Biogeochemistry **61:** 1–19, 2002.

Stable isotope and radiocarbon compositions of methane emitted from tropical rice paddies and swamps in Southern Thailand

FUMIKO NAKAGAWA[1,5,*], NAOHIRO YOSHIDA[1,5], ATSUKO SUGIMOTO[2], EITARO WADA[2], TAKAHITO YOSHIOKA[1], SHINGO UEDA[3,6] and PISOOT VIJARNSORN[4]

*[1]Institute for Hydrospheric-Atmospheric Sciences, Nagoya University, Chikusaku, Nagoya, 464-8601, Aichi, Japan; [2]Center for Ecological Research, Kyoto University, 809-3 Otsuka, Kamitanakami-Hirano, Otsu, 520-2113, Shiga, Japan; [3]National Institute for Resources and Environment, 16-3 Onogawa, Tsukuba, 305-8569, Ibaraki, Japan; [4]Department of Land Development, Ministry of Agriculture and Cooperatives, Chatuchuck, 10900, Bangkok, Thailand; [5]Current address: Current address: Department of Environmental Science and Technology, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, 226-8502, Yokohama, Japan; [6]Current address: College of Bioresource Sciences, Nihon University, 1866 Kameino, Fujisawa, 252-8510, Kanagawa, Japan; *Author for correspondence (e-mail: fuminaka@depe.titech.ac.jp; phone: +81-45-924-5517, +81-45-924-5506; fax: +81-45-924-5519)*

Received 24 December 2000; accepted in revised form 20 August 2001

Key words: Methane, Radiocarbon, Rice paddy, Stable carbon isotope, Stable hydrogen isotope, Tropical swamp

Abstract. Stable isotopes ($\delta^{13}C$, δD) and radiocarbon were measured in methane bubbles emitted from rice paddies and swamps in southern Thailand. Methane emitted from the Thai rice paddies was enriched in ^{13}C (mean $\delta^{13}C$; −51.5 ± 7.1‰ and −56.5 ± 4.6‰ for mineral soil and peat soil paddies, respectively) relative to the reported mean value of methane from temperate rice paddies (− 63 ± 5‰). Large seasonal variation was observed in $\delta^{13}C$(∼ 32‰) in the rice paddies, whereas variation in δD was much more smaller (∼ 20‰), indicating that variation in $\delta^{13}C$ is due mainly to changes in methane production pathways. Values of $\delta^{13}C$ were lower in swamps (−66.1 ± 5.1‰) than in rice paddies. The calculated contribution of acetate fermentation from $\delta^{13}C$ value was greater in rice paddies (mineral soils: 62–81%, peat soils: 57–73%) than in swamps (27–42%). δD in methane from Thai rice paddies (−324± 7‰ (n=46)) is relatively higher than those from 14 stations in Japanese rice paddies ranging from −362 ± 5‰ (Mito: n=2) to −322 ± 8‰ (Okinawa: n=3), due to higher δD in floodwaters. ^{14}C content in methane produced from Thai rice paddies (127±1 pMC) show higher ^{14}C activity compared with previous work in paddy fields and those from Thai swamps (110±2 pMC).

Introduction

Methane (CH_4) is an important greenhouse gas in the atmosphere and plays a major role in stratospheric and tropospheric chemistry (Cicerone and Oremland 1988). Measurements of methane in modern air and air trapped in polar ice cores indicate that concentrations of atmospheric methane have more than doubled during the past

three centuries (Craig and Chou 1982; Rasmussen and Khalil 1984; Stauffer et al. 1985; Pearman et al. 1986; Etheridge et al. 1998). Anthropogenic emissions are considered the main cause of this increase. Flooded rice paddies are known to be one of the major anthropogenic sources of methane (Koyama 1963), and it is important to note that the total area covered by paddy fields is spreading with global population growth. Recent estimates of rice paddies as a global source of methane range from 20 to 100 Tg/yr (Houghton 1994), which is equivalent to 5–28% of the total methane from all anthropogenic sources. Uncertainty in this estimation is due to the wide range of local methane fluxes for the different climatic conditions, soil types, and cultivation practices of the rice-growing regions of the world.

Stable and radiocarbon isotopes provide important information for estimating the sources and sinks of methane. In addition, they have become important tools for studying methane production and secondary isotope fractionation processes (methane oxidation and transportation processes). For example, methane ^{14}C content provides a useful estimate of the contribution from fossil carbon (^{14}C free), which comes from natural gas, coal mining, and natural seepage from gas reservoirs (Lowe et al. 1988; Wahlen et al. 1989). Furthermore, ^{14}C gives information about the mean residence time of methane (age of methane) in anaerobic sediments. In the case of stable isotopes, $\delta^{13}C$ varies widely in methane from anaerobic environments, mainly because of changes in methanogenic pathways (acetate fermentation: $\delta^{13}C = -30 \sim -40‰$ and CO_2 reduction: $\delta^{13}C < -70‰$ (Sugimoto and Wada 1993)), whereas δD seems to be independent of methanogenic pathways, but is linked to the δD of coexisting water (Sugimoto and Wada 1995; Waldron et al. 1998). Enrichment with both ^{13}C and D occurs during methane oxidation by methanotrophic bacteria (Barker and Fritz 1981; Coleman et al. 1981; Alperin et al. 1988; Happell et al. 1994; Tyler et al. 1994).

Detailed isotopic characterization of major methane sources, including paddy fields, is required to lessen the uncertainty about global methane budgets. Some measurements of $\delta^{13}C$ (e.g. Tyler et al. (1988); Wahlen et al. (1989); Uzaki et al. (1991)) and δD (Chanton et al. 1997) in methane from paddy fields taken sporadically have been published. Variation in $^{13}C_{CH4}$ in both gas bubbles (Stevens and Engelkemeir 1988) and emitted gases (Tyler et al. 1994) during a complete rice-growing season in Japanese rice paddies indicated the necessity of obtaining isotopic measurements throughout a season. The same variation was observed in Chinese rice paddies, suggesting that the pattern might represent general behavior of methane emissions from rice plants, due to systematic changes that occur during the vegetation cycle. Moreover, the study in Chinese rice paddies also suggested that δD varies temporally (Bergamaschi 1997).

However, these stable isotope studies of methane have been carried out in temperate areas, and few studies have been done in tropical areas, where 70% of worldwide paddy fields exist. Furthermore, cultivation management differs from region to region. Most temperate rice paddies are irrigated, whereas in tropical areas only half of the paddy fields are irrigated, while the remainder is rain fed (FAO 1988). In our study, the isotopic composition (^{13}C, D, ^{14}C) of methane from rain feded paddy fields in tropical Thailand was determined. Gas bubbles in shallow

part of the sediment, where the gas exchange with the atmosphere via three transport processes (bubble ebullition, gas transport within plants, and gas diffusion) will occur, were collected to understand the methane production mechanism of emitted methane. The purposes of this study are (1) understanding the seasonal variation of methanogenic pathways and methane oxidation in tropical paddy fields, (2) determining the carbon-14 content of methane carbon sources in tropical area, and (3) determining the relationship between δD of methane and surface water in rice paddies. In addition, isotopic determination of methane from Thai swamps and Japanese rice paddies were also carried out for comparison.

Materials and Methods

The study site was located in Narathiwat province, Thailand (6°N, 102°E). The climate in this region is characterized by uniformly high temperatures (27.6 °C on average) and humidity (80% on average). There is a distinct seasonal rainfall pattern, with heavy precipitation during the wet season from September to December, followed by a dry season from January through August. The mean annual rainfall over the 30-year period from 1951 to 1980 was 2,619 mm. In this region, rice is cultivated during the wet season.

In Narathiwat province, coastal swamps exist in depressions between former beaches. They contain peat layers more than 1-m thick, underlain by marine sediment that is rich in pyrite (Vijarnsorn 1992).

Samples were collected from paddy fields with peat and mineral soils (grayish clay containing large amounts of pyrite) in the Pikunthong Royal Development Center. Sampling took place every one to four weeks from December 1990 to March 1992. Gas samples were also collected in the summers and winters of 1991 and 1992 from To Daeng and Bacho Swamps and from the Bang Nara River (Figure 1). To Daeng Swamp is an original-growth forest, and most of the area is likely to be permanently flooded. Bacho Swamp is a secondary-growth forest; the original forest was cleared and appears to have been extensively drained. However, the water table still lies close to the soil surface most of the year, except during the dry season, when the water level is lower (Vijarnsorn 1992). Gas bubbles were stirred up from the shallow part of the sediment (below ca. $\sim$20 cm from the surface) with a long rod. Gas bubble samples were collected by displacing water using an inverted funnel with a rubber cap. Samples were stored in glass bottles (20 ml) with HCl.

The concentrations of major gases (CH_4, CO_2, N_2 and O_2) in the gas-bubble samples were analyzed on a gas chromatograph equipped with far UV detector for CH_4 and CO_2, and with TCD (Ar carrier gas) for N_2 and O_2. The stable carbon isotope compositions of CH_4 and CO_2 were measured by a previously described method (Sugimoto et al. 1991) using a GC/C/IRMS (Gas chromatography (Varian 3400)/Combustion/Mass spectrometer (Finnigan MAT delta S)) system.

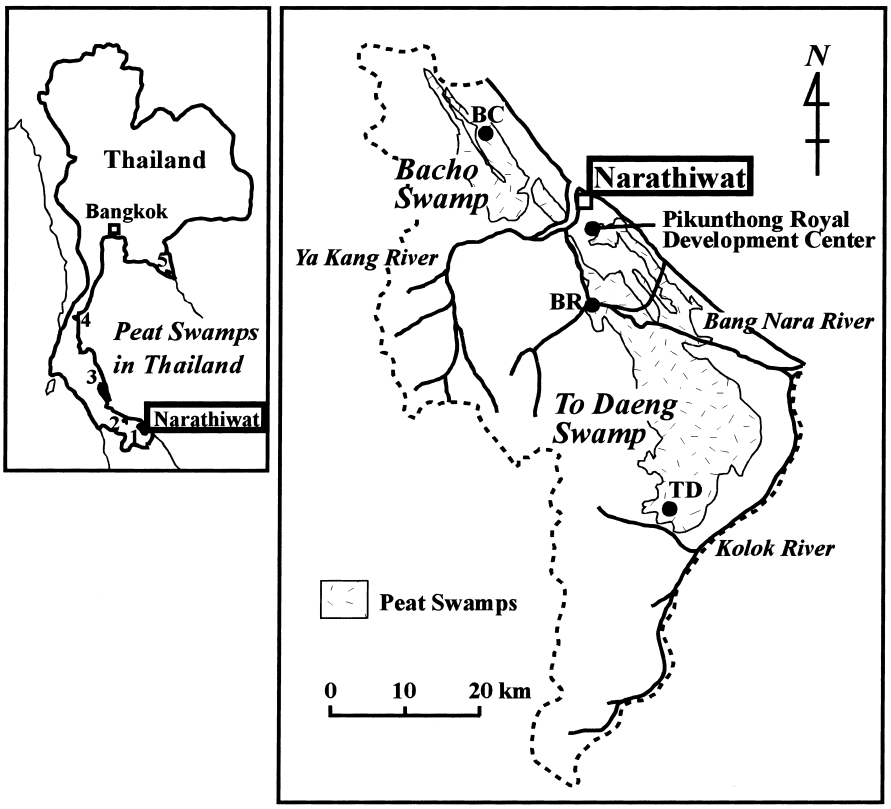

Figure 1. Location map for sampling sites. Rice paddy samples are taken from the Pikunthong Royal Development Center. TD, BC, and BR indicates the sampling sites of To Daeng Swamp, Bacho Swamp, and Bang Nara River, respectively.

Gas samples were prepared for deuterium and radiocarbon analyses in a vacuum system. Methane was oxidized in a CuO furnace (850 °C) after removing CO_2 and H_2O at liquid nitrogen temperature. CO_2 and H_2O formed by CH_4 combustion were trapped at the temperature of liquid nitrogen, and CO_2 was subsequently separated from H_2O at the temperature of dry-ice/methanol. Remaining H_2O was converted to H_2 by zinc reduction (Coleman et al. 1982). Hydrogen isotope analyses were performed using an MAT251 isotope ratio mass spectrometer (TheremoQuest, Tokyo). CH_4-derived CO_2 was converted to graphite via reaction with H_2 and an iron catalyst (Kitagawa et al. 1993). The ^{14}C analyses were done on a Tandetron Analyzer, Model 4130A (General Ionex Corp., Massachusetts), at the Center for Chronological Research at Nagoya University.

Stable isotope composition is expressed as

$$\delta(‰) = ((R_{\text{sample}}/R_{\text{standard}}) - 1)\times 1000 \quad (1)$$

where R is $^{13}C/^{12}C$ or D/H and $\delta^{13}C$ and δD are reported relative to VPDB and VSMOW, respectively. The overall error of the analyses for $\delta^{13}C$ was ±0.3‰ and for δD was ± 1‰. Radiocarbon data are expressed as

$$pM(\%) = (({}^{14}C/ {}^{12}C)_{sample}/({}^{14}C/ {}^{12}C)_{standard}) \times 100 \quad (2)$$

The percentage of the $^{14}C/^{12}C$ ratio (normalized to $\delta^{13}C = -25‰$) is relative to that of an oxalic acid standard from 1950.

Gas bubble and floodwater samples from rice paddies were collected at 14 locations in Japan during the summer of 1989 (Uzaki et al. 1991). The sampling method and preparation for carbon isotope measurements are described elsewhere (Uzaki et al. 1991). The stable hydrogen isotopic composition of floodwater and methane was determined using a Micromass 602E IRMS (Micromass UK Ltd., Manchester) at Toyama University, after the reduction of H_2O and H_2O derived from methane combustion to H_2 with the use of uranium. The overall error of the $\delta^{13}C$ and δD analyses was ±0.1‰ and ±1‰, respectively.

Results and Discussion

Methane contribution in bubbles

The concentrations of the major constituents and the stable isotope compositions of methane from paddy fields and swamps in Thailand are summarized in Table 1. The methane concentration in both peat soil and mineral soil rice paddies varied widely throughout the year. Methane concentrations were high in the wet season (maximum of 66% in peat soil and 68% in mineral soil from September to December) and low or zero in the dry season (January to August) (Figure 2a). This seasonal variance is due to changes in water level that influence oxidation-reduction potentials in the soil. The pattern of variation in methane concentrations differed between the two types of paddy; however this difference is likely to come from variations in water level induced by water management rather than from differences in soil type.

Methane concentrations in swamps varied spatially, due to water level differences (Table 1); lower water level leads to the enhancement of gas exchange between the atmosphere and sediments (Chanton et al. 1989). The Bang Nara River, where the water level is always high (depth: 2 m to 6 m), had a high methane concentration of 80.8±3.4% (n=6). Bacho Swamp, where the water table lies close to the soil surface (depth: 0 m), had lower methane concentrations of 24.6±13.5% (n=6). The methane concentrations in To Daeng Swamp were higher (51.1±17.4% (n=10)) than those in Bacho Swamp, because the water levels were higher (depth: 0.3 m to 0.7 m) at To Daeng.

Table 1. Concentration of major constituents and stable isotopes (mean value and standard deviation) of methane and carbon dioxide in gas bubbles from southern Thailand.

	n	CH_4 %	N_2 %	CO_2 %	O_2 %	$\delta^{13}C_{CO2}$	$\delta^{13}C_{CH4}$	δD_{CH4}
Rice Paddy (Mineral Soil)	47	24.6 (21.5)	69.9 (21.6)	0.9 (1.4)	4.4 (1.8)	−18.6 (4.1) (n=4)	−51.5 (7.1)	−325 (8)
Rice Paddy (Peat Soil)	49	25.0 (20.5)	69.9 (19.5)	0.6 (0.6)	4.5 (3.1)	−21.6 (3.4) (n=8)	−56.5 (4.6)	−322 (6)
Bang Nara River	6	80.8 (3.4)	15.5 (5.1)	2.0 (3.3)	1.6 (1.1)	−14.8 (3.9) (n=5)	−68.3 (3.1)	−288 (25)
To Daeng Swamp	10	51.1 (17.4)	45.3 (17.4)	1.0 (1.2)	2.6 (1.8)	−9.9 (5.1) (n=5)	−64.0 (4.5)	−323 (14)
Bacho Swamp	6	24.6 (13.5)	71.6 (12.7)	0.4 (0.4)	2.9 (0.9)	−23.4 (n=1)	−67.6 (7.4)	−343 (2)

Stable isotope ratios of methane in gas bubbles

Seasonal variation in the methane concentration and stable isotope compositions of gas bubbles in the paddy fields is shown in Figure 2. There are no isotope data from the seasonal dry period when methane concentrations were below determination limits for isotope ratios (April to June for peat soil paddies and May to June for mineral soil paddies). $\delta^{13}C$ in methane from peat soil rice paddies ranged from −61.4 to −44.9‰; these values are similar to those for Japanese rice paddies (−68 ∼ −48‰, Uzaki et al. (1991)), but are slightly higher than those for paddy fields in Louisiana (−61 ∼ −57‰, Chanton et al. (1997)) and China (−71 ∼ −58‰, Bergamaschi (1997)). Higher values, ranging from −63.1 to −31.3‰, were obtained from mineral soil rice paddies. High $\delta^{13}C$ values have been reported for rice paddies in tropical areas, such as the Philippines (−61 ∼ −45‰, Wada et al. (1995)) and Malaysia (−46 ∼ −42‰, Wada et al. (1995)). Large seasonal variation in $\delta^{13}C_{CH4}$ was observed in both types of paddy field (16‰ for those with peat soils and 32‰ for those with mineral soils, Figure 2b). These variations are larger than those observed in other areas, including China (13‰, Bergamaschi (1997)) and Japan (5 ∼ 12‰, Uzaki et al. (1991)). Methane that was relatively depleted in ^{13}C was obtained from December through March, with values ranging from −63 to −55‰, whereas highly ^{13}C-enriched methane was detected immediately after the dry period, when methane concentrations started to increase. $\delta^{13}C_{CH4}$ values in mineral soils were higher than those of peat soils throughout the September to December growing season, with maximum values of −31.3‰ and −44.9‰ for min-

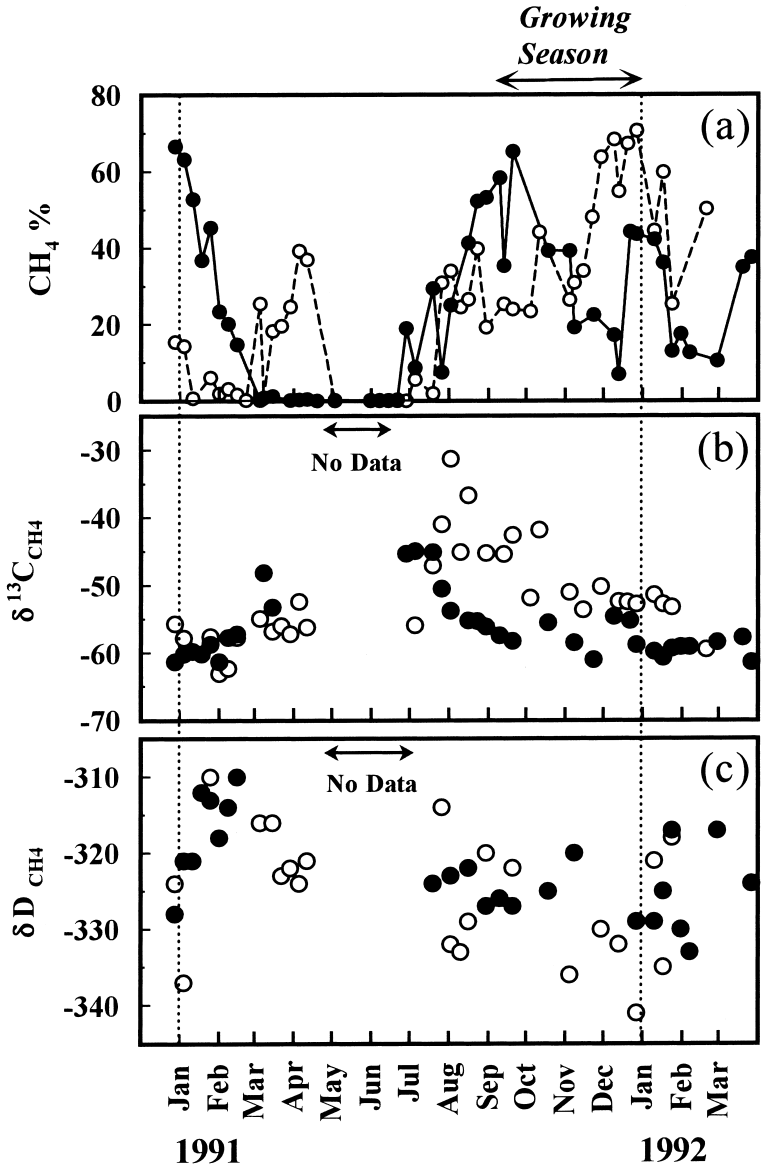

Figure 2. Seasonal variation of (a)methane concentration, (b)$\delta^{13}C$ in methane, and (c)δD in methane from rice paddies in Southern Thailand. ● indicates the methane from mineral soils and ○ indicates the methane from peat soils. There are no isotope data during the very dry period when the methane concentration was too low for isotope measurements (April to June in peat soils, May to June in mineral soils).

eral soils and peat soils, respectively. The variation is thought to arise from 1) changes in the methane formation pathway, 2) variation in isotopic composition of

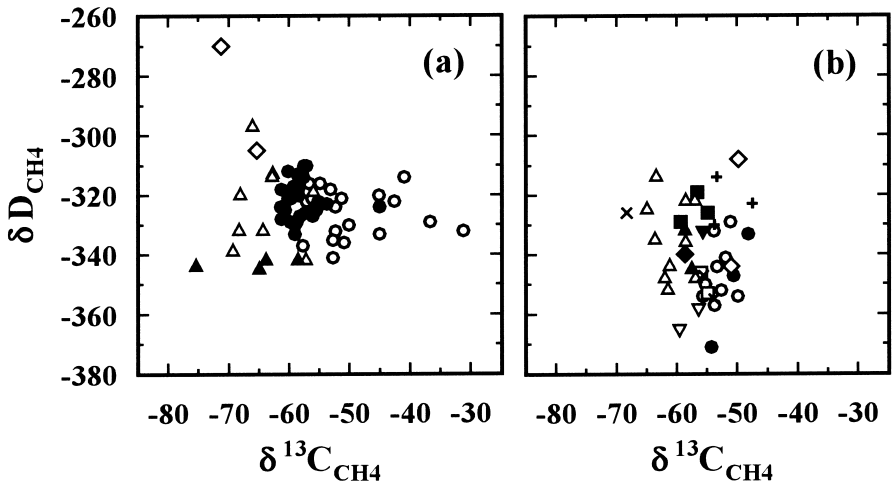

Figure 3. Stable hydrogen and carbon isotopes of methane from (a)rice paddies and swamps in Thailand and from (b)Japanese rice paddies. Legends for figure 2a are as follows; ○:rice paddy (mineral soils), ●:rice paddy (peat soils), ◇:Bang Nara River, △:To Daeng swamp, ▲:Bacho swamp. Legends for figure 2b are as follows; ○:Hokkaido, ●:Morioka, □:Miyagi, ■:Chiba, △:Yokohama, ▲:Toyama, ▽:Mito, ▼:Mie, ◇:Hiroshima, ◆:Fukuoka, ×:Kagoshima, +:Okinawa.

methanogenic precursors, and 3) isotope fractionation due to methane oxidation (Whiticar et al. 1986; Alperin et al. 1992; Sugimoto and Wada 1993).

Small seasonal variation was observed in the δD of methane emitted from paddy soils, with a range of −341 to −310‰ for mineral soils and −333 to −310‰ for peat soils (Figure 2c). Seasonal variation in δD differed from that of $\delta^{13}C_{CH4}$. Lower δD values were obtained during the November to December rainy season and relatively high δD values were detected throughout the dry season, when evaporation rates exceed precipitation rates. The enrichment of δD in methane is thought to come from a combination of two effects: 1) evaporation that results in the δD enrichment of floodwater and 2) methane oxidation.

The methane produced from swamp soil in Thailand was more depleted in ^{13}C than the methane in paddy fields (Figure 3, Table 1). Swamp soil methane ranged from −75.5 to −56.0‰, with a mean value of −66‰, similar to $\delta^{13}C_{CH4}$ from other wetlands (e.g., Alaska tundra: −73 ∼ −55‰, Quay et al. (1988); Minnesota peat bogs: −86 ∼ −50‰, Quay et al. (1988); Florida Everglades: −70 ∼ −63‰, Chanton and Martens (1988); Amazon floodplains: −63 ∼ −65‰, Tyler et al. (1987)). The δD of the methane from the two Thai swamps ranged widely from −345 to −268‰; these values are similar to those for methane from wetlands with similar δD present in the surface waters (Woltemate et al. 1984; Waldron et al. 1999).

Stable hydrogen isotope ratios in methane from 14 stations in Japanese rice paddies ranged from −365 to −308‰; these values are lower than those for Thailand (Figure 2). Lower δD values in methane from Japanese rice paddies are likely due to lower δD in floodwaters; this will be discussed later.

Methane oxidation

Methane oxidation often occurs in anoxic aqueous environments, such as those of paddy fields and wetlands. Most of the methane are oxidized in the oxic zones of sediments or water columns (Rudd et al. 1974). Anaerobic methane oxidation may also occur using sulfate as oxidant, in some cases (Davis and Yarbrough 1966). The degree of oxidation is influenced mainly by water levels; methane oxidation becomes active when the water level decreases below soil surface and the aerobic environment is extended (Moore and Roulet 1993). Since methane oxidation results in the enrichment of methane with heavy stable isotopes, positive correlation between $\delta^{13}C$ and δD are expected in either aerobic or anaerobic environments with slopes of 8.5 $\sim$ 13.5 or 7 $\sim$ 18, respectively (Coleman et al. 1981; Alperin et al. 1988). If methane oxidation greatly influenced the carbon isotope ratio of methane with a range of about 30‰, the variation in the hydrogen isotope ratio of methane would be approximately 210–540‰. However, δD in the methane varied by only 20‰ in paddy fields (Figure 3), therefore the variation of $\delta^{13}C$ in the methane is suggested to be due to changes in methanogenic pathways rather than an oxidation effect. In the case of swamps, relatively larger variation of δD in the methane (ca. $\sim$80‰) was observed, indicating some contribution of methane oxidation in swamps.

Methanogenic pathways induced from the stable carbon isotope ratio

The methane in anoxic sediments is produced biologically from simple compounds, including carbon monoxide, carbon dioxide, acetate, formate, methylamines, methanol, and dimethylsulfide (Conrad 1989). The primary pathways of bacterial methane formation are (i) carbon dioxide reduction and (ii) acetate fermentation (Whiticar et al. 1986; Sugimoto and Wada 1993) as follows:

$$CO_2 + 4H_2 \rightarrow CH_4 + H_2O \quad \text{(i)}$$

$$CH_4COOH \rightarrow CH_4 + CO_2 \quad \text{(ii)}$$

The $\delta^{13}C$ in methane produced through each pathway is different, because of differences in isotopic fractionation in each pathway and differences in $\delta^{13}C$ for each substrate (CO_2 or acetate). The contribution of these two methanogenic pathways (f) is determined from the mass balance equation:

$$\delta^{13}CH_4 = (f_{CO_2})\alpha_{CO_2}(\delta^{13}C_{CO_2}) + (f_{ac})\alpha_{ac}(\delta^{13}C_{ac}) \quad (3)$$

where $\delta^{13}CH_4$ is the measured carbon isotopic composition in methane, $\delta^{13}C$ is the isotopic composition of the precursor and α is the isotopic fractionation factor during the formation process. The fractionation factor (α) is defined by the following equations:

$$\alpha_{CO_2} = \frac{(\delta^{13}C_{CO_2} + 10^3)}{(\delta^{13}C_{CH_4} + 10^3)} \quad (4)$$

$$\alpha_{ac} = \frac{(\delta^{13}C_{ac} + 10^3)}{(\delta^{13}C_{CH_4} + 10^3)} \quad (5)$$

where the subscripts CO_2 and ac denote the CO_2 reduction and acetate fermentation pathways, respectively. Alternatively, using the enrichment factor ε, defined as $\varepsilon = (1/\alpha - 1) \times 1000$, the mass balance equation is expressed as follows:

$$\delta^{13}C_{CH_4} = (f_{CO_2})(\delta^{13}C_{CO_2} + \epsilon_{CO_2}) + (f_{ac})(\delta^{13}C_{ac} + \epsilon_{ac}) \quad (6)$$

$\delta^{13}C$ values of methane from CO_2 reduction were calculated using equation (4). Isotopic fractionation factor of CO_2 reduction reported from pure culture studies of *Methanococcales* at temperatures of 35 °C ranged from 1.063 to 1.079 (Botz et al. 1996). Since our measurements of $\delta^{13}C$ in carbon dioxide were limited to gas bubble samples taken in 1992, we used the mean value (mineral soil paddy field: −18.6 ± 4.1‰, peat soil paddy field: −21.6 ± 3.4‰, Bang Nara River: −14.8 ± 3.9‰, To Daeng Swamp: −9.9 ± 5.1‰) to calculate the $\delta^{13}C$ in methane produced by the CO_2 reduction pathway. Our calculations produced values ranging from −77 to −89‰, which correspond to the $\delta^{13}C$ values (< −77‰) obtained in the incubation experiments of rice paddy soils reported by Sugimoto and Wada (1993).

On the other hand, isotope fractionation during acetate fermentation in pure culture studies of *Methanosarcina barkeri* (ε = 21.2‰, Gelwicks et al. (1994); ε = 21.3 ± 0.3‰, Krzycki et al. (1987)) and natural communities (ε = 19.2 ± 0.3‰, Krzycki et al. (1987)) is reported to be significantly smaller than the isotope fractionation of CO_2 reduction. Methane from acetate fermentation is derived from the methyl group of acetate. Since the $\delta^{13}C$ values of acetate in Thai rice paddies and swamps are unknown, we used values obtained in other studies to estimate the fraction for both pathways.

Using the $\delta^{13}C$ of methyl carbon from lake sediments (−21.4‰) reported by Krzycki et al. (1987), the $\delta^{13}C$ of methane produced from acetate fermentation in paddy fields in Thailand was calculated to be −42.7 ∼ −40.6‰. These values correspond to results reported by Avery et al. (1999) (−43.8 ± 11.9‰ in May and −44.5 ± 5.4‰ in June), who calculated the $\delta^{13}C$ of methane generated from acetate fermentation during peat incubation experiments. From these calculations, the $\delta^{13}C$ of methane was estimated to be −43‰ in cases in which large amounts of fresh organic materials were supplied.

However, downcore variation in $\delta^{13}C_{methylcarbon}$ (−8.3 to −24.9‰) was observed in coastal marine sediments (Blair and Carter 1992). The enrichment of in $^{13}C_{acetate}$ may occur during the isotopic effect of acetate consumption by both oxidative and dissimilative processes. Hence, the $\delta^{13}C$ of methane from acetate fermentation will be higher in sediments in which labile organic materials are depleted. ^{13}C enrich-

Table 2. Estimation of acetate fermentation contribution for methane from rice paddies and swamps in southern Thailand.

	Acetate fermentation %			Acetate fermentation %	
	Case 1*	Case 2**		Case 1*	Case 2**
RICE PADDY					
Mineral Soil			*Peat Soil*		
Jan	67	52	Jan	63	50
Feb	58	45	Feb	66	52
Mar	69	53	Mar	84	65
Apr	74	57	Apr	–	–
May	–	–	May	–	–
Jun	–	–	Jun	–	–
Jul	88	68	Jul	93	72
Aug	108	83	Aug	74	58
Sep	98	75	Sep	68	53
Oct	91	70	Oct	73	57
Nov	80	61	Nov	64	50
Dec	78	60	Dec	72	56
Average	81	62	Average	73	57
SWAMP					
Bang Nara River			*To Daeng Swamp*		
Jul	31	23	Jul	39	29
Dec	38	29	Dec	48	35
Average	36	27	Average	42	31

* Case 1: calculated assuming the $\delta^{13}C$ in methyl group of acetate to be −43‰.
** Case 2: calculated assuming the $\delta^{13}C$ in methyl group of acetate to be −30‰.

ment in acetate was also seen in paddy soil incubation experiments (Sugimoto and Wada 1993). From anaerobic incubations of paddy soils, these authors estimated $\delta^{13}C_{CH4}$ from acetate fermentation to be −43 to −30‰. Based on these results, we made estimations for two cases: (1) acetate fermentation in sediments in which sufficient fresh organic materials are supplied and thus have a low $\delta^{13}C_{CH4}$ (−43‰) and (2) acetate fermentation in sediments that are extremely depleted in fresh organic materials and thus have a higher $\delta^{13}C_{CH4}$ (−30‰).

The calculated contribution of acetate fermentation is shown in Table 2. Monthly and annual averages for rice paddies were calculated using the data from 1991. The mean values for the Bang Nara River and To Daeng Swamp were calculated using all the data. Generally, the contribution of acetate fermentation was relatively greater in rice paddies (mineral soils: 62–81%, peat soils: 57–73%) than in swamps (27–42%), probably due to the abundance of acetate in paddy fields and the depletion of acetate in swamps, since acetate is likely oxidize to CO_2 by sulfate reducing bacteria where higher amounts of sulfate exists (Winfrey and Zeikus 1977; Winfrey and Ward 1983).

Almost 100% of the methane was produced by acetate fermentation from July through September, a few weeks after the dry period, when methane concentrations started to increase. In incubation experiments with rice paddy soil, most of the methane produced via acetate fermentation (62–100%) was observed in weeks one through three, after very low contribution of acetate fermentation in week 1 (less than 12%) (Sugimoto and Wada 1993). This indicates that a few weeks after onset, rice paddy sediments become anaerobic, and the accumulation of acetate is sufficient to activate acetate-utilizing bacteria. After rapid consumption of acetate, the acetate fermentation activity reaches steady state (the contribution of acetate fermentation was 50–70%). Since ^{13}C enrichment of methane after a few weeks of irrigation has been observed in other paddy fields (Uzaki et al. 1991; Tyler et al. 1994; Bergamaschi 1997), active methane formation by acetate-utilizing bacteria after the accumulation of acetate (a week to a few weeks: the difference in the period depends on the environmental conditions of rice paddies; temperature, precipitation, cultivation practice, soil types, and so on) of irrigation may be a general feature in paddy fields. In order to understand the contribution of methanogenic pathways more accurately, it is necessary to measure the $\delta^{13}C$ of the acetate methyl group.

Relationship between δD of methane and environmental water

Assuming that methane from marine environments is mainly produced via the CO_2 reduction pathway, and methane from freshwater environments by acetate fermentation, the relationship between the δD of water and methane is a useful tool to distinguish these primary methanogenic pathways (Whiticar et al. 1986), since these two pathways have large differences in hydrogen fractionation factors (CO_2 reduction: 180‰, 1.22, acetate fermentation: 320‰, 1.47). However, exception to the assumption do occur in both marine and freshwater environments; higher contribution of acetate fermentation in marine sediments where the sedimentation rates are high, and lower contribution of acetate fermentation in freshwater sediments. Lansdown et al. (1992), tested the relation between δD of water and methane in temperature bog and the methane production pathway proposed by Whiticar et al. (1986) and concluded the difficulty in distinguishing the methanogenic pathways using δD of methane. Furthermore, a large fractionation (317±20‰) for CO_2 reduction has been obtained from incubation experiments of freshwater soil (Sugimoto and Wada 1995), indicating that there is no significant difference in the δD of methane between the two methanogenic pathways. Therefore, the δD in methane from freshwater environments can be related to δD in environmental water. All the hydrogen in methane produced via CO_2 reduction originates from the formation water (Pine and Barker 1956; Daniels et al. 1980), therefore the slope of the relationship between the δD of methane and water will be $1/\alpha_D$, where α_D is a hydro-

gen fractionation factor defined by the following equation:

$$\alpha_D = \frac{(\delta D_{H_2O} + 10^3)}{(\delta D_{CH_4} + 10^3)} \quad (7)$$

In the case of methane produced via acetate fermentation, three quarters of the hydrogen is derived from the methyl group and the remaining one quarter from the formation water (Pine and Barker 1956; Daniels et al. 1980), with the slope of δD_{CH4} and water being $1/(4\alpha_D)$. However, some of the hydrogen atoms in the acetate methyl group are likely to be exchanged with the formation water, therefore more than one quarter of the hydrogen in methane originates from water (Sugimoto and Wada 1995).

The relationships between the δD of water and methane in Thai and Japanese rice paddies, and for Thai swamps, are presented in Figure 4. Excluding the swamp data, there is a linear relationship between δD in methane and water, with a regression line of $\delta D_{CH4} = 0.54 \times \delta D_{H2O} - 314$ (R^2=0.39). This relationship lies between the lines (dashed line in Figure 3) for CO_2 reduction and acetate fermentation obtained from incubation experiments (Sugimoto and Wada 1995). Accordingly, hydrogen isotopic fractionation during the production of microbial methane is large, about 300 to 330‰, with little regard to methanogenic pathways in paddy fields. The maximum difference of δD_{CH4} (the maximum range of δD in surface water of rice paddies is 100‰ (−80 ∼ +20‰), which were estimated using the δD value of precipitation in tropical and temperate zones reported (Yurtsever and Gat 1981) and the evaporation effect of 20‰ because surface water in wetlands is generally enriched in the heavy isotope relative to rainwater, as a result of isotopic fractionation during evaporation) from rice paddies caused by difference in δD_{H2O} is calculated to be approximately 50‰, since rice paddies exist in tropical and temperate zones.

For swamps, a large variation in hydrogen isotopic composition (from −345 to −270‰) was observed (Figure 4); lower δD value in Bacho Swamp, which has low water levels and low methane concentrations, and higher δD value in the Bang Nara River, which has high water levels and high methane concentrations. Methane oxidation in the water columns might lead to deuterium enrichment of methane in swamps with higher water level (Rudd et al. 1974). Moreover, extremely high δD value of methane in the Bang Nara River is likely due to higher concentrations of SO_4^{2-} in the river water (two orders of magnitude higher than the SO_4^{2-} concentration of swamps, (Ueda et al. 2000), which will lead to D-enrichment of methane via anaerobic methane oxidation using sulfate (Davis and Yarbrough 1966) and/or D-enrichment of hydrogen stimulated by sulfate-reducing bacteria that preferentially utilizes light hydrogen.

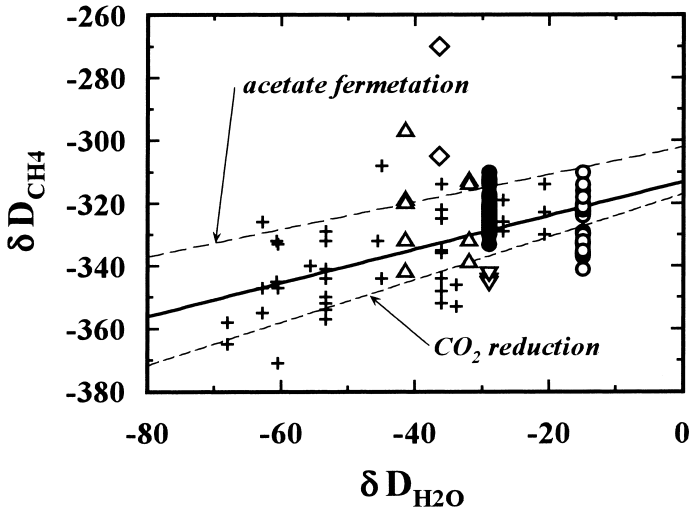

Figure 4. Hydrogen isotope composition of methane and floodwater. ○:Rice Paddy (mineral soils), ●:rice paddy (peat soils), ◇:Bang Nara River, △:To Daeng swamp, ▽:Bacho swamp, +:Japanese rice paddies. Solid line is the regression line for methane from rice paddies excluding swamps (δD_{CH4} = 0.54 × δD_{H20} − 314 (R^2=0.39)). Dash line is the relationship for CO_2 reduction and acetate fermentation obtained from the incubation experiments reported by Sugimoto and Wada (1995). CO_2 reduction:δD_{CH4}=(0.683±0.020) δD_{H2O} − (317±20), Acetate fermentation:δD_{CH4}=(0.437 ± 0.045) δD_{H2O} − (302 ± 15)

The carbon-14 content of methane

^{14}C is the most useful parameter to estimate the contribution of methane from fossil carbon (0 pMC) to the atmospheric inventory. However, the ^{14}C data of methane sources including wetlands and paddy fields are very limited, especially in tropical area.

The results for ^{14}C in methane are summarized in Table 3. The methane produced from rice paddies with both peat soils and mineral soils was enriched in radiocarbon (127 pMC in peat soils and 128 pMC in mineral soils) relative to 1990 atmospheric CO_2 levels (115 pMC; an estimated value for the ^{14}C content in atmospheric CO_2 in 1990, (Levin et al. 1992)). This indicates that the methane from the rice paddies was produced from organic materials that were fixed recently. Since the ^{14}C in the methane was similar to that of atmospheric CO_2 from 1978 (Levin et al. 1992), the mean age of the methane was estimated to be about 12±1 years. Comparisons with previous work in paddy fields indicate that our results show higher ^{14}C activity than in rice paddies in Louisiana (Wahlen et al. 1989) and Japan (Tyler et al. 1994), both of which had activity equal to or slightly lower than contemporary carbon (100–120 pMC). This suggests that organic matter degrades faster in rice paddies in tropical areas, because of the year-round higher temperatures and humidity, than it does in temperate rice paddies, which might have slower degradation rates.

Table 3. Summarized radiocarbon content of methane from paddy fields and wetlands

Study Area		$^{14}C^{*}_{CH4}$ (pMC)	$^{14}C^{**}_{CH4(Ave)}$ (pMC)	Sampling Year
RICE PADDY				
Thailand[a]	Mineral Soil	128 ± 2.0	127 ± 1	1991
	Peat Soil	127 ± 0.9		
Louisiana[b]			110 ± 10	1987
Japan[c]			111 ± 4	1990–1991
WETLANDS				
Thai Swamp[a]	Bang Nara	108 ± 2.0	110 ± 2	1991
	To Daeng	110 ± 1.6		
	To Daeng	108 ± 2.0		
	Bacho	112 ± 1.0		
Siberian Alass[d]			104 ± 6	1993
Alaskan Tundra[e]			111 ± 4	1987
Alaskan Tundra[f]			109 ± 9	1988
Canadian Tundra[b]			112 ± 2	1987
Canadian Peat land[g]			119 ± 5	1993–1994
Minnesota Peat bog[e]			123 ± 6	1987
Minnesota Peat bog[h]			115 ± 1	1991
New York Swamp[b]			113 ± 2	1986–1988
West Virginia Peat bog[b]			117 ± 2	1986
Amazon Floodplain[e]			120 ± 2	1987

*Mean values and standard deviation of AMS analyses (5 measurements) for each sample is listed.
**Mean values (σ^2 average) for Thai rice paddies are averaged for mineral soils and peat soils, and for Thai swamps for Bang Nara River, To Daeng and Bacho Swamps.
[a]This study
[b]Wahlen et al. (1989)
[c]Tyler et al. (1994)
[d]Nakagawa et al. (2002)
[e]Quay et al. (1991)
[f]Martens et al. (1992)
[g]Bellisario et al. (1999)
[h]Chanton et al. (1995)

On the other hand, the ^{14}C concentration of the methane from the swamps was 110±2 pMC, which is 15–20% lower than the ^{14}C levels from the paddy fields. These results correspond with ^{14}C dates reported from other wetlands (Wahlen et al. 1989; Quay et al. 1991; Chanton et al. 1995). ^{14}C-depleted methane values in wetlands are likely due to the contribution of older methane that was produced from recalcitrant material.

Conclusions

The contribution of acetate fermentation was estimated using the $\delta^{13}C$ of methane, which is higher in rice paddies (mineral soils: − 51.5 ±7.1‰, peat soils: −56.5 ± 4.6‰) than in swamps (−66.1 ± 5.1‰). Large seasonal variation in $\delta^{13}C$, with a range of 32‰, was observed in rice paddies, whereas variation in δD was smaller, with a range of 20‰, indicating that variation in $\delta^{13}C$ is mainly due to changes in methane production pathways. Almost 100% of the methane was produced by acetate fermentation from July through September, immediately after the dry period, when methane concentrations started to increase. Conversely, the contribution of methane from acetate fermentation was reduced by 50 to 70% in winter. In swamps, CO_2 reduction pathways dominated over acetate fermentation, because of the depletion of acetate in these environments.

The relationship obtained between the δD of methane and surface water from rice paddy environments ($\delta D_{CH4} = 0.54 \times \delta D_{H2O} - 314$ ($R^2 = 0.39$)) was in agreement with results obtained from previous incubation experiments of rice paddy soils (Sugimoto and Wada 1995). The maximum difference of the δD_{CH4} from rice paddies caused by difference of δD_{H2O} was calculated to be approximately 50‰, indicating that the δD of methane is not greatly influenced by the region of rice paddies, since they are restricted to tropical, subtropical, and temperate regions. In the case of swamps, large variation in hydrogen isotope composition (from −345 to −270‰) was observed, probably due to D-enrichment of methane during methane oxidation and D-enrichment of hydrogen stimulated by sulfate-reducing bacteria in sulfate rich swamp.

Methane from rice paddies was enriched in ^{14}C (127±1 pMC) relative to 1990 levels of atmospheric CO_2, which shows higher ^{14}C activity compared with previous work in paddy fields. Methane from swamps was depleted in ^{14}C by 15–20% (110±2 pMC) relative to paddy fields, likely due to the contribution of older methane that was produced from recalcitrant material.

Acknowledgements

We thank T. Nakamura, A. Ikeda, and K. Oguri for their cooperation in conducting the radiocarbon measurements, and M. Uzaki, T. Yoneguchi, and Y. Mizutani for the isotope measurements of methane in Japanese rice paddies. We also thank O. Abe, T. Nakatsuka, and E. Matsumoto for their valuable contributions during the analyses. We are greatly indebted to the staff of the Pikunthong Royal Development Study Center for their kind help in collecting samples. We also thank two anonymous reviewers for their constructive comments. This work was financially supported by a Grant-in-Aid for Creative Basic Research from the Ministry of Education, Science, Sports, and Culture of Japan.

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