, 1993.

Cicerone, R.J. and J.D. Shetter, Sources of atmospheric methane: measurements in rice paddies and a discussion, J. Geophys. Res., 86, 7203-7209, 1981.

Cicerone, R.J., J.D. Shetter, and C.C. Delwiche, Seasonal variation of methane flux from a California rice paddy, J. Geophys. Res., 88,. 11022-11024, 1983.

Cicerone, R.J., C.C. Delwiche, S.C. Tyler, and P.R. Zimmerman, Methane emissions from California rice paddies with varied treatments, Global Biogeochem. Cycles, 6, 233-248, 1992.

Conrad, R., Control of methane production in terrestrial ecosystems, in: Exchange of trace gases between terrestrial ecosystems and the atmosphere, edited by M.O. Andrae and D.S. Schimmel, Wiley & Sons Ltd, 39-58, 1989.

Conrad, R. and R. Rothfuss, Methane oxidation in the soil surface layer of a flooded rice field and the effect of ammonium, Biol. Fertil. Soils, 12, 28-32, 1991.

Dalton, H., Ammonia oxidation by the methane-oxidizing bacterium Methylococcus capsulatus strain Bath, Arch. Microbiol. 114, 272-279, 1977.

De Datta, S.K., Principles and practices of rice production, 618 p., Wiley & Sons, New York, 1981.

Denier van der Gon, H.A.C., H.-U. Neue, R.S. Lantin, R. Wassman, M.C.R. Alberto, J.B. Aduna, and M.J.P. Tan, Controlling factors of methane emissions from rice fields, In: World Inventory of Soil Emission Potentials, Proceedings of an International Workshop, ISRIC, Wageningen, The Netherlands, 1992.

Denier van der Gon, H.A.C. and N. van Breemen, Diffusion-controlled transport of methane from soil to atmosphere as mediated by rice plants, Biogeochem., 21, 177-190, 1993.

Denier van der Gon, H.A.C. and H.U. Neue, Impact of gypsum application on the methane emission from a wetland rice field, Global Biogeochem. Cycles, 8, 127-134, 1994.

Denier van der Gon, H.A.C. and H.U. Neue, Methane emission from a wetland rice field as affected by salinity, Plant and Soil, 170, 307-313, 1995.

Denier van der Gon, H.A.C. and H.U. Neue, Influence of organic matter incorporation on the methane emission from a wetland rice field, Global Biogeochem.Cycles, 9, 11-22, 1995.

Denier van der Gon, H.A.C. and H.U. Neue, Oxidation of methane in the rhizosphere of rice plants, Biol. Fertil. Soils, 22, 359-366, 1996.

Denier van der Gon, H.A.C., N. van Breemen, H.-U. Neue, R.S. Lantin, J.B. Aduna, M.C.R. Alberto, and R. Wassmann, Release of entrapped methane from wetland rice fields upon soil drying, Global Biogeochem. Cycles, 10, 1-7, 1996.

Epp, M.A. and J.P Chanton, Rhizospheric methane oxidation determined via the methyl fluoride inhibition technique, J. Geophys. Res., 98, 18413-18422, 1993.

Frenzel, P., F. Rothfuss and R. Conrad, Oxygen profiles and methane turnover in a flooded rice microcosm, Biol. Fertil. Soils, 14, 84-89, 1992.

Hein, R. and M. Heimann, Determination of global scale emissions of atmospheric methane using an inverse modelling method, In: Non-CO2 greenhouse gases: Why and how to control?, edited by J. van Ham, L.J.H.M. Janssen and R.J. Swart, Kluwer Acedemic Publishers, Dordrecht Netherlands, 271-282, 1994.

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

Holzapfel-Pschorn, A., R. Conrad and W. Seiler, Effects of vegetation on the emission of methane from submerged paddy soil, Plant and Soil, 92, p. 223-233, 1986.

Intergovernmental Panel on Climate Change (IPCC), Climate Change 1994, Radiative forcing of climate change and an evaluation of the IPCC IS92 emission scenarios, Cambridge University Press, New York, 1994.

International Rice Research Institute IRRI, Agricultural Economics Database, P.O. Box 933, Manila, Philippines, 1988.

International Rice Research Institute IRRI, World Rice Statistics 1993-94, P.O. Box 933, Manila, Philippines, 1995.

Jenkinson, D.S., Studies on the decomposition of plant material in soil. V. The effects of plant cover and soil type on the loss of carbon from ^{14}C labelled ryegrass decomposing under field conditions, J. Soil Sci., 28, 424-434, 1977.

Jermsawatdipong, P., J. Murase, P. Prabuddham, Y. Hasathon, N. Khomthong, K. Naklang, A. Watanabe, H. Haraguchi, and M. Kimura, Methane emission from plots with differences in fertilizer application in Thai paddy fields, Soil Sci. Plant Nutr., 40, 63-71, 1994.

Kimura, M., Y. Miura, A. Watanabe, J. Murase and S. Kuwatsuka, Methane production and its fate in paddy fields 1. Effects of rice straw application and percolation rate on the leaching of methane and other soil components into the subsoil, Soil Sci. Plant Nutr., 38 665-672, 1992.

King, G.M., Dynamics and controls of methane oxidation in a Danish wetland sediment, FEMS Microbiol. Ecol., 74, 309-324, 1990.

King, G.M., P. Roslev, and H. Skovgaard, Distribution and rate of methane oxidation in sediments of the Florida Everglades, Appl. Environ. Microbiol., 56, 2902-2911, 1990.

King, G.M., Ecological aspects of methane oxidation, a key determinant of global methane dynamics, Adv. Microbial Ecol., 12, 431-468, 1992.

Kludze, H.K., R.D. DeLaune, and W.H. Patrick, Jr., Aerenchyma formation and methane and oxygen exchange in rice, Soil Sci. Soc. Am. J., 57, 386-391, 1993.

Knowless, R., Methane: Processes of production and consumption, In: Agricultural ecosystem effects on trace gases and global climate change, ASA Special Publication no. 55, pp. 145-155, 1993.

Koyama, T., Gaseous metabolism in lake sediments and paddy soils and the production of atmospheric methane and hydrogen, J. Geophys. Res., 68, 3971-3973, 1963.

Lindau, C.W., P.K. Bollich, R.D. Delaune, A.R. Mosier, and K.F. Bronson, Methane mitigation in flooded Louisiana rice fields, Biol. Fertil. Soils, 15, 174-178, 1993.

Lindau, C.W., P.K. Bollich, and R.D. Delaune, Effect of rice variety on methane emission from Louisiana rice, Agricult. Ecosyst. & Environ., 54, 109-114, 1995.

Lovley, D.R. and M.J. Klug, Sulfate reducers can outcompete methanogens at freshwater sulfate concentrations, Appl. Environ. Microbiol., 45, 187-192, 1983.

Minami, K., Effects of agricultural management on methane emission from rice paddies, Contribution to IPCC-RSWG Workshop: Greenhouse gas emissions from agricultural systems, 1990

Neue, H.-U., Rice growing soils: Constraints, utilization and research needs, In: Wetland Soils: Characterization, Classification and Utilization, International Rice Research Institute, P.O. Box 933, Manila, Philippines, 1989.

Neue, H.U. and P.A. Roger, Potential of methane emission in major rice ecologies, in: Climate Biosphere Interaction, edited by R.G. Zepp, pp. 65-93, Wiley and Sons, New York, 1994.

Neue, H.U. and R. Sass, Trace gas emissions from rice fields, in: Global Atmospheric-Biospheric Chemistry, edited by R.G. Prinn, pp. 119-148, Plenum Press, New York, 1994.

Neue, H.U., Agronomic practices affecting methane fluxes from rice cultivation, Ecol. Bull., 42, 174-182, 1992.

Neue, H.U., R.S. Lantin, R. Wassmann, J.B. Aduna, M.C.R. Alberto and M.J.F. Andales, Methane emission from rice soils of the Philippines, in: CH_4 and N_2O: Global emissions and controls from rice fields and other agricultural and Industrial sources, edited by K. Minami, A. Mosier, and R. Sass, pp. 55-63, National Institute of Agro-Environmental Sciences, Tsukuba, Japan, 1994.

Oremland, R.S., Biogeochemistry of methanogenic bacteria, in: Biology of anaerobic microorganisms, edited by A.J.B. Zehnder, Wiley & Sons, New York, pp. 641-705, 1988.

Patel, G.B. and L.A. Roth, Effect of sodium chloride on growth and methane production of methanogens, Can. J. Microbiol., 23, 893-897, 1977.

Patrick, W.H., Jr and C.N. Reddy, Chemical changes in rice soils, in: Soils and Rice, International Rice Research Institute, P.O. Box 933, Manila, Philippines, 1978.

Ponnamperuma, F. N., The chemistry of submerged soils, Adv. Agron., 24, 29-96, 1972.

Oades, J.M., The retention of organic matter in soils, Biogeochem., 5, 35-70, 1988.

Salvas, P.L. and B.F. Taylor, Blockage of methanogenesis in marine sediments by the nitrification inhibitor 2-chloro-6-trichloromethylpyridine nitrapyrin or n-serve, Curr. Microbiol. 4, 305-308, 1980.

Sass, R.L., F.M. Fisher, P.A. Harcombe, and F.T. Turner, Methane production and emmision in a Texas rice field, Global Biogeochem. Cycles, 4, 47-68, 1990.

Sass, R.L., F.M. Fisher, P.A. Harcombe, and F.T. Turner, Mitigation of methane emissions from rice fields: Possible adverse effects of incorporated rice straw, Global Biogeochem. Cycles, 5,275-287, 1991a.

Sass, R.L., F.M. Fisher, F.T. Turner, and M.F. Fund, Methane emission from rice fields as influenced by solar radiation, temperature, and straw incorporation, Global Biogeochem. Cycles, 5, 335-350, 1991b.

Sass, R.L., F.M. Fisher, Y.B. Wang, F.T. Turner, and M.F. Jund, Methane emissions from rice fields: The effect of floodwater management, Global Biogeochem. Cycles, 6, 249-262, 1992.

Sass, R.L. and F.M. Fisher, CH_4 emission from paddy fields in the United States Gulf Coast Area, in: CH_4 and N2O: Global emissions and controls from rice fields and other agricultural and Industrial sources, edited by K. Minami, A. Mosier, and R. Sass, pp. 65-77, National Institute of Agro-Environmental Sciences, Tsukuba, Japan, 1994.

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

Schütz, H., W. Seiler, and R. Conrad, Processes involved in formation and emission of methane in rice paddies, Biogeochem., 7, 33-53, 1989b.

Schütz, H, P. Schroder, and H. Rennenberg, Role of plants in regulating the methane flux to the atmosphere, in: Trace Gas Emissions by Plants, edited by T.D. Sharkey, E.A. Holland, and H.A. Mooney, Academic Press, San Diego, pp. 29-63, 1991.

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

Steudler, P.A., R.D. Bowden, J.M. Mellilo, and J.D. Aber, Influence of nitrogen fertilization on methane uptake in temperate forest soils, Nature, 341, 314-316, 1989.

Tsutsuki, K. and F.N. Ponnamperuma, Behaviour of anaerobic decomposition products in submerged soils. Effects of organic material amendment, soil properties and temperature, Soil Sci. Plant Nutr., 33, 13-33, 1987.

Vergara, B.S., B. Jackson, and S.K. DeDatta, Deepwater rice and its response to deep water stress, in: Climate and Rice, pp 301-319, International Rice Research Institute IRRI, P.O. Box 933, Manila, Philippines, 1988.

Wang, Z.P., R.D. DeLaune, P.H. Masscheleyn, and W.H. Patrick, Jr., Soil redox and pH effects on methane production in a flooded soil, Soil Sci. Soc. Am. J., 57, 382-385, 1993.

Wang, Z.P., C.W Lindau, R.D. Delaune, W.H. Patrick, Jr., Methane emission and entrapment in flooded rice soils as affected by soil properties, Biol. Fertil. Soils, 16, 163-168, 1993.

Wassmann, R., H. Schütz, H. Papen, H. Rennenberg, W. Seiler, D. Aiguo, R.X. Shen, X.J. Shangguan, and M.X. Wang, Quantification of methane emissions from Chinese rice fields Zhejiang province as influenced by fertilizer treatment, Biogeochem., 20, 83-101, 1993.

Wassmann, R., M.X. Wang, X.J. Shangguan, X.L. Xie, R.X. Shen, Y.S. Wang, H. Papen, H. Rennenberg, and W. Seiler, 1st Records of a field experiment on fertilizer effects on methane emission from rice fields in Hunan-Province PR-China, Geophys. Res. Lett., 20, 2071-2074, 1993.

Wassmann, R., H.U. Neue, R.S. Lantin, J.B. Aduna, M.C.R. Alberto, M.J. Andales, M.J. Tan, H.A.C. Denier van der Gon, H. Hoffmann, H. Papen, Temporal patterns of methane emissions from wetland rice fields treated by different modes of N-application, J. Geophys. Res., 99, 16457-16462, 1994.

Whitton, B.A. and J.A. Rother, Environmental features of deepwater rice fields in Bangladesh during the flood season, in: 1987 International Deepwater Rice Workshop, International Rice Research Institute, P.O. Box 933, Manila, Philippines, 1988.

Yagi, K. and K. Minami, Effect of organic matter application on methane emission from some Japanese paddy fields, Soil Sci. Plant Nutr., 36, 599-610, 1990.

Yagi, K., P. Chairoj, H. Tsuruta, W. Cholitkul, and K. Minami, Methane emission from rice paddy fields in the central plain of Thailand, Soil Sci. Plant Nutr., 40, 29-37, 1994.

Yoshida, S., Fundamentals of rice crop science, 269 p., International Rice Research Institute IRRI, P.O. Box 933, Manila, Philippines, 1981.

Appendix to chapter 9

Options to mitigate methane emission from rice agriculture

This paper was published in a special issue of the Globe[1] (issue 26, 1995) addressing technological and policy instruments to mitigate causes and adverse impacts of global environmental change. It is of a more speculative nature than an original research paper but it seems an appropriate appendix to chapter 9 since it illustrates how the research described in this thesis may contribute to environmental and policy issues, which is an important reason why this research was funded.

[1] The Globe is published by the UK Global Environmental Research Office with the objective to contribute to the exchange of informtion between those involved or interested in research and policy making on global change.

Options to mitigate methane emission from rice agriculture

Introduction

Methane (CH_4) is one of the principal greenhouse gases. Its estimated contribution to the radiative forcing of climate in 1990 was about 18% (IPCC, 1992). CH_4 merits attention due to its relatively short atmospheric life time. Lelieveld et al. (1993) estimated that to stabilise the atmospheric concentration of the three major greenhouse gases, CO_2, N_2O and CH_4, reductions in their global emissions of >60%, 70-80% and of ≈10%, respectively, are necessary. Therefore, from a policy point of view, CH_4 emission reduction is a promising target because a 10% reduction of global CH_4 emission may be achievable in the short term. Indeed, it would be a very encouraging achievement if the global community could succeed in stabilising the atmospheric concentration of one of the major greenhouse gases.

Manageable methane sources

There are four major anthropogenic sources of methane that are manageable; from fossil fuel exploitation, landfill sites, cattle husbandry and rice agriculture. Emissions from fossil fuel exploitation seem the most appropriate for mitigation because they are from point sources and any reduction in losses is economically beneficial. This may also apply to CH_4 from landfills because the harvested CH_4 can be used as an energy source. However, despite the rapid progress in recent years,uncertainties in the CH_4 source strengths make it difficult to estimate how much CH_4 would not be emitted if a particular mitigation strategy was adopted globally. Furthermore, it is doubtful whether mitigation of one major source only could reduce the global emission of CH_4 by 10-15% especially given that the anthropogenic CH_4 emissions appear to be linked to the growing world population. So, mitigation options for all manageable CH_4 sources should be studied. Studies that evaluate the (social) impact, chances of success and cost-benefit ratio are required to decide which mitigation options are to be implemented. This article discusses options to mitigate CH_4 from rice fields which accounts for about 20% of the global anthropogenic CH_4 emission.

Mitigation options

Change of rice to other crops

Methane is produced in strict anaerobic environments only. (Therefore, upland rice is not a source of CH_4). The most efficient mitigation option is to prevent flooding of the rice fields, which causes the anaerobic environment, and cultivate upland rice or other crops. However, large areas of the world are suited to flooded rice only and yields from upland rice are low compared to flooded rice. Nevertheless, in some areas other crops than rice may be attractive. For example, in China there has been a shift in recent years from double or triple rice cropping towards rice-wheat rotation because wheat is less labour intensive, yields are similar and less water is needed. Although the impacts of such changes in agronomic practice need to be assessed, change of cropping cycle may be promoted in other areas as well. The FAO could play an important role in developing this mitigation option and estimate its impact. Of course food production remains the priority, not greenhouse gas emission reduction.

Water management

Increased water percolation and/or well-timed, short drainage periods during the growing season were found to reduce CH_4 emission and do not necessarily reduce the rice yield. (e.g., Sass et al., 1992). However, there are several complications with this mitigation option. 1) Recent studies, both in the greenhouse (Byrnes et al., 1995) and the field (Denier van der Gon et al., 1995), showed that large amounts of soil entrapped CH_4 are released to the atmosphere upon soil drying and thus escape oxidation in the soil. The amount of CH_4 emitted during soil drying has to be taken into account, reducing the efficiency of floodwater management as a mitigation option. 2) Intermittent wetting and drying of the rice soil may cause emissions of N_2O, another potent greenhouse gas. 3) Most water management regimes suggested as mitigation options will use more water. In many areas, even wetland rice growing regions, water is becoming a scarce commodity. In such cases, the farmer may put his yield at risk because rice is very sensitive to water stress. 4) What is the incentive for the farmer if the yield does not increase and more labour (regulating the floodwater) is involved?

Still, water management offers possibilities as an mitigation option. Some floodwater regimes that were found to be water-saving strategies (Soriano and Bhuiyan, 1989) are likely to reduce CH_4 emissions. Development of feasible water management practices that reduce CH_4 emission, reduce water use, do not enhance N_2O emission and maintain rice yields should be promoted. In rice growing areas with limited water supply such water management is a promising and sustainable mitigation option with a clear incentive for the farmer.

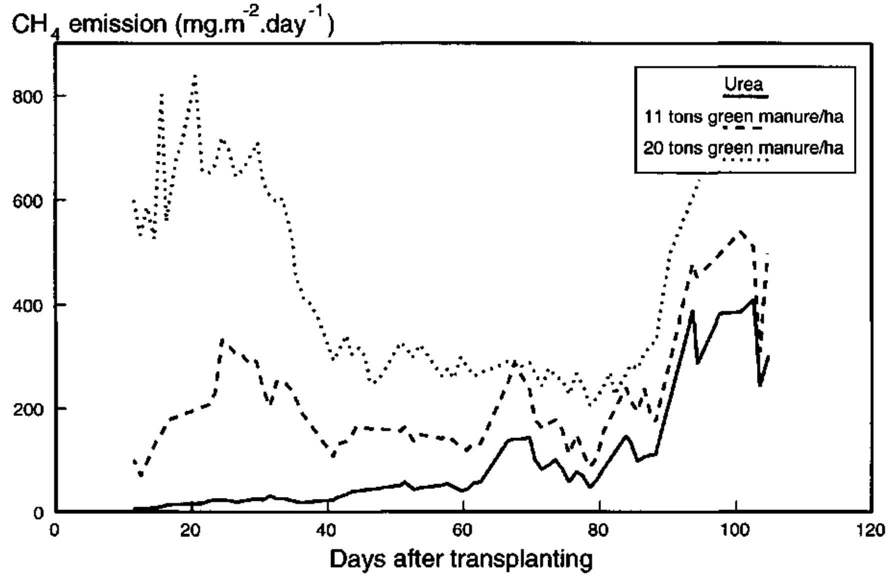

Figure 9a.1 Methane emission from a Philippine rice field fertilized with urea or green manure throughout the rice growing season (wet season of 1992; adapted from Denier van der Gon and Neue, 1995).

Fertilizer applications

A frequently suggested mitigation option is the use of sulfate-containing fertilizers such as ammonium sulfate ($(NH_4)_2SO_4$) because sulfate-reducing bacteria can out-compete methane-producing bacteria and thus reduce the amount of CH_4 produced in the rice field. Addition of large amounts of sulfate to a rice field showed that this mechanism worked and reduced CH_4 emissions by 50-70% (Denier van der Gon and Neue, 1994). However, normal fertilizer application rates (50-200 kg.ha^{-1} ammonium sulfate) do not contain enough sulfate to guarantee successfull outcompetition of methane producers and had contradicting effects on CH_4 emission. So, CH_4 emission reduction can be achieved by adding additional sulfate (e.g., in the form of gypsum) to the rice ecosystem but the addition would have to be repeated after some time. Repetitive additions may have negative effects on soil fertility. This argument is also applicable to other chemical substances that block or reduce CH_4 production in a rice field (e.g., nitrification inhibitors, calcium carbide coating of fertilizer granules; Lindau et al., 1993). CH_4 production is a natural process in flooded soils. Thorough studies on the fate of the introduced chemicals and side-effects for the rice ecosystem are necessary before we decide to block CH_4 production with chemicals.

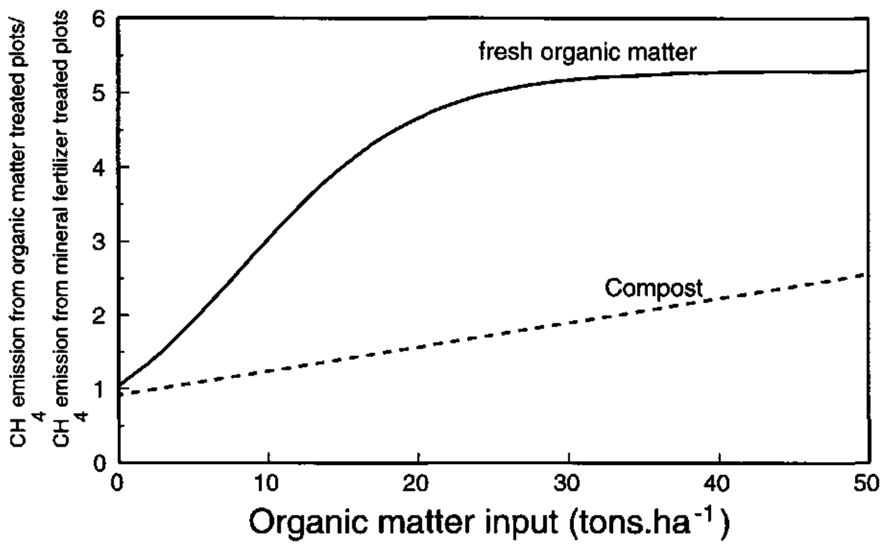

Figure 9a.2 Effect of incorporation fresh organic matter and compost (or fermented residues of biogas pits) on seasonal CH_4 emission from rice fields relative to the seasonal CH_4 emission from mineral N-fertilized rice fields (adapted from Denier van der Gon and Neue, 1995)

Addition of organic material to a rice field such as animal manure, rice straw or green manure enhances CH_4 emission (Figure 9a.1). To mitigate CH_4 from rice fields, organic amendments should be minimized. However, this may conflict with the local availability of fertilizers as well as with soil fertility aspects because long-term field experiments indicate that moderate organic amendments are essential to sustain or increase soil fertility and rice yields. It was found that compost had only a slightly stimulating effect on CH_4 emissions, especially in the common aplication range of 3-15 tons.ha^{-1} (Figure 9a.2). So, aerobic composting is a promising mitigation option which also gives the beneficial effects of moderate organic amendments. A positive effect of composting rice straw would also be that rice straw is now often burned in the field. This burning of biomass is an important source of greenhouse gases. The main problem with composting as a mitigation option seems to be that there is no clear incentive for farmers to do it.

Other cultural practices

The effects of cultural practices (such as tillage, puddling, seeding, transplanting, pest control) on CH_4 emission are not well documented and received little attention up to now. This is partly due to the fact that the most popular technique to measure CH_4 emissions from rice fields (the so-called closed chamber technique) is not well suited to study the impact of cultural practices on CH_4 emission. Nevertheless, evaluation of cultural practices that mitigate CH_4 emissions without sacrificing rice yields is desired. Several cultural practices are likely to cause less CH_4 emission than their common alternatives, e.g., dry (or direct) seeding versus transplanting and dryland (or zero) tillage versus wet tillage, although actual field conditions will often not allow a change of cultural practice. The application of micro-meteorological techniques to measure CH_4 emission may be of great value here because they allow simultaneous measurement of CH_4 and implementation of the specific cultural practise.

Rice cultivars

Up to 90% of the methane released from the rice soil is emitted via the rice plant. Reducing the plant-mediated CH_4 emission is therefore a very potent mitigation option. This can be achieved in two ways. 1) Reduction of plant-factors that may stimulate CH_4 production in the soil e.g., root exudation, root turnover and total below ground biomass, and 2) enhancing the CH_4 oxidation in the rhizosphere. Recent studies, indicate that about 30% of the CH_4 potentially emitted via the rice plant is oxidized and not 70-90% as was previously thought. This means that enhancing CH_4 oxidation in the rhizosphere has a high potential to reduce the CH_4 flux from rice fields. Since the variability in root-oxidizing power among rice cultivars is high (Ando et al., 1983) it may be possible to breed high yielding varieties with high root oxidizing power. Unfortunately, the link between certain varietal traits and CH_4 oxidation or CH_4 production in the rhizosphere are still unknown. Once the mechanisms are singled out, certain plant characteristics that support low emission levels can be provided to plant breeders. The outcome of such a strategy may be that the future high yielding varieties, that the farmer will grow for his own benefit, are also low CH_4 emitting varieties. This calls for long term planning of specialized research but is one of the most promising mitigation strategies. The place where such developments can potentially take place is the International Rice Research Institute (IRRI) but other research programmes may play an important role as well, especially in discovering the varietal traits that reduce CH_4 emission.

Conclusions

According to IRRI annual rice production must increase by 65% over the next three decades to meet the demand of the growing world population. As a result the CH_4 source strength of wetland rice will continue to increase unless new technologies or mitigation options are developed that reduce methane emissions while allowing the necessary increases in rice yield. Reducing methane emission from rice fields will be difficult. The majority of rice farmers live in developing countries, farm on relatively small pieces of land and have small economic margins. Mitigation options can only be successful if the rice farmer can benefit from the implementation. Experience shows that new technologies that improve yields and farmers income spread fast. In other words mitigation options that lower CH_4 emissions should also have one or more of the following characteristics: higher yields, lower water use, lower fertilizer use/costs, less labour intensive or offer an alternative, more profitable, crop. There is not one mitigation option that is the best, in different regions different mitigation options will be applicable. Furthermore, CH_4 emissions from rice fields are not equal all over the globe. There are more and less CH_4 emitting regions or rice ecosystems. These have to be identified and mitigation options should focus on, and be tailored for, those regions or rice ecosystems to be maximum cost-effective.

References

Ando, T., S. Yoshida, and I. Nishiyama, Nature of oxidizing power of rice plants, Plant Soil, 72, 57-71, 1983.

Byrnes, B.H., E.R. Austin, and B.K. Tays, Methane emissions from flooded rice soils and plants under controlled conditions, Soil Biol. Biochem., 27, 331-339, 1995.

Denier van der Gon, H.A.C. and H.-U. Neue, Impact of gypsum application on the methane emission from a wetland rice field, Global Biogeochem. Cycles., 8, 127-134, 1994.

Denier van der Gon, H.A.C. and H.-U. Neue, Influence of organic matter incorporation on the methane emission from a wetland rice field, Global Biogeochem. Cycles., 9, 11-22, 1995.

Denier van der Gon, H.A.C., N. van Breemen, H.-U. Neue, R.S. Lantin, R. Wassmann, J.B. Aduna, and M.C.R. Alberto, Release of entrapped methane from wetland rice fields upon soil drying, Global Biogeochem. Cycles, 10, 1-7, 1996.

Intergovernmental Panel on Climate Change (IPCC), Climate Change 1992, The supplementary report to the IPCC scientific assessment, 200 pp, Cambridge University Press, New York, 1992.

Lelieveld, J., P.J. Crutzen, and C. Brühl, Climate effects of atmospheric methane, Chemosphere, 26, 739-768, 1993.

Soriano, R. and S.I. Bhuiyan, Irrigation application alternatives and their effects on water use and rice yield, IRRI Saturday Seminar, 1989.

Lindau, C.W., P.K. Bollich, R.D. Delaune, A.R. Mosier, and K.F. Bronson, Methane mitigation in flooded Louisiana rice fields, Biol. Fertil. Soils, 15, 174-178, 1993.

Sass, R.L., F.M. Fisher, Y.B. Wang, F.T. Turner, and M.F. Jund, Methane emissions from rice fields: The effect of floodwater management, Global Biogeochem. Cycles., 6, 249-262, 1992.

Samenvatting

Methaan (CH_4) is een belangrijk broeikasgas, met een geschatte bijdrage van 15-20% aan het versterkte broeikaseffect, en speelt tevens een belangrijke rol in de atmosferische chemie. Om zowel de huidige trends te begrijpen, toekomstige methaanconcentraties in de atmosfeer te voorspellen en kost-effectieve reductie strategieën te ontwikkelen is een betrouwbaar budget van alle bronnen en putten van atmosferisch methaan noodzakelijk. Natte rijstbouw is een belangrijke bron van methaan, verantwoordelijk voor circa 20% van de anthropogene methaanemissie en, in principe, beheersbaar. In een samenwerkingsverband met het International Rice Research Institute (IRRI, Filipijnen) en het Fraunhofer Institut für Atmosphärische Umweltforschung (IFU, Duitsland) is geprobeerd de invloed van (bodem)parameters op de emissie van methaan uit natte rijstvelden te kwantificeren. Methaanfluxen van natte rijstvelden in de Filipijnen met verschillende behandelingen zijn gemeten met de zogenaamde "closed chamber" techniek. De methaanfluxen werden semi-continu gemeten gedurende twee natte seizoenen ('91 en '92) en een droog seizoen ('92). Daarnaast zijn enkele kas- en laboratoriumexperimenten uitgevoerd om meer inzicht in de processen te verkrijgen die methaan emissie uit rijstvelden controleren. De resultaten van verschillende experimenten worden hier puntsgewijs besproken.

Invloed van sulfaatbeschikbaarheid in de bodem De methaanemissie van velden waaraan 7 ton.ha^{-1} gips ($CaSO_4$) was toegevoegd verminderde met 55-70% vergeleken bij niet met gips behandelde velden terwijl de rijstopbrengsten gelijk bleven. De afname van de methaanemissie werd naar alle waarschijnlijkheid veroorzaakt door competitie tussen sulfaatreducerende bacteriën en methaanproducerende bacteriën. Toevoeging van gips is een veel voorkomende bodemverbeteringspraktijk op alkalische gronden, bijv. in India en Pakistan. De resultaten van het experiment geven aan dat methaanemissie uit rijstbouw op met gips behandelde bodems aanzienlijk minder is dan tot nu toe aangenomen. Daarnaast wordt de sulfaathoudende meststof ammoniumsulfaat veel gebruikt in de natte rijstbouw. De afname van methaanemissie door gebruik van ammoniumsulfaat is echter beperkt daar de absolute hoeveelheid sulfaat die hiermee in het systeem gebracht wordt relatief gering is.

Methaanemissie uit rijstvelden op zoute gronden Uit laboratorium experimenten met methaanproducerende bacteriën is bekend dat hoge zoutconcentraties de methaanproductie remmen. De hypothese dat daarom ook de methaanemissie uit natte rijstbouw op zoute gronden veel minder is dan uit vergelijkbare, niet-zoute gronden is getest door zout aan een rijstveld toe te voegen totdat een matige verzouting (poriewatergeleidbaarheid = ~ 4 $dS.m^{-1}$) was bereikt. Dit resulteerde in een vermindering van de methaanemissie met slechts 25%. Onderzoek naar de methaanproductie in de bodem wees uit dat de methaanproductie met veel meer dan 25% was afgenomen doch doordat ook de methaanoxidatie sterk geremd werd was het netto resultaat slechts een relatief geringe afname van de methaanemissie. De sterke remming van methaanoxiderende bacteriën in aanwezigheid van zout behoeft verder onderzoek. Geconcludeerd kan worden dat de methaanemissie uit rijstbouw op zoute gronden weliswaar geringer is dan vanuit vergelijkbare niet-zoute gronden doch niet proportioneel met de afname in methaanproductie.

Methaanemissie uit rijstvelden op kalkhoudende gronden Methaanemissies uit rijstvelden op kalkhoudende lemige bodem was hoger dan uit niet-kalkhoudende kleigronden. Het verloop van de methaanemissie gedurende het rijstseizoen was anders; op de kalkhoudende bodem waren de methaanemissie pieken, zowel in het begin als halverwege het seizoen, hoger. Dit is mogelijk het gevolg van een gunstige pH voor methaanproductie in kalkhoudende bodems en buffering van de pH op deze gunstige waarde. Echter in deze studie kan geen onderscheid gemaakt worden tussen het effect van kalkhoudend materiaal en lichtere textuur. Bemesting met organische stof (groenbemester) stimuleerde de methaanemissie van zowel kalkhoudende als niet-kalkhoudende bodems en deed het onderlinge verschil in emissie verdwijnen. Blijkbaar is de toevoeging van extra organisch materiaal van groter belang dan de aanwezigheid van kalkhoudend materiaal of verschillen in textuur.

Invloed van organische bemesting (groenbemester) op de methaanemissie Gebruik van groenbemester resulteerde in een sterke toename van de methaanemissie uit de rijstvelden. Naast transport via de rijstplant, is in (zwaar) organisch bemeste velden bellentransport ("opborrelen") een belangrijk transportmechanisme van methaan naar de atmosfeer. De toename van de methaanemissie na toediening van organische mest was te voorspellen met een dosis-respons relatie indien de methaanemissie uit het veld bij niet-organische bemesting bekend was. Deze aanpak bleek ook succesvol voor veldproeven op andere lokaties waarvan de benodigde gegevens uit de literatuur werden verkregen.

Ontgassing bij droogvallen van de rijstbodem In de onder water staande bodem gevormde gassen kunnen gedurende het groeiseizoen slechts ten dele naar de atmosfeer ontsnappen. Zodoende vindt er in de bodem een opeenhoping van verschillende gassen, waaronder methaan, plaats. Zodra de bodem van het rijstveld droog valt bijvoorbeeld door drainage, stoppen van irrigatie, of langdurige droogte, kan het in de bodem aanwezige gas in zeer korte tijd naar de atmosfeer ontsnappen. Dit proces leidt tot extreem hoge methaanemissies in een tijdsbestek van 1 tot 4 dagen. Na deze periode van hoge emissie zijn de methaanfluxen uit het, inmiddels droge, rijstveld verwaarloosbaar en vindt er geen methaanproductie meer plaats. De korte periode van hoge methaanemissie tijdens droging van de bodem blijkt een significant deel (~10%) van de totale methaanemissie uit een rijstveld te zijn. Dientengevolge moet de methaanemissie tijdens droging van de bodem worden meegenomen bij de bepaling van de totale methaanemissie gedurende een volledige rijstoogstcyclus.

Transport van methaan door de rijstplant De belangrijkste transportweg voor methaan vanuit de rijstbodem naar de atmosfeer is door de rijstplant. Een goed begrip van dit transportmechanisme is essentieel voor de procesmodellering van methaanemissie uit natte rijstvelden. Door de gassamenstelling in kasproeven met rijstplanten te variëren is aangetoond dat het transport van methaangas via de rijstplant gecontroleerd wordt door diffusie. De belangrijkste barrière waarover de diffusie moet plaatsvinden lijkt de wortel-spruit overgang te zijn.

Oxydatie van methaan in de wortelzone van de rijstplant De rijstplant transporteert zuurstof uit de lucht naar zijn wortels voor respiratie in de verder zuurstofloze bodem van het natte rijstveld. Hetzelfde traject, maar dan in omgekeerde richting, wordt door methaan, dat in de anaërobe bodem geproduceerd wordt, afgelegd. Een deel van de naar de wortel getransporteerde zuurstof diffundeert door de wortelwand naar de anaërobe bodem. Hierdoor ontstaat er rondom de wortel een zuurstofgradiënt en tevens een zone waarin zowel zuurstof als methaan naast elkaar voorkomen. Dit is een goed medium voor methaanoxiderende bacteriën die zowel methaan als zuurstof nodig hebben om te groeien. De methaanoxidatie in de rhizosfeer blijkt afhankelijk te zijn van het groeistadium van de rijstplant, mogelijk een gevolg van de veranderende fysiologie en functie van de wortel over het groeiseizoen. De methaanemissie via de rijstplant was zonder methaanoxidatie in de rhizosfeer maximaal 30% hoger. Hoewel dit aanzienlijk minder is dan eerdere schattingen van methaanoxidatie in de rhizosfeer op basis van indirecte metingen, illustreert dit toch het belang van methaanoxidatie in het rijst-bodem-water systeem als put voor methaan. Verhoging van de methaanoxidatie in de rhizosfeer zou een aanzienlijke vermindering van de methaanemissie ten gevolge hebben.

Implicaties van de onderzoeksresultaten De processtudies laten zien dat een afname van de methaanproductie niet altijd leidt tot een evenredige afname van de methaanemissie. Zowel methaanproductie als methaanoxidatie zijn afhankelijk van omgevingsfactoren en daarmee ook de methaanemissie, die de resultante van beide processen is. Dit moet in beschouwing worden genomen bij de ontwikkeling van strategieën om de methaanemissie uit natte rijstbouw te beperken maar ook bij extrapolatie van (laboratorium) experimenten naar veldemissies.

De observatie dat gedurende het droogvallen van de rijstvelden belangrijke methaanemissie optreedt betekent dat de seizoensemissie in eerder gepubliceerde studies waarschijnlijk onderschat is met 10-15%. Hoewel slechts een beperkt aantal bodemtypen en bodemfactoren onderzocht zijn, bieden de resultaten een wetenschappelijke basis om aan bepaalde bodemtypen een specifieke correctiefactor te hangen die recht doet aan hun capaciteit om methaan te produceren en te emitteren. Uiteindelijk moet dit leiden tot een beter onderbouwde schatting van de mondiale methaanemissie uit rijstvelden. Op basis hiervan kunnen in de toekomst gebieden met hoge emissies geselecteerd worden waar maatregelen om de methaanemissie te beperken relatief veel effect zullen hebben.

Summary

Methane (CH_4) is one of the principal greenhouse gases with an estimated contribution to the enhanced greenhouse effect of 15-20%. The atmospheric CH_4 concentration has more than doubled over the last century and shows a strong correlation with global population growth. To understand the observed trends, predict future atmospheric methane concentrations, and design cost-effective mitigation options an accurate budget of the sources and sinks of atmospheric CH_4 is required. To achieve this, uncertainties in individual CH_4 sources need to be reduced. Wetland rice fields are an important source of methane, accounting for approximately 20% of the global anthropogenic methane emission. In cooperation with the International Rice Research Institute (IRRI, Philippines) and the Fraunhofer-Institut für Atmosphärische Umweltforschung (IFU, Germany), CH_4 fluxes from wetland rice fields with different treatments were monitored in 1991 and 1992 with the so-called closed chamber technique. Results from field experiments investigating the influence of soil (type) related properties on CH_4 emission from rice fields are summarized below, Next, laboratory experiments with plants grown in the greenhouse to study two processes, plant-mediated CH_4 transport and rhizospheric CH_4 oxidation are summarized.

Effects of sulfate on CH_4 emissions from rice fields The methane emission from plots amended with 7 tons.ha^{-1} gypsum ($CaSO_4$) was reduced by 55-70% compared to emission from non-amended plots. The reduced CH_4 emission upon gypsum application was most likely due to inhibition of methanogenesis by sulfate-reducing bacteria. 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. Addition of gypsum is a common treatment on alkaline soils and may have a distinct influence on the production of methane in the soil by introducing large amounts of sulfate. The data indicate that CH_4 emissions from rice grown on high-sulfate containing soils or gypsum-amended soils is low compared to non or low-sulfate containing soils. However, fertilization of rice fields with $(NH_4)_2SO_4$ will not necessarily result in lower CH_4 emissions because the amounts of sulfate added are relatively low.

Impact of salinity on CH_4 emissions from rice fields Saline soils are widely distributed in arid and semi-arid areas and in coastal areas. An estimated 4-5 million ha of saline soils is grown to rice at present. The impact of salinity on CH_4 emission was studied in the 1992 dry season by adding salt to a Philippine rice paddy, increasing pore water

electrical conductivity to about 4 $dS.m^{-1}$. The addition of salt reduced CH_4 emissions by only 25%. Measurements of the potential CH_4 production with depth, however, showed that the CH_4 production in the salt-amended field was reduced more severely. Calculation of the percentage of the anaerobic CH_4 flux that was oxidized indicated that CH_4 oxidation in the salt-amended plot was even more inhibited than CH_4 production. The net result was about equal aerobic CH_4 fluxes from cores of salt-amended plots and non-amended plots. The data show that the ratio between CH_4 production and CH_4 oxidation may depend on environmental conditions. This illustrates the importance to consider both CH_4 production and CH_4 oxidation when estimating or modelling CH_4 emission. The reduction in CH_4 emission from rice paddies upon addition of non-sulfate salt is considerably smaller than the reduction in CH_4 emission observed in a similar study where fields were amended with sulfate containing salt. The results indicate that CH_4 emissions from wetland rice fields on saline, low-sulfate soils are lower than CH_4 emissions from otherwise comparable non-saline rice fields. However, the reduction in CH_4 emission is not proportional to the reduction in CH_4 production.

Emissions from rice grown on calcareous soils CH_4 emissions from rice grown on a calcareous soil were higher than from a non-calcareous soil. The seasonal pattern of CH_4 emission was different, with a more pronounced emission peak early in the season, probably due to the favourable pH for CH_4 production in the calcareous soil. However, in this study we could not distinguish the effect of calcareous material from the effect of a lighter texture since the calcareous soil was a sandy-loam and the control field a clay soil. The difference in emission between the two soil types was no longer observed when the fields were fertilized with green manure, indicating that here the "soil"-factor may be overruled by the input of organic matter.

Influence of organic amendments on CH_4 emissions from rice fields Application of green manure strongly stimulated CH_4 emissions. In plots that received more than 11 $tons.ha^{-1}$ of fresh green manure, CH_4 emission was highest during the first half of the growing season. This early emission drastically altered the seasonal emission pattern compared to the urea-fertilized control field. When CH_4 emission from organically-amended plots was expressed relative to emissions from mineral fertilizer-treated plots, the impact of organic amendments on CH_4 emission can be described by a dose-response curve. A single curve accounted for data from locations with different climates, soil types, and field managements. A correction factor is needed for composted and fermented organic matter to account for the lower percentage of easy decomposable carbon. To reduce CH_4 emission from rice fields, organic amendments should be minimized. However, this may conflict with soil fertility aspects as well as with the local availability of fertilizers. Compost has only a slightly stimulating effect on CH_4 emissions as opposed to straw or green manure amendments which greatly enhance CH_4 emissions. Therefore, stimulation of composting appears to be a promising mitigation option.

Release of entrapped methane upon drainage of wetland rice fields After harvest, the rice fields were still flooded but irrigation was stopped and the fields were allowed to evaporatively dry. While the fields were still flooded, CH_4 emissions continued at pre-harvest levels. Next, from all plots we observed a sudden, strong increase of CH_4 emissions to the atmosphere for 2 to 4 days just after the soil fell dry. As soil drying continued, the soils began to crack and CH_4 emissions decreased to nil. The release of CH_4 during soil drying was observed for fields on three different soil types and both for urea or organically manured rice fields in both seasons. The ratio between the amount of CH_4 released upon soil drying and CH_4 emitted during the growing season was quite constant for all treatments (0.10 ± 0.04). This suggests that about 10% of the CH_4 emitted during a full rice crop cycle is released during drying of the fields and thus needs to be included in estimates of the total CH_4 emission from rice agriculture. If soil drying occurs more than once, e.g., due to droughts and/or if the fields remain flooded for a considerable period after harvest, this figure may be higher.

Plant-mediated CH_4 transport In rice fields 80-90% of the CH_4 emission may be due to plant-mediated transport. A proper understanding of the CH_4 transport through the plant is essential for mechanistic modelling of CH_4 emission on a field scale. Based on the kinetic theory of gases an experiment was designed to test the hypothesis that plant-mediated CH_4 transport is driven by diffusion. CH_4 emission from rice reacted quickly (within 1-2 hours) to a change in the atmospheric composition, following the binary diffusion coefficients, showing that plant-mediated CH_4 transport is driven by diffusion. The results combined with data from the literature suggest that the rate limiting step in plant-mediated methane transport is diffusion of CH_4 across the root/shoot junction.

Rhizospheric CH_4 oxidation Methanotrophy is a major factor limiting CH_4 fluxes from wetlands and rice fields. In rice fields, methanotrophs occur and are active in the floodwater-soil interface and the rice rhizosphere. The significance of CH_4 oxidizing activity in the rice rhizosphere was investigated by using methyl fluoride (CH_3F) as a

specific inhibitor for CH_4 oxidation. CH_4 oxidation in the rice rhizosphere depended on the growth stage of the rice plant and became of much less importance when the rice plant reached the ripening stage. To investigate whether the CH_4 oxidizing activity in the rhizosphere was limited by O_2 availability, CH_4 emission was also measured from plants incubated under air, 100% N_2 or air with 40% O_2. Both in the early and late growth stages, incubation under a N_2 atmosphere enhanced the CH_4 flux much stronger than blocking of CH_4 oxidation alone. Apparently N_2 incubation not only blocked CH_4 oxidation but also stimulated methanogenesis in the rhizosphere. Incubation under 40% O_2 decreased the CH_4 flux indicating that rice varieties with enhanced rhizospheric oxidation may be low CH_4 emitters. The O_2 pressure in the rhizosphere is an important factor that reduces the plant-mediated CH_4 flux. The results differ substantially from high CH_4 oxidation rates (> 90% of CH_4 produced oxidized) reported in studies that assess CH_4 oxidation indirectly. Furthermore, seasonal patterns of CH_4 emission in rice fields do not only depend on changes in CH_4 production but also on changes in CH_4 oxidation.

Significance of the research results The results indicate that it is necessary to include the effect of soil characteristics on CH_4 emission when estimating the regional or global CH_4 source strength from flooded rice fields. Also, the observation that during soil drying considerable amounts of CH_4 may be released from flooded rice fields has implications for the estimated total CH_4 source strength. In previous monitoring studies these drying periods were not included, which may cause an underestimation of total seasonal emission by 10-15%. Process studies on production, oxidation and emission of CH_4 showed that a reduction in CH_4 production does not necessarily cause a proportional reduction in CH_4 emission. This is important when looking for mitigation options to reduce methane emission from rice fields.

CURRICULUM VITAE

Hugo Anne Cornelis Denier van der Gon werd geboren op 26 mei 1961 te Amsterdam. In 1979 behaalde hij het Atheneum-B diploma aan de Rijksscholengemeenschap "Schoonoord" te Zeist. In datzelfde jaar begon hij de studie Milieuhygiëne aan de Landbouwuniversiteit Wageningen. Gedurende de studie werden stages gedaan bij Ingenieursbureau TAUW te Deventer en bij het Laboratory for Wetland Soils and Sediments, Louisiana State University, Baton Rouge, U.S.A. In 1987 slaagde hij cum laude voor het doctoraalexamen Milieuhygiëne, specialisatie bodemverontreiniging, met als hoofdvakken Bodemverontreiniging en Hydrogeologie en een bijvak Ecopedologie. Na een half jaar aanstelling bij de vakgroep Bodemkunde en Geologie aan de Landbouwuniversiteit Wageningen vervulde hij van september 1988 tot maart 1990 zijn vervangende dienstplicht bij het Rijksinstituut voor Volksgezondheid en Milieuhygiëne. Hier deed hij onderzoek op het gebied van de vermesting en verzuring van bodem en grondwater bij het Laboratorium voor Bodem- en Grondwateronderzoek. Van maart 1990 tot september 1990 werd hij aangesteld bij het Laboratorium voor Bodem- en Grondwateronderzoek van het RIVM voor onderzoek naar de phytotoxiciteit en het sorptie- en desorptie gedrag van het bestrijdingsmiddel Paraquat. Vanaf september 1990 werkte hij als wetenschappelijk medewerker bij de sectie ecopedologie, vakgroep Bodemkunde en Geologie, Landbouwuniversiteit Wageningen op het project "invloed van bodemparameters op de methaanemissie uit natte rijstvelden", gefinancierd door het Nationaal Onderzoeksprogramma Mondiale Luchtverontreiniging en Klimaatsverandering (NOP-I). Het onderzoek vond plaats in samenwerking met en deels op het International Rice Research Institute (IRRI) op de Filipijnen. Vanaf oktober 1995 werkt hij als onderzoeker en coördinator aan het project "Upscaling and Downscaling of Regional Methane Sources -Rice agriculture as a case study", bij de vakgroep Bodemkunde en Geologie, Landbouwuniversiteit Wageningen, gefinancierd door de tweede fase van het Nationaal Onderzoeksprogramma Mondiale Luchtverontreiniging en Klimaatsverandering (NOP-II).

CURRICULUM VITAE

Hugo Anne Cornelis Denier van der Gon was born May 26 1961 in Amsterdam, The Netherlands. He started his study Environmental Sciences at the Wageningen Agricultural University, The Netherlands in September 1979. During his study he did practical periods at a Dutch consulting firm, TAUW and the Laboratory for Wetland Soils and Sediments, Louisiana State University, Baton Rouge, U.S.A. In 1987 he graduated from the Wageningen Agricultural University (cum laude) with specializations in soil pollution, soil formation and hydrogeology. After his study he worked for 6 months at the department of Soil Science and Geology, Wageningen Agricultural University on the construction of "living soil profiles" to illustrate soil formation. Next, he joined the National Institute for Public Health and Environmental Protection, Bilthoven, The Netherlands to work on acidification and eutrophication of Dutch soils and groundwater and sorption and desorption of the pesticide Paraquat on Dutch soils. In September 1990, he joined the department of Soil Science and Geology, Wageningen Agricultural University as a researcher on the project "Soil parameters influencing methane production and methane emission in/from rice paddies". The project was financed by the Dutch National Research Programme on Global Air Pollution and Climate Change (NRP-I) and resulted in this thesis. The majority of his research within this project took place in cooperation with and at the International Rice Research Institute (IRRI), The Philippines. Starting October 1995 he works as a researcher and coordinator on the project "Upscaling and Downscaling of Regional Methane Sources -Rice agriculture as a case study" financed by the second phase of the Dutch National Research Programme on Global Air Pollution and Climate Change (NRP-II). He is based at the department of Soil Science and Geology, Wageningen Agricultural University.