

# POTENTIAL OF METHANE EMISSION IN MAJOR RICE ECOLOGIES

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## 1. SUMMARY

Water regime, soil properties, and rice plants are major factors in the production and flux of methane in ricefields. Flooding, or at least saturation with water, is a prerequisite for the anoxic soil conditions needed to produce methane. Soil properties—mainly soil organic matter and iron oxide content, texture, and bulk density—govern the pattern of methane formation within floodwater regimes of each rice ecology. While production of methane is governed mainly by water and soil, emission is controlled and mediated mainly by rice. In flooded ricefields, methanogenesis is favored by anoxic conditions; the availability of organic matter from roots, stubbles, and the photosynthetic aquatic biomass; a soil pH near neutral; and soil temperatures between 20 and 30°C—during the rice-growing seasons. Soil temperature and soil pH do not limit methanogenesis but control its intensity. Most of the methane diffusing into the soil–water interface is oxidized. The extent to which methane production is enhanced by root exudates and methane is oxidized in the rhizosphere is still unknown.

Irrigated rice ecologies seem to be the major source of global methane emissions from ricefields. The assured supply and control of water, the intensive soil preparation, and the resultant improved growth of rice favor

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methane production and emission and mediate methane flux to the atmosphere. Methane emissions should be much lower in rainfed rice because of drought periods during the growing season and the poorer growth of rice. The variability of methane production and emission in space and time in this ecosystem should be very high. Upland rice is not a source of methane because upland rice is never flooded for a significant period of time.

## 2. INTRODUCTION

Recent atmospheric measurements indicate that concentrations of greenhouse gases are increasing. Atmospheric methane concentrations have increased with accelerating speed by about 1% annually to 1.7 ppmv during recent decades (Khalil and Rasmussen, 1987). The effect of this increase on global warming is highly significant because the warming efficiency of methane is 32 times that of carbon dioxide (Blake and Rowland, 1988; Dickinson and Cicerone, 1986). Data from polar ice cores indicate an approximately exponential increase in tropospheric methane concentrations over the past 300 years (Khalil and Rasmussen, 1989). The rate of increase of emission (Fig. 1) accelerated from the mid-1920s to 1950 and slowed down thereafter. The increase of methane concentrations in the troposphere correlates closely with global population growth and suggest a strong link to anthropogenic activities. The total annual global emission of methane is estimated to be 320–590 teragrams per year (Tg/year) (Bingemer and Crutzen, 1987; Cicerone and Oremland, 1988), 70–80% of which is of biogenic origin (Bouwman, 1990). Methane emissions from wetland rice agriculture have been estimated up to 170 Tg year<sup>-1</sup> which account for approximately 26% of the global anthropogenic methane budget. Flooded ricefields are the largest agricultural source of methane, followed by ruminant enteric digestion ( $\approx$  100 Tg/year), biomass

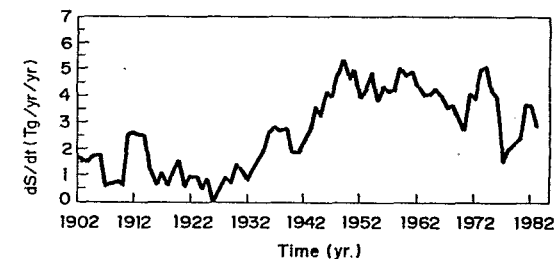


FIGURE 1. Rate of change of yearly methane emission over the last century. (After Shearer and Khalil, 1989.)

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related to climate, landform, floodwater regime, soil, and cropping system. Since submergence of soils causes methane formation through anaerobic decomposition of organic matter, floodwater regimes—and by that, rice ecologies—are the major discriminators for the potential of methane production. The potential of upland rice for methane production is not significant since upland rice is never flooded for a significant period of time. Irrigated rice has the highest potential for producing methane because flooding is assured. Floodwater control may allow temporary drainage and/or aeration of soils, especially if the water supply is fully controlled. The potential for methane production is rainfed rice widely varies in time and space since its floodwater regime is controlled primarily by rainfall within the watershed. Aside from the wide range of maximal floodwater depth, periods of severe droughts, and/or floods during the growing season are characteristic for rainfed rice.

The harvested area of each rice ecology determines the global methane emission. Table 2 gives the rice area harvested in different regions of the world.

Since the 1960s, rice production dramatically increased because of high-yielding rice cultivars, large investments in irrigation schemes, and improved

TABLE 2. Distribution of Harvested Ricelands (million ha) by Rice Ecology

Region	Irrigated	Rainfed	Deep-water	Upland	Total Area	Yield (t/ha)	Rough Rice Production (million tons)
East Asia <sup>a</sup>	34.0	2.8	—	—	36.8	5.4	200.0
Southeast Asia <sup>b</sup>	13.9	13.7	3.75	4.65	36.0	2.9	102.5
South Asia <sup>c</sup>	19.4	20.0	7.3	6.7	53.4	2.0	105.5
Near East <sup>d</sup>	1.25	—	—	—	1.25	3.3	4.1
South/Central America, Caribbean, United States	2.5	0.5	0.4	5.65	9.05	2.9	26.5
Africa	0.9	1.95	—	2.70	5.5	1.8	9.9
Former Soviet Union	0.66	—	—	—	0.66	4.1	2.7
Europe	0.42	—	—	—	0.42	5.4	2.3
Oceania	0.12	—	—	—	0.12	6.6	0.79
Australia	0.11	—	—	—	0.11	7.1	0.76
World	73.26	38.95	11.45	19.70	143.36	3.2	455.05

<sup>a</sup>China, Taiwan, Korea DPR, Korea RP, Japan.

<sup>b</sup>Cambodia, Indonesia, Laos, Malaysia, Myanmar, Philippines, Thailand, Vietnam.

<sup>c</sup>Bangladesh, Bhutan, India, Nepal, Pakistan, Sri Lanka.

<sup>d</sup>Afghanistan, Iran, Iraq.

Source: IRRI (1988).

soil, water, and pest management. The assured supply of irrigation water and the shorter growth duration of most modern cultivars increased the area cropped to rice twice a year. However, expansion of residential and industrial areas as well as diversification of crops resulted in only a slight increase in total harvested area of rice (Fig. 2). Although many factors determined the relative contribution of each rice ecology to rice supplies in the future, irrigated areas will continue to dominate rice production. At present, about 50% of the harvested area is grown to irrigated rice but it contributes about 70% to total production. In the last decades, rice production has been improved in all rice ecologies, but the expansion and improved technology of irrigated rice have especially increased methane emissions.

#### 4. METHANOGENS

As strict anaerobes, methanogens are sensitive to O<sub>2</sub> (< 10 ppm). Oxygen causes an irreversible dissociation of the F<sub>420</sub>-hydrogenase enzyme complex probably because of the lack of protective superoxide dismutase (Schönheit et al., 1981). Methanogens are found in strictly anaerobic environments of aquatic freshwater, brackish and marine sediments, hot springs, midocean ridges, decomposing algal mats, heartwood of living trees, intestinal tracts of humans and animals (especially the rumen of herbivores), and sewage digesters. Methanogenesis occurs in the anoxic water of meromictic lakes (Winfrey and Zeikus, 1979; Oremland and DesMarais, 1983) and possibly in the anoxic water of deepwater rice.

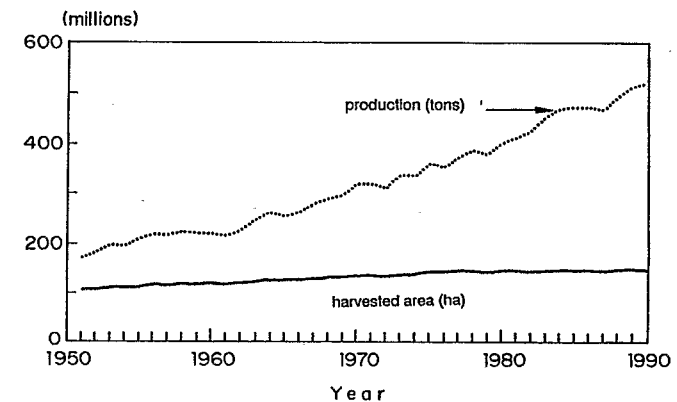


FIGURE 2. Global rough rice production and harvested area.

The taxonomy and ecology of methanogens were recently reviewed by Garcia (1990). More than 18 genera of methane-producing bacteria have been described, but only a few, including *Methanobacterium* and *Methanosarcina*, have been isolated from rice soils (Rajagopal et al., 1988). Information summarized from Garcia's review (1990) in Table 3 indicates that *Methanospirillum*, *Methanocorpusculum* (which were isolated from freshwater sediments) as well as methanogens found as endosymbionts in sapropelic ameba should also be present in wetland ricefields.

The distribution of methanogens in natural environments depends on their adaptation to temperature, pH, and salinity ranges. They can grow from 4 to 97°C. Most methanogens grow over a relatively narrow pH range of 6–8. No acidophilic strains have been reported; however, methanogenesis was observed in acidic peat bogs (Williams and Crawford, 1984). Alkaliphilic species with a growth optimum at pH 8–9 have been reported in the genus *Methanobacterium* (Blotvogel et al., 1985; Worakit et al., 1986).

The anaerobic degradation of organic matter involves four major steps:

- Hydrolysis of polymers by hydrolytic organisms
- Acid formation from simple organic compounds by fermentative bacteria
- Acetate formation from metabolites of fermentations by homoacetogenic or syntrophic bacteria
- Methane formation from H<sub>2</sub> and CO<sub>2</sub>, acetate, simple methylated compounds or alcohols, and CO<sub>2</sub>

Methanogenesis in sediments is characterized by a complete degradation of organic matter while in the rumen of ruminants and the intestine of most animals. Mineralization is incomplete since intermediate products are absorbed as food. According to Garcia (1990), methanogenic bacteria use a wide range of substrates:

- *Hydrogenotrophic methanogens* (~75% of the described species) oxidize H<sub>2</sub> and reduce CO<sub>2</sub> to form methane. Hydrogen availability is a key factor for methanogenesis (Abram and Nedwell, 1978; Oremland and Taylor, 1978; Strayer and Tiedje, 1978). According to Conrad et al. (1985), H<sub>2</sub>-dependent methanogenesis in sediments results mostly from H<sub>2</sub> transfer between microbial associations within flocks or consortia.
- *Methylotrophic methanogens* (~25% of the species) can use methyl compounds as methanol, methylamines, or dimethylsulfide; some are obligately methylotrophs.

TABLE 3. Simplified Classification of Methanogenic Bacteria and Their Habitats

<i>Methanobacteriales</i>	
Methanobacteriaceae <i>Methanobacterium</i>	Various freshwater habitats; half of the species are thermophilic; a few are alkaliphilic
<i>Methanobrevibacter</i>	Specialized habitats such as trees (Zeikus and Henning, 1975), rumen (Smith and Hungate, 1958), sewage sludge, intestinal tracts of animals (Miller and Wolin, 1985)
<i>Methanosphaera</i>	Feces or digestive tracts of animals (Biavati et al., 1988)
Methanothermaceae <i>Methanothermus</i>	Extreme thermophile from volcanic springs
<i>Methanococcales</i>	
Methanomicrobiaceae <i>Methanococcus</i>	Isolated mostly from marine or coastal environments
<i>Methanomicrobiales</i>	
Methanomicrobiaceae <i>Methanolacinia</i>	Marine sediments
<i>Methanospirillum</i>	Mesophilic strains from various habitats
<i>Methanoculleus</i>	
<i>Methanocorpusculum</i>	Sewage sludge, lacustrine sediments (Zhao et al., 1989)
Methanoplanaceae <i>Methanoplanus</i>	Symbiont of marine ciliate
Methanosarcinaceae <i>Methanosarcina</i>	Freshwater and marine sediments, rumen, lagoons, and anaerobic sewage-sludge digestors
<i>Genera Not Ascribed to a Family</i> (Mostly Isolated from Salted Biotopes)	
<i>Methanolobus</i> and <i>Methanococcoides</i>	(Sowers and Ferry, 1983)
<i>Methanohalophilus</i>	(Paterek and Smith, 1988; Mathrani et al., 1988)
<i>Halomethanococcus</i>	(Yu and Kawamura, 1987)
<i>Methanohalobium</i>	(Zhilina and Zavarzin, 1987)
<i>Methanotherix</i>	(Macario and de Macario, 1987)
<i>Methanopyrus</i>	Methanogenic archaeobacteria growing at 110°C (Huber et al., 1989)

Source: Adapted from Garcia (1990).

- *Acetotrophic methanogens* (~10% of the species) utilize acetate. The growth of virtually all methanogens is stimulated by acetate. Its importance as methane precursor in sediments has earlier been documented (Cappenberg, 1974; Cappenberg and Prins, 1974; Winfrey and Zeikus, 1977).

Most of the hydrogenotrophic species that are neither methylotrophic nor acetotrophic also use formate. Few species use  $H_2$  to reduce methanol in methane (hydrogenomethylotrophic methanogens); others can form methane in the presence of  $CO_2$  and alcohols as hydrogen donors (alcoholotrophic methanogens). The importance of methanol and methylated amines as methane precursor in sediments varies with the abundance of decomposing plant materials such as algal mat (King, 1988). Methanogens can use  $H_2$ ,  $CO_2$ , formate, or acetate produced by fermentative bacteria either directly or in obligate association (syntrophy) with obligate  $H_2$ -producing acetogenic bacteria. This phenomenon of "interspecies  $H_2$ -transfer" (Ivanotti et al., 1973) has been observed with few genera of bacteria that require syntrophy with methanogens for the oxidation of fatty acids, benzoic acid, and fructose. In the absence of the  $H_2$  scavenger, the reaction is endogenic and cannot develop. When  $H_2$  is consumed by the methanogen, the reaction becomes exogenic and the syntroph can oxidize the substrate and grow. All methanogens use  $NH_4^+$  as a N source and a few species are known to fix molecular nitrogen (Belay et al., 1984; Murray and Zinder, 1984).

A variety of chemical substances can physiologically inhibit methanogenesis. They have been reviewed by Oremland and Capone (1988). It seems that hydrogenotrophic homoacetogens do not compete significantly with methanogens for  $H_2$  in sediments (Lovley and Klug, 1983). Mineral terminal electron acceptors such as nitrate or sulfate inhibit methanogenesis in sediments by channeling electron flow to thermodynamically more efficient bacteria such as denitrifiers or sulfate reducers (Balderston and Payne, 1976; Ward and Winfrey, 1985). In anaerobic environments, methanogens, sulfate reducers, and homoacetogenic bacteria compete for  $H_2$  produced by fermentative bacteria. Since  $H_2$  concentration is usually very low in such environments (Strayer and Tiedje, 1978), sulfate reducers are able to outcompete hydrogenotrophic methanogens in the presence of sulfate because of their higher affinity for  $H_2$  and faster growth (Winfrey and Zeikus, 1977; Abram and Nedwell, 1978).

Methanogenesis and sulfate reduction are not mutually exclusive when methane is produced from methanol and/or methylated amines, for which sulfate reducers show little affinity (Oremland et al., 1982; Oremland and

Polcin, 1982). This occurs in saline environments where degradation of osmoregulatory compounds as glycinebetaine produces methylamines (King, 1984). Methanol is formed during anaerobic decomposition of plant pectins (Schink and Zeikus, 1980).

## 5. PROPERTIES OF FLOODED RICE SOILS THAT AFFECT METHANOGENESIS

Flooded soils can be grouped with regard to water regime. The duration of flooding and saturation are appropriate criteria. Saturation can be caused by groundwater (aquic moisture regime) or surface water (epiaquic moisture regime). Neue (1989) characterized a typical soil profile of a flooded rice soil during the middle of a growing season as follows:

1. *Horizon Ofw*. A layer of standing water that becomes the habitat of bacteria, phytoplankton, macrophytes (submerged and floating weeds), zooplankton, and aquatic invertebrates and vertebrates. The chemical status of the floodwater depends on the water source, soil, nature, and biomass of aquatic fauna and flora, cultural practices, and rice growth. The pH of the standing water is determined by the alkalinity of the water source, soil pH, algal activity, and fertilization. Because of algae growth and aquatic weeds, the pH and  $O_2$  content undergo marked diurnal fluctuations. In daytime, pH may reach > 10, and the standing water becomes oversaturated with  $O_2$  as a result of photosynthesis in the aquatic biomass. Standing water stabilizes the soil water regime, moderates the soil temperature regime, prevents soil erosion, and enhances C and N supply.
2. *Horizon Apox*. The floodwater-soil interface that receives sufficient  $O_2$  from the floodwater to maintain  $pE + pH$  above the range where  $NH_4^+$  becomes the most stable form of N. The thickness of the layer may range from several millimeters to several centimeters depending on pedoturbation by soil fauna and the percolation rate of water.
3. *Horizon Apg*. The reduced puddled layer is characterized by the absence of free  $O_2$  in the soil solution and a  $pE + pH$  low enough to reduce iron oxides.
4. *Horizon Apx*. This layer has increased bulk density, high mechanical strength, and low permeability. It is frequently referred to as the "plow pan" or "traffic pan."
5. *Horizon B*. The characteristics of the B horizon depend highly on water regime. In epiaquic moisture regimes, the horizon generally remains oxidized, and mottling occurs along cracks and in wide pores. In aquic

moisture regimes, the whole horizon or at least the interior of soil peds remains reduced during most years.

The chemistry and biology of rice soils have been frequently reviewed (Ponnamperuma, 1972, 1981, 1984, 1985; Patrick and Reddy, 1978; De Datta, 1981; Yu, 1985; Patrick et al., 1985; Watanabe and Roger, 1985; Roger et al., 1987; Neue, 1988).

Flooding an air-dried cultivated soil drastically changes the hydrosphere, atmosphere, and biosphere of that soil. Flooding highly limits the diffusion of air into the soil. The  $O_2$  supply cannot meet the demand of aerobic organisms and facultative and anaerobic organisms proliferate by using oxidized soil substrates as electron acceptors in their respiration. Consequently, the redox potential falls sharply according to a sequence predicted by thermodynamics and  $CO_2$  and  $HCO_3^-$  concentrations increase to very high levels. As a result, the pH of acid soils increases, while that of sodic and calcareous soils decreases. The pH may finally stabilize between 6.5 and 7.2. Flooding and puddling render most soils in an ideal growth medium for rice by supplying abundant water, buffering soil pH near neutral, enhancing  $N_2$  fixation, and increasing diffusion rates, mass flow, and availability of most nutrients. In less favorable soils, flooding may result in toxicities of Fe,  $H_2S$ , or organic acids, or deficiencies of Zn or S.

The anaerobic fermentation produces an array of organic substances, many of them transitory and not found in aerobic soils. The major gaseous end products are  $CO_2$ ,  $H_2S$ , and  $CH_4$ . The amount and pattern of  $CH_4$  produced depends highly on soil properties.

The description of the paddy soil profile clearly indicates that methane formation mainly takes place in the reduced Apg horizon. In aquatic moisture regimes the B horizon may become a source of methane. Carbon contents of B horizons are generally low, and B horizon organic matter is less degradable. In epiaquic moisture regimes methane oxidation may predominate in the B horizon. The same holds true for the Apox layer. Harrison and Aiyer (1913) had already established that all methane diffusing into the aerobic surface layer is oxidized. This was reconfirmed by Bont et al. (1978). They found that 10 ml of a suspension of paddy soil oxidized 2 ml of methane within 24 h when incubated aerobically. Methane may also be oxidized in shallow floodwater since it is often oversaturated with  $O_2$  as a result of assimilation of the aquatic flora.

Floodwater of deepwater ricefields has been recently shown to become anoxic during the crop cycle (Whitton and Rother, 1988). Considering the large quantity of organic material available from rice culms and nodal roots in deepwater ricefields, their floodwater may be an environment permitting methanogenesis.

## 6. TEMPERATURE REGIMES OF TROPICAL RICE SOILS

Rice is grown under widely differing temperature regimes. The temperature of flooded soils at planting may range from  $15^\circ C$  in northern latitudes to  $40^\circ C$  in equatorial wetlands. Rice physiologists have studied extensively the effects of air and water temperature on rice growth characteristics (Yoshida, 1981; Matsushima et al., 1964a, 1964b), but there is only little information on the temperature regimes of flooded rice soils and their effects on the chemistry of the soils (Kondo, 1952; Cho and Ponnamperuma 1971; Gupta, 1974, Sharma and De Datta, 1985). Holzapfel-Pschorn and Seiler (1986) reported a marked influence of soil temperature on the methane flux with doubling of emission rates at a temperature increase of  $20-25^\circ C$ . Diurnal variation of methane emission is correlated with temperature (Schütz et al., 1989). Acharya (1935) found the optimum temperature for methane formation to be  $30-35^\circ C$ .

In flooded conditions, soil temperature varies in response to the meteorological regime acting on the atmosphere-floodwater and floodwater-soil interfaces. The changing properties of soil and floodwater (i.e., temporal changes in reflectivity, heat capacity, thermal conductivity, incoming water temperature, and water flow) as well as vegetation interact with these external influences. Hackman (1979) reported that floodwater temperatures are above minimum air temperature but below maximum air temperature if daily amplitudes of air temperature are high, while water temperatures are above maximum air temperatures if daily fluctuations are low.

Neue (1988) reported that floodwater temperature in Philippine ricefields always exceeded ambient air temperature and showed lower daily fluctuations. The temperature of the puddled layer closely followed the temperature of the floodwater and decreased with depth. The annual mean soil temperature at 2:00 p.m. was  $33^\circ C$  at 7-cm depth, and its daily maximum equaled or exceeded the maximum air temperature on most days.

Floodwater transmits shortwave radiation to the soil while reducing the upward escape of emitted longwave radiation. Thus a "greenhouse effect" is produced, heating floodwater and soil. Diurnal temperature amplitudes of floodwater are highly moderated because of the high heat capacity of water, and because evaporation of water consumes energy from the floodwater but not directly from the soil. The high thermal conductivity of flooded soils, in which the bulk densities may be reduced to only  $0.2-0.5 \text{ g/cm}^3$  by puddling, enhances the downward conduction to the dense layer. Dissolved and suspended particles and aquatic biomass in the floodwater change the absorption of radiation, and depth of floodwater changes the heat capacity. The temperature of both floodwater and soils may rise above  $40^\circ C$  in bare soils with muddy floodwater of shallow depth. Floodwater temperature is lowered by

canopy shading, flow of water, and through rainfall. In ricefields where standing floodwater has been drained for transplanting or seeding, soil temperature may reach 50°C in the top centimeter because of increased heat absorption and reduced heat capacity, thermal conductivity, evaporation, and ventilation.

Aselmann and Crutzen (1990) computed monthly distributions of global methane emissions from linearly temperature-dependent methane fluxes in the range of 300–1000 m/g<sup>2</sup> daily for temperatures of 20–30°C and constant emission of 300 m/g<sup>2</sup> per day for temperatures below 20°C. Emissions of methane in the Northern Hemisphere reveal low monthly values (1.5–3 Tg) in December to April and a bell-shaped distribution between May and November with a clear peak of about 16.5 Tg in August. The Southern Hemisphere reveals the highest emission rates ( $\approx$  2 Tg) in the months of February and March. The largest sources where computed between 20 and 30°N (southern China, northern India, Pakistan, Bangladesh, northern Myanmar) with 37.6 Tg/year, followed by 10–20°N (southern India, southern Myanmar, Thailand, Cambodia, Laos, Vietnam, northern and central Philippines, Brunei, Kalimantan) with 22.4 Tg/year, 30–40°N (central China, Japan, Korea) with 8 Tg/year, 0–10°S with 6.5 Tg/year (most of Indonesia) and 0–10°N (Sri Lanka, Malaysia, southern Philippines, Brunei, Kalimantan) with 4.8 Tg/year. Although rice ecologies have not been differentiated explicitly, the computed distribution of emission rates clearly reflects the importance of irrigated rice ecologies (double- and triple-cropped areas may account for irrigated rice).

## 7. ORGANIC MATTER

Easily degradable organic substrates are the main source of methane in wetland rice soils. The net primary production of wetland rice soils (Table 4) has been deduced from yield statistics and estimates of aquatic biomass and weed growth during fallow periods.

In 1988, the world rough rice production was 477 million tons. Of these, upland rice contributed about 28 million tons. The 124 million of wetland rice therefore produced 449 million tons of rough rice. With a shoot:grain ratio of 3:2 (Ponnamperuma, 1984) and a root:shoot ratio of 0.17 (Yoshida, 1981; Watanabe and Roger, 1985), total dry-matter production of wetland rice amounts to 1123 million tons. Adding 74 million tons of dry matter of aquatic biomass [600 kg/ha  $\times$  season (Roger and Watanabe, 1984; Watanabe and Roger, 1985)] and 200 million tons of weed dry matter [2 t/ha (t = tons) during fallow periods (Buresh and De Datta, 1991)], amounts to a total dry-matter production of 1512 million tons or 1220 g/m<sup>2</sup> per year. It is

TABLE 4. Annual Net Primary Production in Wetland Rice Fields

Source	Dry Weight (million tons)	Returned to Soil	
		%	(million tons)
Wetland rough rice	449	—	—
Wetland rice straw <sup>a</sup>	674	15	101
Wetland rice roots <sup>b</sup>	115	100	115
Aquatic biomass (algae, weeds)	74	100	74
Fallow weeds	200	50	100
Total	1512	26	390

<sup>a</sup>Shoot:grain ratio = 1.50.

<sup>b</sup>Root:shoot ratio = 0.17.

assumed that, on an average, 15% of the straw, 50% of the weeds, and all roots and aquatic biomass (amounting to 390 million tons of dry matter or 156 million tons of carbon) are returned to the soil. If a maximum of 30% of the returned carbon is transformed to methane [as found by Neue (1985) in studies with <sup>14</sup>C-labeled straw in soils prone to methane formation], 62.4 Tg of methane would be globally produced in wetland ricelands annually.

The input of degradable organic carbon is probably higher as a result of organic amendments. Reliable data on amounts of organic manures added are missing. Based on the content of easily degradable carbon, humified substrates, like compost, should produce less methane per unit carbon, while green manures should produce more. Application of compost did not remarkably enhance methane emission, while application of rice straw significantly increased methane emission irrespective of soil type (Yagi and Minami, 1990).

Although the use of organic amendments is propagated to sustain soil resources, actual application of organic substrates into wetland rice fields seems to be declining. In China, the production of green manure (Fig. 3) increased sharply after 1960 and peaked sometime in the 1970s (13.2 million ha), followed by a steep decline to only 6.6 million ha in 1987 (Stone, 1990). In Japan, the decline of green manure cultivation started already in the 1950s (Fig. 4). According to Kanazawa (1984), the total addition of organic substrates to ricefields in Japan decreased from 6 t in 1965 to 2.7 in 1980.

From long-term yield trials in the Philippines, a relation among soil C content, N fertilizer rates, and rice grain yields was established. The optimum C content in puddled and flooded soils was found to be 2–2.5%, corresponding to 0.20–0.25% total N (Neue, 1985, Smith et al., 1987). Since almost 90% of the tropical soils studied by Kawaguchi and Kyuma (1977) had less than the optimum total N content, moderate organic amendments seem to be

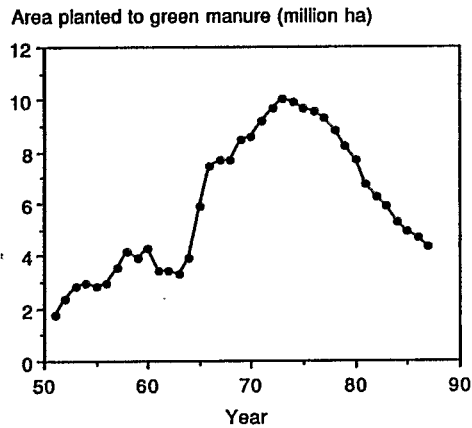


FIGURE 3. Area planted (million hectares) to green manure in China (1952–1987). (Redrawn from Stone, 1990).

essential to sustain or increase soil fertility and rice yields. In some instances, the returned net primary production of organic matter seems to be sufficient. Organic amendments of wetland ricefields should be limited to essential inputs and be replaced by chemical fertilizers to reduce methane formation.

## 8. ORGANIC MATTER DECOMPOSITION

The rate and course of organic matter decomposition are decisive for the rate and pattern of methane formation. Anaerobic fermentation produces an array

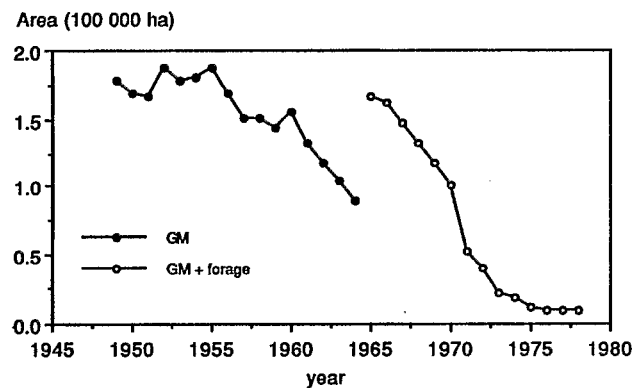


FIGURE 4. Extent of *Astragalus sinicus* cultivation in Japan. (After Watanabe, 1984.)

of organic substances, many of them transitory and not found in well-aerated soils. Ponnampertuma (1984) listed various gases, hydrocarbons, alcohols, carbonyls, volatile fatty acids, nonvolatile fatty acids, phenolic acids, and volatile S compounds. Methanogens constitute the last step in the electron transfer chain generated by the anaerobic degradation of organic matter. Submergence of soils retards initial decomposition of rice straw in the field only slightly compared with upland soils (Neue and Scharpenseel, 1987; Neue, 1988). The rate of decomposition decreases with soil depth (Neue, 1985). Decomposition of the remaining, more resistant metabolites and residues is similar, with half-lives of about 2 years in all soils and water regimes if the following conditions for flooded soils are met:

- Soil is intensively puddled each cropping season.
- Soil temperature of the puddled layer is 30–35°C
- Neutral pH.
- Low soil bulk density and high soil:water ratio.
- Shallow floodwater.
- High and balanced nutrient supply.
- No long-lasting accumulation of organic acids.
- Permanent supply of energy-rich photosynthetic aquatic and benthic biomass.
- High diversity of micro- and macroorganisms that provide successive fermentation down to CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>, and NH<sub>3</sub>.
- Supply of O<sub>2</sub> into the reduced layer by rice root excretion and oligochaete population.
- Diurnal oversaturation of the floodwater with O<sub>2</sub> due to photosynthetic aquatic biomass enhancing the aeration function of oligochaetes.

Decomposition is retarded in wetland rice soils with low and imbalanced nutrient supply, high bulk density, and low biological diversity and activity, as demonstrated in the Aeric Paleaquult of Northeast Thailand (Snitwongse et al., 1988). If the biological activity is restricted to bacterial soil fauna, as in laboratory experiments, the decomposition of rice straw in flooded soils is highly retarded (Capistrano, 1988). Only 7–18% of the incorporated straw was decomposed after 100 days following the order San Manuel clay loam (pH 6.6), > Maahas clay loam (pH 5.5), > Luisiana clay (pH 4.9). These results clearly demonstrate the high limitations of laboratory incubation studies.

Methane production occurred within hours after wet incubation of an alkaline soil (pH 8.2, organic C 1.5%, CEC 10.2 meq/100 g). In a calcareous soil (pH 7.4, organic C 1.6%, CEC 30.4 meq/100 g) methane production

reached its maximum at about 2 weeks. In an acid soil (pH 4.0, organic C 2.6%, CEC 17.9 meq/100 g) methane production was delayed and peaked after 5 weeks only (Fig. 5). In very acid soils, methane may not be formed at any time. Short-term  $H_2$  evolution immediately follows the disappearance of  $O_2$  after flooding. Thereafter,  $CO_2$  production increases, and finally, with decreasing  $CO_2$ , methane formation increases (Takai et al., 1956; Neue and Scharpenseel, 1984). Methane is also preceded by the production of volatile acids. Addition of organic substrates enhances the fermentation process. With increasing temperature up to  $35^\circ C$ , decomposition starts earlier and is more vigorous in every case. At high temperatures, the formation of  $CO_2$  and  $CH_4$  occurs earlier and is stronger (Yamane and Sato, 1961). The period of occurrence and the amount of the gaseous products and volatile acids depend largely on temperature and reducing conditions.

The ratio of  $CO_2$  and  $CH_4$  formation is regulated by the ratio of the oxidizing capacity (amount of reducible  $O_2$ ,  $NO_3^-$ ,  $Mn^{+4}$ , and  $Fe^{+3}$ ) to the reducing capacity (Takai, 1961). The actual capacity is influenced highly by  $O_2$  diffusion from the atmosphere, floodwater, and plant roots; the soil bulk density (soil:water ratio); and fertilization. Methanogenesis is reduced, but emission of methane is enhanced in the presence of tubificidae (earthworms) in topsoil, which enlarge the aerobic top layer. Less methane and higher accumulation of volatile acids are found in soils with higher bulk density (lower soil:water ratio). Methanogenesis is markedly inhibited by brackish water (Garcia et al., 1974; De Laune et al., 1983; Holzappel-Pschorn et al., 1985; Bartlett et al., 1987). Inhibitory effects and interactions with sulfate-

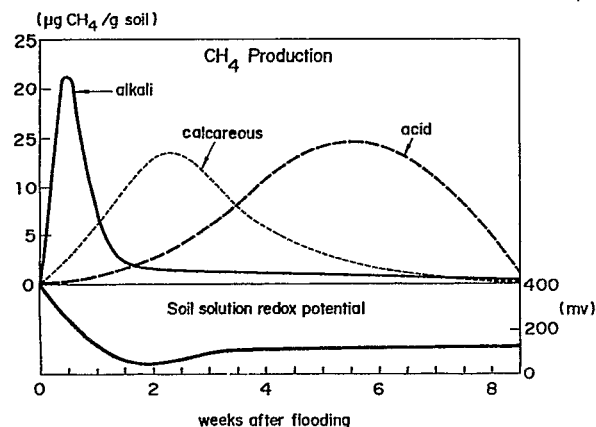


FIGURE 5. Methane formation in alkaline, calcareous, and acid soils.

reducing bacteria are given as possible reasons (Mitsch and Gosselink, 1986). Competition for  $H_2$  and toxicity of sulfide are possible mechanisms.

Consecutive addition of organic substrates through plant growth and photosynthetic biomass production in the floodwater maintains the fermentation chain. The low specific activity of methane produced after adding  $^{14}C$ -labeled rice straw in field experiments (IRRI, 1981) was likely caused by degradation of newly produced photosynthetic biomass and root exudates. In permanently flooded soils, methane is produced in significant amounts only after addition of organic substances.

In wetland rice soil, the potential for methane production is also high because the degree of humification is less, the content of  $H_2$  and N and degree of unsaturation are lower, and the content of carboxyl and phenolic groups is lower; on the other hand, alcoholic and methoxyl groups are higher (Kuwatsuka et al., 1978; Tsutsuki and Kuwatsuka, 1978; Tsutsuki and Kumada, 1980). Humification indices in flooded soils, given as the ratio of non-humified to humified materials (Sequi et al., 1986), are high (low humification) in topsoils and decrease with depth. Very acid rice soils have more humified materials.

Submergence is often equated with retarded decomposition of organic matter. But wetland rice soils in the tropics fall into wet soils with high temperature in all seasons, which show rapid mineralization and weak humification (Bonneau, 1982).

## 9. REDOX POTENTIAL

The supply of biodegradable carbon and the activity of the edaphon are the key to most of the characteristic biochemical and chemical processes in flooded soils (Neue, 1988). These processes include soil reduction and associated electrochemical changes; N immobilization and fixation; production of an array of organic compounds, especially organic acids; and release of  $NH_4^+$ ,  $CO_2$ ,  $H_2S$ , and  $CH_4$ . Since methane is produced only by strictly anaerobic bacteria (methanogens), a sufficiently low redox potential is required.

The magnitude of reduction is determined by the amount and decomposition rate of easily degradable organic substrates and the amounts and kinds of reducible nitrates, iron and manganese oxides, sulfates, and organic compounds. A rapid initial decrease of  $E_h$  after flooding in most soils is caused by high decomposition rates of organic substrates and a low buffer of nitrates and Mn oxides. The most important redox buffer systems in rice soils are Fe(III) oxyhydroxides/Fe(II) and organic compounds stabilizing the  $E_h$  level somewhat between +100 and -100 mV in most soil solutions. Measurements in the bulk soil may reveal  $E_h$  values as low as 300 mV because of direct

contact with reduced surfaces of soil particles. The most important interacting chemical changes after flooding an air-dried acid soil are shown in Figure 6.

Although the reduction of flooded soils proceeds stepwise in a thermodynamic sequence, the given oxidation-reduction systems (Ponnamperuma, 1972; Patrick and Reddy, 1978) are only partially applicable to field conditions. The mineral phases present in soils are not pure and are seldom known, and a large portion of reduced  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  ions are held at ion-exchange sites (Tsuchiya et al., 1986). Changes in pH and activities of reactants and resultants can also alter the order of redox reactions. As a consequence, reduction potentials of a given redox reaction span a fairly wide range. The soil  $E_h$  also varies between microsites in a soil. Nevertheless, redox potentials (corrected to pH 7) of at least  $-150$  mV seem to be needed for the formation of methane.

Chemical reactions that are favored thermodynamically are not necessarily favored kinetically. The lack of effective coupling and the slowness of redox reactions mean that catalysis is required if equilibrium is to be attained. In soils, the catalysis of redox reactions is mediated by microbial organisms. Equilibrium is dependent entirely on the growth and ecological behavior of the soil microbial population and the degree to which the reagents and products can diffuse and mix. Soil organisms are important with regard to

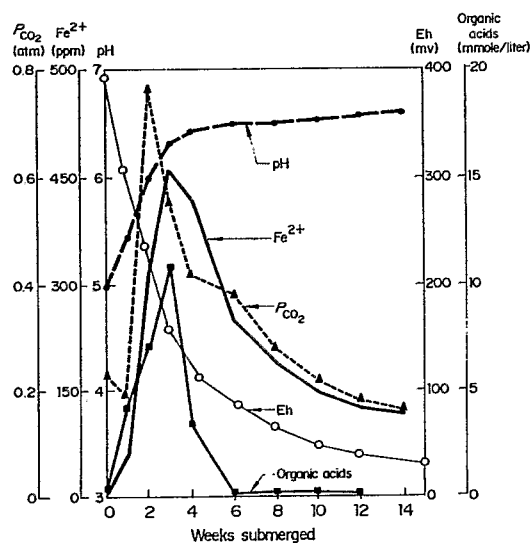


FIGURE 6. Kinetics of pH,  $E_h$ ,  $P_{\text{CO}_2}$ , water-soluble  $\text{Fe}^{2+}$ , and organic acids in the soil solution of a flooded ultisol at  $30^\circ\text{C}$ . (Adapted from Ponnamperuma, 1985.)

kinetic aspects of redox by affecting the rate of a redox reaction but not its standard free-energy change (Sposito, 1981).

Katyal (1977) demonstrated the acceleration and intensification of  $E_h$  and pH change with the addition of plant residues. The effect of vetch, which has a narrow C:N ratio, was greater than that of rice straw (Yu, 1985). Changes were more profound when organic substrates were added to soil low in organic matter (Nagarajah et al., 1989). Increasing the soil bulk density of flooded soils retards organic matter decomposition, increases the concentration and residue time of organic acids, and reduces the speed of  $E_h$  and pH changes as well as methane formation.

Soils low in active iron with high organic matter attain  $E_h$  values of  $-200$  to  $-300$  mV within 2 weeks after submergence (Ponnamperuma, 1972). In soils high in both iron and organic matter, the  $E_h$  may rapidly fall to  $-50$  mV but then slowly decline over weeks or level off. Soils having a ferritic, ferruginous, or oxidic mineralogy and/or a strong acidic or allic reaction are less prone to methane formation (Neue et al., 1990). The partial pressure of  $\text{CO}_2$  directly influences  $\text{CH}_4$  production since  $\text{CO}_2$  is a carbon source for methane. It affects  $\text{CH}_4$  production indirectly because the accumulation of  $\text{CO}_2$  coupled with the formation of  $\text{HCO}_3^-$  buffers the pH near neutral in all flooded soils.

The increase of pH of acid soils is initially brought about by soil reduction of Fe oxyhydroxides. The pH decrease of sodic and calcareous soils and the final regulation of the pH rise in acid soils are the results of  $\text{CO}_2$  accumulation. The pH values at steady state of flooded alkaline, calcareous, and acid soils are highly sensitive to the partial pressure of  $\text{CO}_2$ . Carbon dioxide that accumulates in large amounts profoundly influences the chemical equilibria of almost all divalent cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ ) in flooded soils as well as methane formation. Parashar et al. (1991) found highest emission rates of  $\text{CH}_4$  at a pH of 8.2. Acharya (1935) reported that the preliminary stage of acid formation is more tolerant of pH reactions, but gas formation is greatly impeded outside the pH range 7.5–8.

Up to  $2.6$  t  $\text{CO}_2/\text{ha}$  is produced in the puddled layer during the first few weeks of flooding (IRRI, 1964). After addition of organic substrates, the partial pressure of  $\text{CO}_2$  in a flooded soil may reach a peak of almost  $100$  kPa (Neue and Bloom, 1989; Ponnamperuma, 1985). Typical values in flooded soils range of  $5$ – $20$  kPa (Kundu, 1987; Patra, 1987). Carbon dioxide concentrations  $> 15$  kPa retard root development, leading to wilting and reduced nutrient uptake (Dent, 1986).

At soil temperatures found in flooded tropical soils,  $\text{CO}_2$  and  $\text{CH}_4$  formation occur sooner and in larger amounts than in cooler climates (Tsutsuki and Ponnamperuma, 1987). The amount of  $\text{CH}_4$  found in the soil solution and in

gas bubbles of flooded soils may be up to 3 times higher than that of  $\text{CO}_2$  after the initial stage of flooding (Martin et al., 1983). The change in favor of  $\text{CH}_4$  is likely caused by assimilation of  $\text{CO}_2$  and precipitation of carbonates rather than reduction of  $\text{CO}_2$  to  $\text{CH}_4$ , but the controlling processes still need elucidation. According to Takai (1970), the bulk of  $\text{CH}_4$  is formed through decarboxylation of acetic acid, which would result in a 1:1 ratio of  $\text{CO}_2$  and  $\text{CH}_4$  formation.

## 10. RICE CULTIVARS

Rice plants play an important role in the flux of methane. Up to 90% of the methane released from the rice soil to the atmosphere is emitted via the rice plant (Bont et al., 1978; Seiler, 1984; Holzappel-Pschorn et al., 1986). The aerenchyma and intracellular space of rice plants mediate the transport of  $\text{CH}_4$  from the reduced soil to the atmosphere (Raimbault et al., 1977). However, up to 80% of the methane produced is apparently oxidized in the rhizosphere (Holzapfel-Pschorn et al., 1985).

The aerenchyma of rice plants acts as a chimney, but the transport mechanisms have still to be elucidated. The well-developed airspaces in leaf blades, leaf sheath, culm, and roots provide an efficient gas exchange between the atmosphere and the anaerobic soil. Atmospheric  $\text{O}_2$  is supplied via the aerenchyma to the roots for respiration. Oxygen diffusion from rice roots seems to constitute an important part of the roots, oxidizing power aside from enzymatic oxidation due to  $\text{H}_2\text{O}_2$  production. Large cultivar differences in the amount of  $\text{O}_2$  released from rice roots have been found (Yoshida, 1981). Because of the abundance of methane-oxidizing bacteria present in the rhizosphere, its potential for methane oxidation is very high. At tillering, Bont et al. (1978) counted in the rhizosphere 10 times more methane-oxidizing bacteria than those in the bulk anaerobic soil and one-third more than those in the oxidized soil-water interface. They found significant increases in  $\text{CH}_4$  emission of IR36 when  $\text{CH}_4$  oxidation is suppressed with acetylene at the soil-water interface. However, acetylene had only a small effect on emission rates when applied to the rhizosphere (Fig. 7). Bont et al. (1978) concluded that the utilization of  $\text{O}_2$  by reduced substances and microbial activity in the root-soil interfacial region exceeds the supply of  $\text{O}_2$  by the root. Consequently, the aerobic zone surrounding the root is too thin to get the diffusing  $\text{CH}_4$  oxidized or the rhizosphere is, for the most part, anaerobic.

Rice plant may not only mediate the flux of  $\text{CH}_4$ , their root exudates and degrading roots may be an important source for  $\text{CH}_4$  formation, especially at later growth stages.

Large cultivar differences in oxidation power (Yoshida, 1981) and emis-

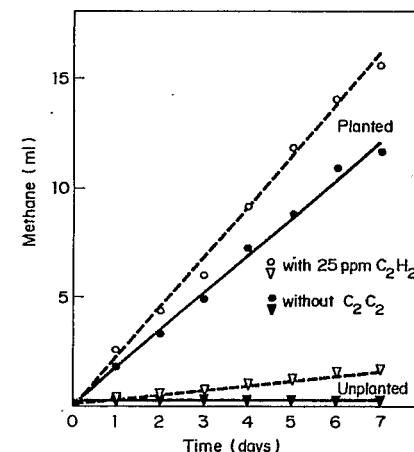


FIGURE 7. Effect of rice plants and methane oxidizing bacteria on  $\text{CH}_4$  emission. (After Bont et al., 1978.)

emit less methane. The inheritance of underlying traits still has to be elucidated.

## 11. CONCLUSION

Irrigated ricefields provide an ideal environment for methanogenesis because of high, easily degradable carbon inputs, anaerobic conditions, and optimum temperature for methane-producing bacteria. The environment also provides favorable conditions for methane fluxes because of the "chimney effect" of the rice plant.

The high carbon input in rice soils due to a high primary production by the crop, the photosynthetic aquatic biomass, and organic amendments favor methane emission from ricefields. Methane from ricefields may contribute about one-fourth of the global anthropogenic methane emission.

Mitigation technologies are required in the long term to stabilize atmospheric methane concentration. Possible methods include reducing inputs of easily degradable carbon, increasing methane oxidation, reducing emission pathways through the selection of adequate rice varieties, and preventing or reducing anaerobiosis through intermittent aeration. However, such technologies should be environmentally and socioeconomically sound, and acceptable to farmers.

During the last two decades, emphasis has been placed on the potential of biological nitrogen fixation as an alternative source of N and the recycling of organic materials as a source of nutrients for crops. Such technologies increase organic matter inputs in soils and favor methane emission from wetland ricefields. Sound technologies have to consider both maintaining or increasing soil fertility and reducing methane emission.

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