Journal of Scientific & Industrial Research
Vol. 63, February 2004, pp. 101-115

Emission of methane from rice fields — A review

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Methane (CH_4) with its current concentration of 1.72 ppmV in the atmosphere accounts for 15 per cent of the enhanced greenhouse effect. The atmospheric concentration of CH_4 is increasing at 0.3 per cent/y. Lowland rice soil is considered to be one of the major contributors of atmospheric methane. Various soil, climate, and management factors control methanogenesis, the geochemical process that occurs in all anaerobic environments in which organic matter undergoes decomposition, resulting in the formation of CH_4. Methane formed in soil escapes to the atmosphere through vascular transport, ebullition or diffusion. Emission of CH_4 from rice fields can be reduced by: (i) Midseason drainage instead of continuous flooding, (ii) Use of cultivars with low emission potential, (iii) Use of low C:N organic manure, and (iv) Direct establishment of rice crop like dry direct seeded rice.

Keywords: Global warming, Lowland rice soil, Methane emission, Mitigation options, Soil properties

Introduction

Methane (CH_4) is one of the important greenhouse gases accounting for 15 per cent of the total enhanced global warming[1]. Its concentration in the atmosphere has increased from 0.7 ppmV in the pre-industrial time to 1.72 ppm V at present and is increasing at 0.3 per cent/y (ref. 2). The residence time of this gas in the atmosphere is relatively short (10 y) as compared to that of other greenhouse gases (GHG), such as CO_2 (100 y) and N_2O (170 y) (ref. 3). Therefore, reduction of the global methane sources offers possibilities for curtailing the increasing trend of global warming on a short time scale. Lowland rice fields are one of the main anthropogenic sources of CH_4[1,4]. The waterlogged condition in rice field creates an anoxic environment, which is conducive for CH_4 production by the anaerobic methanogenic bacteria[5]. In order to meet the demand of teaming population, the world's annual rice production needs to be increased by 65 per cent over the next three decades or an increase of 1.7 per cent /y (ref. 6). In south Asia, rice production has to be doubled by the year 2020. Therefore, CH_4 emission from rice fields is a matter of concern.

Methane as a Natural Gas

Methane is the simplest hydrocarbon with a tetrahedral shape having four hydrogen atoms covalently linked to one central carbon atom. It is a colourless and odourless gas with a wide distribution in nature. At room temperature, it is less dense than air. Its melting and boiling points are: –183 and –164°C, respectively, and is sparingly soluble in water (17 mg/L at 35°C). Methane is combustible and a mixture of about 5 to 15 per cent in air is explosive. It is not toxic when inhaled, but it can produce suffocation by reducing the concentration of oxygen. Methane is synthesized commercially by the distillation of bituminous coal and by heating a mixture of carbon and hydrogen. It can be produced in the laboratory by heating sodium acetate with sodium hydroxide and by the reaction of aluminum carbide (Al_4C_3) with water.

Migeotte[7], who observed strong absorption bands in the IR region of electromagnetic spectrum, caused by atmospheric CH_4, discovered the presence of CH_4 in the atmosphere. In the early 1970s, Ehhalt and Heidt[8] had measured vertical profiles of CH_4 concentration in the atmosphere of Northern hemisphere and reported that CH_4 had nearly a uniform distribution in the troposphere with an average concentration of 1.41 ppmV. Ehhalt[9] subsequently showed a latitudinal gradient of CH_4 concentration with a lower value, about 1.3 ppmV, in the Southern hemisphere than that of in the Northern hemisphere. From these measurements, it was recognized that a total amount of about 4 Pg (Pg = 10^{15} g) of CH_4 was present in the atmosphere and the CH_4 cycle contributed 1 per cent to the atmospheric carbon cycle.

Beginning 1980s the evidence that the concentration of atmospheric CH_4 had rapidly increased, was reported

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by time-series measurements of the atmospheric components at many different locations[10]. Measurements on ice cores at Byrd Station and Dye, both in Antarctica, showed that atmospheric methane concentration was about 0.35 ppmV at 20,000 y BP (≈ last glaciation) in comparison with a mean pre-industrial level of about 0.7 ppmV and the current atmospheric concentration of methane around 1.72 ppmV.

Methane in the atmosphere interacts with planetary IR radiations and acts as one of the potential greenhouse gases contributing significantly to the global warming[5]. Donner and Ramanathan[11] have calculated that the presence of 1.5 ppmV of CH_4 in the atmosphere caused the globally average surface temperature to be about 1.3K higher than it would be with no CH_4 in the atmosphere. According to Thompson *et al.* [12], the global temperature increase could be reduced by 25 per cent if CH_4 emissions could be stabilized. It is predicted that by the year 2100 methane levels may rise by 3.0 to 4.0 ppmV (ref.13). Therefore, it is of concern that the increasing concentration of CH_4 may exerts significant effect on the global heat balance, causing an elevation of the global temperature.

Sources and Sinks of Atmospheric CH_4

A wide range of natural and anthropogenic sources of atmospheric CH_4 are identified (Table 1). Total annual global emission of CH_4 is estimated to be about 535 Tg (Tg = 10^{12} g) (ref. 5), about 70 per cent of which is of anthropogenic origin[14]. Fossil fuel burning, cattle and rice fields are the major sources of anthropogenic CH_4. However the strength of individual source is still highly uncertain and wide variation among different estimates is due to lack of direct measurements and extreme temporal and spatial variability in CH_4 emission from different natural and anthropogenic sources.

The major sink[15] for atmospheric CH_4 is the reaction with OH radical in the troposphere the concentration of which is controlled by a complex set of reactions involving CH_4, CO, NOx, and tropospheric O_3. Microbial oxidation of atmospheric CH_4 in the soil is the only known biological sink process that consumes up to 10 per cent of the total global emission[16]. However, land

Table 1 —Estimates of global sources and sinks of atmospheric methane (Tg CH_4/y)

Sources/sinks	IPCC (1994)	
	Emission range	Emission average
Natural		
Wetlands	55-150	115
Termites	10-50	20
Oceans, fresh water	5-50	15
Others	10-40	15
Total	110-210	160
Anthropogenic		
Fossil fuel (coal/gas production/ distribution)	70-120	100
Cattle	65-100	85
Rice paddies	20-100	60
Other sources		
Biomass burning	20-80	40
Landfills	20-70	40
Animal waste	20-30	25
Domestic sewage	15-80	25
Total	300-450	375
Total Identified sources	410-660	535
Total Sinks	430-600	515
Atmospheric increase	35-40	37

Source: ref.118

management, nitrogen fertilizers, and acidity significantly affect the sink strength.

Wetland Rice Fields as a Source of CH_4

Rice fields have been considered to be one of the most important sources of CH_4 emission. The potential for CH_4 release from rice fields was noted by Harrison and Aiyer as early as in 1913 (ref. 17). The first *in situ* measurement of the CH_4 flux was done in California, the US by Cicerone and Shetter[18], followed by extensive studies in other parts of the world. The field experiments stressed the importance of rice plant as a conduct pipe for CH_4 transport from soil to the atmosphere. At present the CH_4 source strength of wetland rice fields is estimated at 60 Tg/y, with a range of 20 – 100 Tg /y. However this estimate is still tentative and efforts are being made to make it more realistic. International Panel on Climate Change (IPCC) has started a worldwide campaign to update the inventory of CH_4 emission from various sources.

Methanogenesis

Methanogenesis the biological formation of CH_4, is a geochemically important process that occurs in all-anaerobic environments in which organic matter undergoes decomposition. The biogenic CH_4 results from the metabolic activities of a small and highly specific bacterial group, which are terminal members of the food chain in their ecosystem and are called methanogens. Methane is produced by the reduction of soil organic carbon by methanogens under strict anaerobic conditions having redox potential of less than –150 mV. When soil is under oxidized environment, aerobic decomposition occurs with the consequent release of carbon dioxide.

Anaerobic conditions occur in wetland rice fields as a result of soil submergence[5]. Water saturation of soil limits the transport of O_2 into the soil. Under this anaerobic condition, microorganisms start using alternative electron acceptors in their respiration causing further soil reduction. The redox potential drops sharply in a sequence, eventually leading to methanogenesis. The sequence of the redox reactions is given below[20]:

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \qquad -475\text{kJ}$$

$$CH_2O + 4NO_3^- \rightarrow 4HCO_3^- + CO_2 + 3H_2O + 2N_2 \qquad -448\text{kJ}$$

$$CH_2O + 2MnO_2 + 3CO_2 + H_2O \rightarrow 2Mn^{++} + 4HCO_3^- \qquad -349\text{ kJ}$$

$$CH_2O + 4Fe(OH)_3 + 7CO_2 \rightarrow 4Fe^{++} + 8HCO_3^- + 3H_2O \qquad -114\text{ kJ}$$

$$2CH_2O + SO_4^- \rightarrow H_2S + 2HCO_3^- \qquad -77\text{ kJ}$$

$$2CH_2O + H_2O \rightarrow CH_4 + CO_2 + H_2O \qquad -58\text{ kJ}$$

The sequence is strictly in accordance with the yield of free energy. The process of soil reduction tends to stabilize the soil pH near neutral, which is optimal for methanogenesis[21]. High salinity and sulphate concentration increase competitive interactions of sulphur reducing bacteria and methanogens[22]. Application of organic manure and fertilizers, and submergence with deep water increase the population and activities of methanogenic bacteria in the paddy soils[23].

Under anaerobic and reduced conditions, methanogens produce CH_4 from either the reduction of CO_2 with H_2 (hydrogenotrophic) or from the fermentation of acetate to CH_4 and CO_2 (aceticlastic)[24]. In nature the later mechanism accounts for about two-third of the CH_4 emission from soil. Under steady-state conditions in anoxic rice fields the aceticlastic pathway is dominant and accounts for about 75-80 per cent of the total CH_4 emitted[25]. These bacteria being strictly anaerobic, convert fermentation products formed by other microorganisms, notably CO_2, H_2, esters, and salts of methanoic acid (HCOOH) into CH_4, but other substrates may be used as well[5]. The reactions with reference to the type of methanogens involved in forming CH_4 as an end product are given below[26].

a) H_2 reduction of CO_2 by chemoautotrophic methanogens:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

b) Several strains of methanogens can also use HCOOH or CO as a substrate for producing CH_4 in addition to CO_2 and H_2:

$$4\,HCOOH \rightarrow CH_4 + 3\,CO_2 + 2\,H_2O$$

$$4\,CO + 2\,H_2O \rightarrow CH_4 + 3\,CO_2$$

c) Methane can also be produced by methylotrophic methanogens, which use methyl-group containing substrates such as methanol, acetate and trimethylamine:

$$4\,CH_3OH \rightarrow 3\,CH_4 + CO_2 + 2\,H_2O$$

$$CH_3COOH \rightarrow CH_4 + CO_2$$

$$4\,(CH_3)_3N + 6\,H_2O \rightarrow CH_4 + 3\,CO_2 + 4\,NH_3$$

Methane Consumption

There are some aerobic microsites in rice soils which function as sinks for CH_4. Such transformation of CH_4 to CO_2 by the oxidation process is carried out by methanotropic bacteria[27]. Conrad and Rothfuss[28] have observed that about 80 per cent of the potential diffusive CH_4 flux through the soil-water interface was oxidized in the oxic surface layers. The oxidation pathway is represented below:

$$CH_4 \xrightarrow{\text{Monoxygenase}} CH_3OH \xrightarrow{\substack{\text{Methanol}\\ \text{dehydrogenase}}} HCHO \xrightarrow{\substack{\text{Formaldehyde}\\ \text{dehydrogenase}}} HCOOH \xrightarrow{\substack{\text{Formate}\\ \text{dehydrogenase}}} CO_2$$

Methanotrophs are a subset of physiological group of methylotrophs, which utilize a variety of one-carbon compounds. Some of the microorganisms responsible for the oxidation of CH_4 are strictly aerobic, obligate methylo- or methano-trophic eubacteria. These microorganisms can use CH_4 and other C_1-compounds such as methanol as substrates. Papen and Rennenberg[26] illustrated the reactions as follows:

$$CH_4 + NADH + H^+ + O_2 \xrightarrow{(a)} CH_3OH + NAD^+ + H_2O$$

$$CH_3OH + PQQ \xrightarrow{(b)} CH_2O + PQQH_2$$

$$CH_2O + NAD^+ + H_2O \xrightarrow{(c)} HCOOH + NADH + H^+$$

$$HCOOH + NAD^+ \xrightarrow{(d)} CO_2 + NADH + H^+$$

Where (a) methane-monooxygenase; (b) methanol-dehydrogenase; (c) formaldehyde-dehydrogenase; (d) formate-dehydrogenase; and PQQ = pyroquinoline quinone (methotaxin).

Some aerobic chemoautotrophic NH_4^+ - oxidizers can also use CH_4 in addition to ammonium as a substrate[26]:

$$CH_4 + O_2 + XH_2 \xrightarrow{(e)} CH_3OH + H_2O + X,$$

where (e) ammonia mono-oxygenase; X and XH_2: coenzyme and co-substrate in the reduced and oxidized form, respectively.

Ammonium could possibly inhibit the oxidation of CH_4 by constraining the availability of O_2. However, Paul *et al.*[29] have reported that methane oxidation was stimulated by the application of ammonium-based fertilizers. Sulphate is the only apparent oxidant present in the anaerobic sediments, which causes a significant removal of CH_4 under these conditions.

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O$$

Processes Regulating the Transfer of CH_4 from Soil to the Atmosphere

Vascular Transport

Methane is emitted from paddy fields mostly by transport through rice plant[30]. Rice plants act as bundles of chimneys to transport CH_4 from the rhizosphere to the atmosphere. Aerenchyma helps in transport of O_2 and some other gases in several aquatic plants like rice. The path of CH_4 through the rice plants includes diffusion into the root, conversion into gaseous CH_4 in the root cortex, diffusion through cortex and aerenchyma, and release to the atmosphere through micropores in the leaf sheath[31, 32]. Methane transport capacity of rice plant is dependent mainly on plant aerenchyma size. The concept of plant mediated transport as the predominant mechanism for the emission of CH_4 from the rice fields is strengthened by comparative measurements in rice planted and un-planted soils[33]. Schutz *et al.*[30] have observed that as the rice plants grew, there was an increase not only in the contribution of plant mediated CH_4 emission, but also the percentage of produced CH_4 that was oxidized and hence not emitted. A shift in the CH_4 transport pathway was observed by Wang *et al.*[34], about 50 per cent of the CH_4 was released from the leaf blades before shoot elongation, whereas only a small amount was emitted through leaves as plants grew older. In addition to the presence of micropores on leaf sheath, Wang *et al.*[34] have identified cracks in junction points of internodes. Although CH_4 can also be released through panicles, but this pathway is negligible as long as leaves and nodes were not submerged. CH_4 emission rates increased linearly as the number of nodal culms increased, indicating an effective proportionality between number of culms and release sites. Nouchi *et al.*[35] have reported that CH_4 was mostly released from the culms of rice plants.

Ebullition

Many researchers have identified ebullition of gases entrapped in sediments and peats as a possible form of CH_4 release to the atmosphere. The ebullition process could be influenced by many factors like wind speed, floodwater temperature, solar radiation, flood water level, local water table, and atmospheric pressure[36]. The contribution of ebullition to total CH_4 emission[37] is not more than 20 per cent. It has been observed that fields without rice plants emit 50 per cent methane of the amount of CH_4 emitted by the fields planted with rice. The emissions from the un-planted fields were almost exclusively due to ebullition[30]. In Japan, Takai and Wada[33] had observed that CH_4 ebullition is important during the early stage of flooding, when rice plants are small, whereas vascular transport becomes more important as the rice plants get older.

Diffusion

The diffusion of gases in water is 10^4-times slower than in air, so that the exchange of gases almost stops when soils are waterlogged. The actual diffusion of CH_4 from rice fields is a function of CH_4 supply to the floodwater, CH_4 concentration in the floodwater and prevailing wind speed[38]. Diffusion through the floodwater is usually less than 1 per cent of the total flux[39]. It is suggested that the rate-limiting step in plant-mediated CH_4 transport is the diffusion of CH_4 across the root/shoot junction[40].

Temporal and Spatial Variation in CH_4 Emissions

Generally, CH_4 emission in a given location shows strong diurnal and seasonal variations whose pattern changes from year to year. Methane oxidation by methanotrophs in rice paddies, i.e., an *in situ* sink, shows pronounced seasonal variation[41]. In the early vegetative period, about 50 per cent of the methane produced might be oxidized, increasing to as much as 90 per cent. Integrated measurements over a full growing period in Texan paddies indicate that 58 per cent of total methane produced is oxidized. The seasonal variation of CH_4 emission depends on various factors like growing stage of rice, temperature, day-length, solar radiation, humidity, water regime, fertilization, and weed population. Holzapfel-Pschorn and Seiler[42] have found strong dependence of day-length on CH_4 emissions in an Italian paddy. The seasonal variation of CH_4 fluxes from a Japanese paddy field was mainly related to the variations in CH_4 production in these fields[43]. Schutz *et al.*[30] had observed two maxima in CH_4 production corresponding with the early vegetative period of the rice crop grown in Hongzhou Province in China. During the early vegetative period, maximum CH_4 emissions occurred at noon and at night while the CH_4 emissions peaked only in the night during the late vegetative period. It is due to less O_2 being transported to the root system of rice plants at night so that CH_4 oxidation would be reduced, resulting in higher net emissions[44]. The temporal and spatial variations of CH_4 production are related to rice root biomass, which might be seen as a function of cultivar and soil dependent property[45]. Kanno *et al.*[46] have observed that CH_4 emission was more in gley soil than those from other soil types such as, andosol, upland soils, fine textured lowland soils, medium, and coarse-textured lowland soils and gravelly lowland soils. Wang *et al.*[47] have concluded that soil temperature and CH_4 concentration in the soil solution are the two major factors controlling diel methane emissions. Laboratory incubation of soil cores showed that methanogenesis was the highest near the soil surface in the rice row and decreased gradually with depth and distance from the rice plant[45], so that plant density might form a possible source of spatial variation in CH_4 emissions from paddy fields.

Estimates of CH_4 Emission

The estimates on CH_4 emission from rice fields have varied considerably over time. Koyama[48] has estimated global source strength of rice paddies to be 190 Tg CH_4/y. Later on Enhalt and Schimdt[49] have estimated it to be 280 Tg/y. Cicerone and Shelter[18] gave the revised estimates for CH_4 emission at 59 Tg CH_4/y. Another estimate of the global emission of methane from rice fields is in the range of 30-70 Tg/y based on various model calculations by different groups[50]. The recent estimates of the International Panel for Climate Changes (IPCC) using SRES scenarios are around 300 Tg in 2000, and between 400 and 600 Tg in 2010 (ref..51). Average methane emissions from the different countries are given in Table 2. Measurements in rice paddies in various locations of Asia show that there are large temporal variations of CH_4 emissions differing markedly with climate, soil and paddy characteristics, fertilizers applied, organic matter and other agricultural practices. These observations indicate the average emission range of methane flux from 18.4-1540 kg/ha/y. Further CH_4 emission was as low as 4 kg/ha/y in IRRI, Philippines and the highest being 2110 kg/ha/y in Shenyang, China. Neue[50] has reported that irrigated, rainfed and deep-water rice contribute 75, 22, and 3 per cent of the total global CH_4 emission from rice fields, respectively. Most of the CH_4 emitted from rice fields is expected to be from Asia, as it has 90 per cent of the total world rice harvested area, out of which about 52 per cent is in China and India[52].

Table 2 — Seasonal methane emission from rice fields in different countries

Location	CH_4 kg/ha	No. of observation	Average kg/ha	Ref.
Philippines	49-414	71	175	119, 72
Vietnam	252-500	3	336	53
China	36-610	108	256	70, 120, 78
Indonesia	37-646	48	161	82
Thailand	24-167	20	49	77
Korea	269-424	4	367	106, 121
Japan	30-790	18	182	46,122
Australia	336-1848	4	810	113

The methane emission values from Indian soils in Table 3.

CH_4 Emission Studies in India

The estimates of CH_4 budget from Indian paddy fields are of special significance as India has 42.2 million ha of land under rice cultivation, of which 16.4 million ha is irrigated and the remaining is rainfed (19.7 and 5.9 million ha lowland and upland, respectively).

Several studies have been conducted on CH_4 emission from rice fields in India (Table 3). The seasonal CH_4 emissions were observed to be 16-630, 4-109, 37-530, and 0.1-1650 kg/ha in eastern, central, southern, and northern India, respectively. Wide variations in CH_4 emission are due to variations in soil organic carbon, texture, pH, and other physico-chemical properties and different agronomic practices, including fertilizer and water management and cultivar of rice used at these locations. In 1991, the US Environment Protection Agency (USEPA)[13] reported that 37.8 Tg/y of CH_4 was emitted from rice growing regions of India. A broad measurement campaign (1989-1991) covering selected rice growing regions of India[53], however, indicated a very low source strength ranging from 3.64±1.26 Tg/y (Table 4). According to Watson *et al.*[1], CH_4 emission from rice paddies in India is 2.4-6 Tg/y. However, more recently it has been estimated that total methane emission from Indian rice fields is 2.9 Tg/y. In India, range of CH_4 flux values varied between 0.20-3.6, 0.04-6.6 and 1.1-23.3 mg/m²/h for irrigated and intermittently flooded, flooded and deep-water rice fields, respectively (Bhatia Arti, Pathak H & .Aggarwal P K, 2003, communicated). These estimates, however, require further refinements because of uncertainties caused by scarcity of flux measurements data from larger areas, gaps in the knowledge of rice ecologies, the impact of soil types, crop management and lack of data on *in situ* CH_4 oxidation.

Factors Regulating CH_4 Emission

Methane production and consumption in soil are biologically mediated processes. Therefore, CH_4 emission from rice fields is affected by prevalent weather conditions, water regime, soil properties and various cultural practices like irrigation and drainage, organic amendments, fertilization, and rice cultivars.

Temperature

Temperature plays an important role in the rate of activity of soil microorganisms including those involved in CH_4 production and consumption. According to Van Hulzen *et al.*[54], temperature influences CH_4 production by regulating anaerobic carbon mineralization, availability of alternative electron acceptors and methanogenic activity. At higher temperature,, mineralization increases and more carbon substrate becomes available, resulting in faster depletion of the alternative electron acceptor pool. However the influence of temperature on CH_4 production is mainly through its effect on methanogenic activity. Yagi and Minami[41] have found very little methanogenesis between 5 and 15°C in Japanese paddy fields. According to Neue and Scharpenseel[55], most of the methanogenic bacteria display optimum rates of CH_4 production at around 30°C. Inubushi *et al.*[56] have found that high temperature, especially above 30°C, enhances CH_4

Table 3— Seasonal methane emission from rice fields at different locations in India

Location	CH_4 (kg/ha)	No. of observations	Average	Ref.
Garia, West Bengal	126-290	2	208	123
Purulia, West Bengal	110	1	110	123
Nadia, West Bengal	108	1	108	123
Barrackpore, West Bengal	18-630	3	222	123
Jorhat, Assam	460	1	460	123
Gabberia, West Bengal	145-462	2	305	123
Cuttack, Orissa	16-257	40	89	126, 123
Bhuvaneshwar, Orissa	140-186	2	163	123
IARI, New Delhi	10-221	55	43	102, 123
Andhava, Allahabad, UP	5.2	1	5	123
Kumarganj UP	20	1	20	123
Maruteru, AP	150	1	150	123
Madras	110-182	2	149	123
RRL, Trichur	37	1	37	123
RRL, Trivendrum	90	1	90	123
Kuttanad	530	1	530	123
Kasindra Gujarat	120	1	120	123
Pant Nagar	54-114	4	79	123
Karnal	64-100	2	81	123
BHU, Varanasi	0.1-261	12	126	124
Raipur	4-109	6	34	83
Ludhiana	452-1650	5	875	125

Table 4 — Methane budget estimates from Indian rice paddy fields using Indian methane emission data and Methane Asia Campaign (MAC)

1998 studies data

Rice ecosystem	Category	Sub-category	Aeration frequency	Harvested area (Mha)	Emission (g/m^2)	Seasonal integrated flux (g/m^2)	Total Emission (Tg/y)
Upland				6.35			
Lowland	Rainfed	Flood prone		4.23	16 (10-20)	19±6.0	0.8±0.25
		Drought prone		6.77	8 (0-10)	7.3±2.3	0.49±0.16
	Irrigated	Continuously flooded		6.77	20	15.6±6.3	1.06±0.43
		Intermittently flooded	Single aeration	9.92	10 (4-14)	7.3±2.3	0.72±0.23
			Multiple aeration	5.74	4 (2-6)	1.58±0.74	0.091±0.04
Deep water		Water depth 50-100 cm		2.54	16 (12-20)	19.0±6.0	0.48±0.15
Total							3.64±1.26

Source : Ref. 53

formation. Holzapfel-Pschorn and Seiler[42] have observed almost double rates of CH_4 emission when the soil temperature rose from 20 to 25 °C, corresponding with a Q_{10} (temperature quotient, relative increase in activity after an increase in temperature of 10 °C) of about 4. Wassmann *et al.*[57] have reported that the incubation at 30 and 35°C increased CH_4 production rates following the Arrhenius equation. Temperature also affects CH_4 transport through the rice plant[58], as there is a positive correlation between soil temperature at –5 cm and plant conductance for CH_4 [ref. 59]. Daily variations of CH_4 emission in rice fields are related with temperature variations during the day.

pH

The activity of methanogens is very sensitive to variations in soil pH. Most of the methanogens are neutrophilic, hence CH_4 production is most efficient in a pH range between 6.5 and 7.5. Wang *et al.*[60] have observed highest CH_4 production rates at pH 6.9 to 7.1 and small change in pH sharply lowered CH_4 production. Below pH 5.8 and above 8.8, CH_4 production in the soil suspension was almost completely inhibited. Studies in clay soils in Texas showed that CH_4 emission was four times lower in the most acidic soil with low structural stability.

Redox Potential (Eh)

Methanogenesis can only occur in a strictly anaerobic condition. A sufficiently low redox potential (*Eh*) is required for CH_4 production and *Eh* is negatively related to CH_4 emission[61]. In soils with high contents of Fe and organic matter, *Eh* falls to –50 mV and may then slowly decline over a period of a month to –200 mV. Soils, low in active-Fe with high organic matter contents, attain *Eh* values of –200 to –300 mV within 2 weeks after submergence [62]. Flooded rice soils may have *Eh* values as low as –250 to –300 mV, while *Eh* (corrected to pH 7) of –150 mV to –190 mV are needed for CH_4 formation[60]. However, several researchers reported that the range of *Eh* is not a good indicator for the onset of methanogenesis in general and should only be used when the soil and its CH_4 production behaviour have been carefully characterized [63]. Hou *et al.*[64] have suggested that both zymogenic bacteria number and soil redox potential appear to be predictors of CH_4 emission potential. There are reports that CH_4 production in freshly flooded rice soils is initiated much earlier than generally expected [65]. In spite of high *Eh* values the reason for this early initiation of CH_4 production in some soils could be due to the presence of enough viable methanogenic archaea in the air-dried soils[66]. *Eh* value from –200 to –300 mV induces a ten-fold increase in CH_4 production and a 17-fold increase in its emission[67].

Organic Substrates

Application of organic matter such as, manure and crop residues enhances methanogenesis[68]. Yagi and Minami[41] have found a positive correlation between the annual emission rate of CH_4 and the contents of readily mineralizable carbon in pre-cultivated paddy soils. The amount of CH_4 formed in paddy soils is positively correlated with soil organic-C and water-soluble organic C (ref. 56). Yagi and Minami[41], on the contrary, have found no correlation between CH_4 production rates and total carbon contents in soils. Wang *et al.*[19] have also observed no correlation with soil organic C and water soluble C, suggesting that other factors such as, bacterial population and oxidizing capacity of the soil were important in controlling CH_4 production. Organic matter incorporation favoured more CH_4 emission during the dry season when rice biomass is higher, than during the wet season[69]. Methane production and emission decrease when the C content and the C/N ratio of the incorporated material decrease.

Lu *et al.*[70] have reported that in irrigated rice fields in southeast China, incorporation of organic amendments promoted CH_4 emission. CH_4 emission from fields where biogas residue was applied was 10-16 per cent lower than those given the same quantity (based on N content) of pig manure. Majumdar *et al.*[71] have observed that incorporation of rice straw in the soil increased CH_4 production by 1.2–7.9 -times over that of unammended soil.

Wassmann *et al.*[72] have observed 34-times higher CH_4 fluxes with application of straw than those with urea. Similarly, in Indonesian paddy fields, CH_4 emission increased 1.3-1.6-times by rice straw application[73]. In another study incorporation of rice straw in soil increased methane emission by 51 per cent, and application of rice straw on soil surface by 34 per cent[74]. Application of green manure (*Sesbania rostrata*) gave 3-fold increase in emission as compared with urea treated plots. Methane emission rate from plots receiving a larger quantity of green manure was higher than from plots receiving the normal quantity of green manure during the early rice vegetative development period, while at later rice development stages the reverse was true[75]. According to Adhya *et al.*[76] have organic amendments in conjunction with chemical N (urea) affected higher CH_4 flux over that of chemical N alone. Chaareonsi *et al.*[77] have studied the CH_4 emissions from deepwater rice as affected by different crop management practices. Methane emission from deepwater rice was highest with straw incorporation (83-619 kg CH_4/ha), followed by straw compost incorporation (145 kg CH_4/ha), zero tillage with straw mulching (100-127 kg CH_4/ha) and least with straw ash incorporation (60-69 kg CH_4/ha).

Ying *et al.*[78] have reported that growing *Azolla* as a dual crop could enhance CH_4 emission from rice fields due to mediation of CH_4 transport from floodwater of rice soil into the atmosphere. Due to the presence of *Azolla,* chemical properties of soil could also be modified, stimulating CH_4 production and decreasing *in situ* CH_4 removal. It also appeared to depress soil *Eh*, which increases CH_4 production and also increases NH_4^+-N content that leads to reduction of biological CH_4 oxidation and porosity of rice soil resulting in higher emission of CH_4. Inubushi *et al.*[79] have indicated that the role of aquatic weeds in paddy soil in methane emission should not be overlooked in evaluating mitigation options for reducing methane emission from paddy fields. More than double the amount of methane was emitted from weeded plots due to higher populations of methanogenic bacteria and lower methane oxidation compared with unweeded ones. Hou *et al.*[78] have also reported that rice straw and organic manure increased CH_4 production significantly. Maximum stimulation of CH_4 production was observed with pig manure, followed by chicken and cattle manure. Application of biogas spent slurry as manure in combination with inorganic fertilizer results in lowering CH_4 emissions compared to combined application of FYM and urea from rice fields[62]. Thus, use of biogas slurry could be a practical mitigation option for minimizing CH_4 flux from flooded rice fields.

Cultivars

Plants influence CH_4 efflux by: (i) Providing channels (aerenchyma) for the transport of CH_4 from soil to the atmosphere, (ii) Releasing root exudates or root autolysis products to methanogenic bacteria, and (iii) Creating oxic environment in the anoxic soil through the transport of O_2 into the rhizosphere which stimulates the oxidation of CH_4 and inhibits methanogenesis[81]. Satyanto *et al.*[82] have observed that in irrigated rice, early maturing cultivars like Dodokan had lowest emission (52-101 kg CH_4/ha) and the late maturing cultivar Cisadane had the highest emission (116-142 Kg CH_4/ha). High yielding varieties like, IR-64 and Memberamo had moderately high emission rates. Singh *et al.*[83] also found significant variations in CH_4 emitted from soils growing different cultivars. Mitra *et al.*[61] have reported seasonal methane emission of some rice cultivars in the order of Pusa 933> Pusa 1019 > Pusa Basmati > Pusa 834 > Pusa 677> Pusa 169. Wang *et al.*[81] have reported that such differences in CH_4 emission among the rice cultivars could be due to the differences in amounts of root exudates produced per plant the CH_4 oxidizing capacity of the roots and the population level of methanogenic bacteria in roots. According to Jia *et al.* [84] in rice cultivars *Yanxuan, 72031* and *9516* CH_4 emission flux was positively related with CH_4 production rate and rice plant-mediated CH_4 transport efficiency, but negatively with rhizospheric CH_4 oxidation. The contribution of rice plants to CH_4 production seems to be more important than to rhizospheric CH_4 oxidation and plant-mediated transport in impact of rice plants on CH_4 emission.

Mineral Fertilizers

Methane fluxes are strongly influenced by the type, method and rate of fertilizer application[30]. Lindau *et al.*[85] have reported increasing CH_4 fluxes with increasing rate of fertilizer applications with highest fluxes urea plots followed by ammonium chloride and ammonium sulphate treated plots[86]. Addition of large amount of sulphate can reduce CH_4 emission by 50-70 per cent[87]. Methane emission, on an average, decreased by 42 and 60 per cent in the ammonium sulphate treatments and 7 and 14 per cent in the urea treatments at rates of 100 and 300 kg N/ha, respectively, compared to control[88]. In other studies, use of ammonium sulphate in place of urea resulted in a 25-36 per cent reduction in CH_4 emission[89]. Methane fluxes had a considerable temporal variation (CV 52–77 per cent) and range from 0 05 (ammonium sulphate) to 3.77 mg/m^2/h (urea). There was a significant increase in the CH_4 emission on the application of fertilizers while addition of DCD with fertilizers reduced emissions. Total CH_4 emission in 105 days ranged from 24.5 to 37.2 kg/ha. The NO_3-N application reduced dissolved CH_4 concentration as well as CH_4 emission[90]. The root zone dissolved organic carbon (DOC) appears to be the main source for CH_4 production and the lower DOC concentrations with NO_3-N application are accountable for the low CH_4 emissions[91].

Methane emission seems to be reduced when N-fertiliser is incorporated, as compared with surface application[92]. In a rain-fed lowland rice field, deep placement of urea super-granules reduces CH_4 emissions compared to prilled urea broadcasting[93]. A higher emission when N-fertiliser was surface-applied might be due to an inhibitory effect of ammonium on methanotrophy, which was observed not only in oxic soils[94] but also at the soil-water interface in a submerged soil[28].

Phosphogypsum, a sulphate-containing by-product of industrial production of phosphoric acid, reduced CH_4 emissions by 56-73 per cent when applied in combination with urea[95]. In a field study, P applied as single super phosphate (SSP), inhibited CH_4 emission considerably[89]. Application of P at 50 and 100 mg/kg soil as K_2HPO_4 stimulated CH_4 production in a P-deficient soil, while there was no such stimulation in normal alluvial soil. Supplementary addition of K_2SO_4 with K_2HPO_4 mimicked the inhibitory effect of SSP on CH_4 production. In practice, use of SSP in rice cultivation, in addition to supplying P to the growing crops, could mitigate CH_4 production. According to Furukawa *et al.*[96] methane flux was significantly decreased by application of iron materials, approximately 10 per cent, when 10-40 and 10 t/ha of revolving furnace slag and spent disposable portable body warmer, respectively, were applied. The decrease in total methane flux may be attributed to enhanced methane oxidizing activity rather than inhibition of methanogenic activity. Rice microcosm incubation studies by Jackel *et al.*[97] showed that the total methane emission during the vegetative period of rice was reduced by 43 and 84 per cent after fertilisation with ferric iron oxide ferrihydrate at a rate of 15 and 30 g of ferrihydrate/kg soil, respectively.

Application of pesticides could also have significant impact on methane emission but very limited data are available on the subject. It has been observed that application of insecticide, carbofuran at 2 kg ai/ha to rice fields retarded CH_4 emission through enhanced CH_4 oxidation[95]. Hexachlorocyclohexane also inhibited CH_4 emission. While herbicide bromoxynil and insecticide methomyl inhibited CH_4 oxidation in soil[98]. Mohanty *et al.*[99] have observed that application of a commercial formulation of the herbicide butachlor at 1 kg ai/ha to an alluvial soil planted with direct-seeded flooded rice significantly inhibited both crop-mediated emission and ebullition fluxes (20 and 81 per cent, respectively). Nitrification inhibitors inhibit methanotrophy both in upland and wetland soils. In one study[100], CH_4 emission was lowest in plots treated with the mixture of prilled urea and nimin (a nitrification inhibitor).Application of dicyandiamide (DCD), a nitrification inhibitor, with urea reduced emission of CH_4 in rice-wheat system to 70 per cent while substituting 50 per cent of inorganic N with FYM increased emission by 172 per cent compared to application of entire amount of N through urea[90]. In another study DCD, especially in combination with hydroquinone, enhanced methane oxidation in rice root rhizosphere, particularly from its tillering to booting stage[101].

Water Management

Water regime of soil is important for gas exchange between soil and atmosphere and has a direct impact on the processes involved in CH_4 emission. For methanogenesis to take place, it is of primary importance that the soils should have enough moisture to create an anoxic condition. Drainage is a major modifier of seasonal CH_4 emission pattern[70]. A single mid-season drainage may reduce seasonal emission rates[86] by about 50 per cent. CH_4 emissions could further be reduced by intermittent irrigation yielding a 30 per cent reduction as compared to mid-season drainage[70]. Percolating water also transports organic solutes and dissolved gases into the subsoil or groundwater where leached CH_4 may be oxidized or released to the atmosphere[86]. In a 4 y study in northern India, it has been observed that low emissions were indirectly caused by high percolation rates of the soil and also frequent water replenishment resulted in constant inflow of oxygen in the soil[102]. The intermittent flooding practice is found to be very efficient in reducing the CH_4 emission. Sass *et al.*[103 have] also observed similar phenomenon. Cortan *et al.*[104] have found that mid-season drainage reduced CH_4 emission by 43 per cent due to influx of O_2 into the soil. According to Wassmann *et al.*[72], field drying at mid tillering reduced CH_4 emissions by 15-80 per cent compared to continuous flooding without a significant effect on grain yield. The net impact of mid tillering drainage was diminished firstly when rainfall was strong during the drainage period and secondly, very low levels of organic substrate in the soil suppressed emissions. Continuous flooding and urea application resulted in 79-184 mg $CH_4/m^2/d$ in dry season and 269-503 mg $CH_4/m^2/d$ in wet season[104]. Cumulative CH_4 efflux from control and prilled urea treated lowland rice field was about 4 to10-times higher than that of in irrigated shallow fields[100]. Flooding and draining cycle as well as high rate of water percolation and low organic matter content of the soil resulted in low CH_4 emissions[105]. Transplanting 30-d old seedlings, direct seeding on wet soil and direct seeding on dry soil reduced CH_4 emissions by 5, 13 and 37 per cent, respectively, when compared with transplanting 8-

d-old seedlings[106].

Min *et al.*[76] have suggested that improved water management is an effective method of mitigating methane emission from paddy fields. The methane emission rate from wetting and drying cycle plots was much lower than that from normal irrigation plots during the whole rice season, and was the lowest level observed among the four treatments. Spatial variation of precipitation in winter and corresponding variations of soil moisture regimes control the regional and annual variation of CH_4 emissions from rice fields in China[107]. Keeping soils drained as much as possible during winter seems to be a feasible option to reduce CH_4 emissions during the following rice growing seasons.

Salts

Methane emission is inversely related to salinity and sulphate concentration in soil as sulphate and sulphides are toxic to methanogens[108]. Inubushi *et al.*[109] have found that Na_2SO_4 suppressed the CH_4 formation and methanogenic bacteria were outcompeted by the sulphate reducing bacteria for H_2 and acetic acid. Between the two main pathways of CH_4 formation the reduction of CO_2 is less susceptible to NaCl than the decomposition of acetic acid[110].

Soil Texture

Soil texture and mineralogy through their effect on puddling can affect percolation rate and thereby net emission of CH_4 in waterlogged paddy soils. Clay soils upon drying form cracks and thus facilitate the entrapped CH_4 to go into the atmosphere. Yagi and Minami[41] have found that CH_4 emission decreased in the sequence of peaty soils, alluvial soils, and andosols. Mitra *et al*[112]. have found that soil properties like total N, soil texture (clay and sand fractions mainly), CEC, available K and active Fe content have significant effect on methane production potential of the topsoil and subsoils.

Strategies for Mitigating CH_4 Emission

Possible strategies for mitigating CH_4 emission from rice cultivation can be made by controlling production, oxidation, and transport of CH_4 from soil to the atmosphere. Methane emission varies markedly with water regimes. Altering water management, particularly promoting mid-season aeration by short-term drainage is one of the most promising strategies for reducing CH_4 emission. Improving organic matter management by promoting aerobic degradation through composting or incorporating into soil during off-season drained period is another promising technique[112]. A frequently suggested mitigation option is the use of sulphate-containing fertilizers such as ammonium sulphate and gypsum because sulphate-reducing bacteria can outcompete CH_4 producing bacteria and thus reduce the amount of CH_4 produced in the rice field. Addition of 6-7t/h of gypsum can reduce CH_4 emission by 50-70 per cent[87]. The cost of applying SO_4 containing fertilizers varies across countries. Since a fractional reduction is obtained, the cost efficiency in terms of methane mitigation per unit of SO_4 applied will be highest in high emitting rice production systems[87]. Nitrification inhibitors can reduce significant amount of CH_4 emitted from the flooded rice soils. In addition to their role in controlling various processes of N losses, nitrification inhibitors like, calcium carbide and nitrapyrin have been shown to inhibit CH_4 emission from flooded soil planted with rice[113]. Organic amendments to flooded soils increase CH_4 production and emission[37]. However, application of fermented manure like biogas slurry reduces the emission[62]. In Tanyuan, Hunan Province, China the incorporation of fermented organic matter into the rice fields reduced CH_4 emission by 60 per cent compared with application of unfermented manure[114]. Another mitigation option may be the use of low emitting rice cultivars[115] as different rice cultivars grown in similar conditions show pronounced variations in CH_4 emission[34]. These traits and related emission rates vary widely among cultivars making it possible for breeders to develop rice varieties with low CH_4 emission potential. Screening of rice cultivars with few unproductive tillers, small root system, high root oxidative activity and high harvest index is ideal for mitigating CH_4 emission in rice fields[81]. Cyanobacteria and *A. microphylla*, applied to floodwater, appear to play a major role in mitigation of methane emission from rice fields through enhanced methane oxidation[116].

The IPCC has recommended immediate reductions of 15-20 per cent in anthropogenic emissions of CH_4 to stabilize atmospheric concentrations at current levels[117]. Manipulation of some or all of the factors causing variability in CH_4 emission rates mentioned above might offer a way in which this reduced target can be met. Moreover the strategies to reduce the CH_4 emission should not have any adverse effect on crop yields. Environment friendly technologies must consider both for maintaining and even increasing soil fertility, improving crop yield and mitigating CH_4 emissions. Combined with a package of technologies CH_4 emission can best be reduced by: (i) Combining organic manure (decomposed with lower C:N like biogas slurry) with mineral N-fertiliser; (ii) Deep placement or incorporation of N-fertiliser, which has also additional advantages such as decreasing N-loss by volatilisation, favouring photodependent biological N_2-fixation, and decreasing the incidence of the vectors of human diseases, (iii) Use of sulphate containing fertilizers such as ammonium sulphate and phosphogypsum combined with urea, (iv) Practice of midseason drainage instead of continuous flooding, (v) Direct crop establishment like, dry seeded rice, and (vi) Use of low C:N organic manure such as, chicken manure and rice straw compost[104]. To achieve this goal there is a need for a detailed study on the intrinsic soil properties and their corresponding effects on the CH_4 production and emission from the rice paddy soils.

Areas of Further Research

The review suggests that there are many microbial, climatic, hydrological, soil, crop, and management factors that control the production, consumption, and transport of CH_4 in rice ecosystems in different ways. However, to what extent the controlling factors affect the production and emission of CH_4 from the rice ecosystems and their interactions have not been evaluated quantitatively. Precise estimates are difficult due to the large spatial and temporal variability in CH_4 measured at different sites due to differences in climate, soil properties, duration and pattern of flooding, rice cultivars and crop growth, organic amendments, fertilization, and cultural practices. Therefore, attention must be focused on developing simple and accurate technologies in quantifying CH_4 emissions for different land use types and developing process-based models to have reliable estimates of CH_4 emission from regional or global rice paddies. The efficacy of various mitigation technologies needs to be tested in farmer's fields. Moreover, such technologies need to be assessed for non-target effects and economic feasibility.

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