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Carbon isotope composition of CH_4 from rice paddies in Japan

MINORU UZAKI, HIROSHI MIZUTANI, & EITARO WADA
Laboratory of Biogeochemistry and Sociogeochemistry, Mitsubishi Kasei Institute of Life Sciences, 11 Minamiooya, Machida, Tokyo 194, Japan

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Abstract. Carbon isotope ratios ($\delta^{13}C$) for bubble CH_4 in a submerged paddy soil were studied in Yokohama, Japan, throughout a growing period, and its variation was found. Bubble CH_4 collected from other 33 paddy fields in Japan was also measured for its $\delta^{13}C$ and the results agreed with Yokohama. Furthermore, the variation occurred irrespective of the amount and the type of supplied organic substances to the fields (whole rice straw, rice stubble, or compost). The $\delta^{13}C$ value (average value of $-55.9 \pm 4.24‰$) from these paddy fields was higher than those of the CH_4 emitted from African and North American paddies. The higher value was little affected by their difference in the supplied organic substances. CH_4 oxidation likely occurs for bubble CH_4 in the shallow paddy fields. A rough estimate of the total CH_4 production, using isotope mass balance, showed that 17 to 22% of organic carbon supplied to Japanese paddies transforms to CH_4.

Introduction

While only one fifth of the present world cultivated acreage is for rice, it feeds more than one half the world population (FAO 1989). There are two types of domestic rice and the prevailing one is aquatic, grown in marshy or flooded lands. About 89% of the paddy fields in the world is in Asia and it produces more than 91% of the world's domestic rice. In fact, rice paddies are the most common fresh water-soil ecosystem in Asian agriculture. The largest producer of rice is China, followed by India, Indonesia, Bangladesh, Thailand, Viet Nam, Myanma (Burma), and Japan. Japan alone produces more rice than North and Central America and Europe combined.

In early spring in Japan, the soil is plowed to a depth of 15 to 20 cm, and young rice plants are transplanted. During summer, one half of the Japan's cultivated land is flooded to produce rice. The water depth is about 4 to 7 cm. The annual supply of fresh organics such as organic manure, winter weeds, and rice plant remains and roots actively support soil microorganisms in the paddies. The overlying water induces an oxidized surface layer at the soil surface (400 to 500 mV of redox potential) and a reduced layer underneath (−250 to −100 mV). Thus, both of the two most important atmospheric constituents of carbon, CO_2 and CH_4, are produced in almost all paddies.

As is well publicized, atmospheric CH_4 contributes to the greenhouse effect and influences tropospheric and stratospheric ozone (e.g., Hansen et al. 1988). Its concentration has increased from 0.7 p.p.m.v. to 1.7 p.p.m.v. over the last 300 years (e.g., Raynaud et al. 1988) and continues to do so at the annual rate of about 1%. CH_4 arises primarily from two biological processes (Wolin & Miller 1987): the reduction of CO_2, and the fermentation of acetate. Paddy fields are considered most important of the tropospheric CH_4 sources (Ehhalt and Schmidt 1978; Khalil and Rasmussen 1983; Holzapfel-Pschorn & Seiler 1986). The important agroecosystem to mankind is, thus, attracting attention not because of its product but rather because of its byproduct.

In order to control CH_4 emission from paddies, while maintaining their productivity, it is necessary to know more about the ecosystem and the physiology of rice plants relating to CH_4 production. Stable carbon isotope studies would be of use for this purpose. It can, in principle, distinguish CH_4 through the CO_2 reduction from that through the fermentation. Whiticar et al. (1986), for instance, showed that $\delta^{13}C$ value for CH_4 *via* the CO_2 reduction is −110 to −60‰ while that *via* the fermentating −65 to −50‰. Bacterial CH_4 oxidation shows a significant carbon isotope fractionation up to 1.020 which favors light isotopic molecules (Zyakum et al. 1981).

Curiously, stable isotope research on CH_4 from rice paddies has so far neglected paddies in Asia. Accordingly, we collected bubble CH_4 from a submerged paddy field and measured its carbon isotope ratio throughout the growing season of 1989 in Yokohama, Kanagawa Prefecture, Japan. We also conducted a nationwide survey on CH_4 from Japanese paddy fields.

Methods

Sampling locations

At two sites of the paddy field (50 m × 100 m) at Yokohama, Kanagawa Prefecture, soils and bubbles in it were collected from 5 June (10th day after flooding) to 24 August (90th day), 1989. The soils were a brown alluvium. Organic manure supplied to it is only rice stubble that amounts to 0.12 kg dry weight/m^2/year. In addition, a nationwide collection of gas bubbles and soils were performed in the same 1989 from 33 rice paddies at 13 locations in Japan (Fig. 1). At most locations, more than one paddy was selected for the sampling. There were three types among these

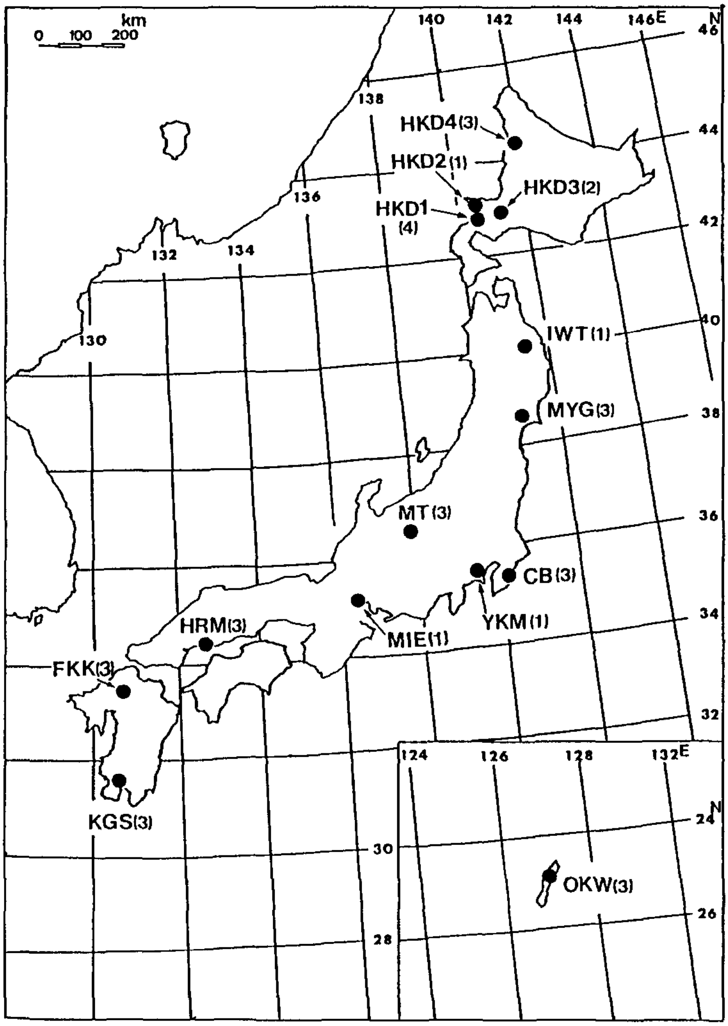

Fig. 1: Sampling locations of nationwide survey. Number of plots studied at each location is given in parentheses. The place of the Yokohama paddy is also shown.

Abbreviations: HKD1 — Hokkaido (Rankoshi-cho), HKD2 — Hokkaido (Kyowa-cho), HKD3 — Hokkaido (Hiroshima-cho), HKD4 — Hokkaido (Shosanbetsu-mura), IWT — Iwate, MYG — Miyagi, CB — Chiba, YKH — Yokohama; MT — Matsumoto, MIE — Mie, HRM — Hiroshima, FKK — Fukuoka, KGS — Kagoshima, OKW — Okinawa paddies concerning applied organic manure: W-type paddy field where whole rice straw containing leaves, stems, and stubbles were applied (about 0.6 kg dry weight/m^2/year); S-type paddy where only rice stubble remained after harvest was the source of organic matter (about 0.1 kg dry weight/m^2/year); and C-type paddy where compost heap made from rice straw was applied (0.6—2.0 kg/m^2/year). According to this classification, the Yokohama field belongs to the S-type.

Sampling methods

Bubbles in the submerged soils (up to 20 cm in depth) were purged by stirring, and trapped in an inverted funnel (15 cm in diameter) initially filled with paddy water. Then, approximately 30 ml of the gas was extracted by a syringe from the funnel through a serum cap and transferred to a glass tube (50 ml) initially filled with the water and capped with a silicone rubber stopper. It was kept upside down until ready for analysis to prevent gas leakage through the stopper.

In order to see if a relationship exists between CH_4 concentration in the bubble and the extent of bubble gas formation, the extent was recorded at the time of bubble sampling according to the following:

- lebel 1, more than 3,000 cm^2 of the field was necessary to collect 50 ml of the gas;
- lebel 2, more than 750 cm^2 and up to 3,000 cm^2 needed;
- lebel 3, more than 200 cm^2 and up to 750cm^2;
- lebel 4, more than 75 cm^2 and up to 200 cm^2;
- lebel 5, less than 75 cm^2;
- lebel 6, frequent bubbling from surface.

Submerged surface soil up to about 15 cm in depth was collected simultaneously for measurement of $\delta^{13}C$ of soil organic matter.

Gas analysis

The collected gas was analyzed by a gas chromatograph (Shimadzu GC3BT) with a thermal conductivity detector (TCD). Chromatographic analyses were carried out with a column serially connected as Porapak Q column (2 m), TCD, blank column (10 m), molecular sieve 5A column (2 m), and TCD (Nakamura 1981). The carrier gas was helium at a flow-rate of about 35 ml/min. The column temperature was 45 °C. Carbon monoxide was not detected in any one of the gas samples ($CO/CH_4 <$ 0.01 as molar ratio).

Sample preparation for carbon isotope measurements

A sample gas (3—25 ml) in the tube was introduced into a vacuum line through a silicone septum by using an airtight syringe, and passed through a series of a dry ice — ethanol trap and a liquid nitrogen trap to remove water vapor, CO_2, and any other condensables. Gases not trapped were then introduced to molecular sieve 5A at a liquid nitrogen temperature and those not adsorbed onto the sieve were pumped out. The adsorbed gases were desorbed at room temperature and introduced into a circuit line equipped with an 850 °C CuO furnace, circulated for 45 min to covert CH_4 to CO_2, and CO_2 was collected with a liquid nitrogen trap (Mizutani and Wada 1985) for the isotope measurement.

Soil samples were freeze-dried, passed through a stainless sieve (2 mm), and ground in a mortar with a pestle to less than 0.5 mm. The carbonates in the powder were then removed by treatment with 2N HC1 solution (room temperature, 24 h). The wet soil samples were neutralized with NaOH solution to pH value of around 5 and dried. Soil samples containing 0.5 to 5 mg organic carbon were analyzed for carbon isotope ratios. Organic carbon was transformed into CO_2 by heating at 850 °C with copper oxide (Minagawa et al. 1984). Analysis of organic carbon and nitrogen contents was also performed by a combustion method using a Yanagimoto MT-3 Model CHN analyzer.

Isotope measurement

A Finnigan MAT-251 mass spectrometer with dual inlet and triple collector systems measured the carbon isotope ratio, which was expressed in ‰ deviation ($\delta^{13}C$) from PDB carbonate standard, where:

$$\delta^{13}C(‰) = \frac{(^{13}C/^{12}C)_{\text{sample}} - (^{13}C/^{12}C)_{\text{PDB}}}{(^{13}C/^{12}C)_{\text{PDB}}} \times 1000.$$

There were two working standards in the present work. One (−19.4‰) was generated by reacting sodium bicarbonate powder with anhydrous phosphoric acid. The other (−11.3‰) was obtained by reacting 0.5 M sodium bicarbonate solution with dilute hydrochloric acid. Their carbon isotopic compositions were calibrated against National Bureau of Standards isotope reference material No. 20 and No. 21. Standard deviation of the carbon isotope measurements was less than 0.1‰.

Results

The CH_4 concentration in the bubbles and its $\delta^{13}C$ at the Yokohama paddy field are summarized in Table 1 together with some soil characteristics. The results of the nationwide survey are given in Table 2.

So far examined in the present study, CH_4 concentration in the bubbles was highly variable (1—59% V/V) and seemed to be related to the rate of CH_4 production in paddies, since the CH_4 concentration increased with increasing *in situ* accumulation of bubbles in the paddies (Fig. 2).

Fig. 3 shows the seasonal variation of the $\delta^{13}C$ (CH_4) value and the concentration at the Yokohama paddy field. Starting from a low value of around −65‰ at the 10—17th day after flooding, it increased rapidly about the 30th day after flooding and reached a maximum on the 45th day. After that, the value appeared to decrease gradually but did not return to the value observed at the early period of flooding. On the other hand, the CH_4 concentration increased rapidly after flooding and reached a minimum of 2% at the 45th day after flooding when the corresponding

Table 1. The seasonal variation at the paddy field of Yokohama. Organic matter supplied to this paddy field is rice stubble (0.12 kg/m^2/year).

			CH_4		Soil organic carbon		
Site	Date	Submerged period (days)	concentration (%)	$\delta^{13}C$ (‰)	concentration (%)	$\delta^{13}C$ (‰)	Soil C/N
Site 1	5 June	10	1.4	−63.5	3.0	−23.7	11.9
	12 June	17	4.0	−63.7	n.a.	n.a.	n.a.
	20 June	25	21.5	−61.2	2.7	−23.8	10.6
	5 July	40	10.1	−61.5	3.4	−24.2	10.2
	10 July	45	2.2	−56.1	2.9	−23.8	10.8
	17 July	52	12.4	−57.1	2.8	−23.6	10.5
	31 July	66	13.4	−58.6	2.9	−23.8	11.5
	7 Aug.	73	7.2	−58.6	3.4	−23.9	10.9
	24 Aug.	90	1.1	−60.6	3.7	−24.0	10.9
Site 2	12 June	17	2.9	−65.0	n.a.	n.a.	n.a.
	20 June	25	10.9	−62.0	2.8	−24.2	11.0
	5 July	40	5.6	−57.0	2.9	−24.1	9.8
	10 July	45	4.8	−52.1	3.0	−24.3	9.7
	17 July	52	10.6	−56.7	3.0	−24.3	9.9
	24 Aug.	90	0.9	n.a.	2.9	−24.4	10.1

n.a.: not analyzed

Table 2. The type of main organic source, submerged period, concentration and $\delta^{13}C$ for bubble methane, organic content and $\delta^{13}C$ for soil organic carbon, and C/N of Japanese paddy soils.

				CH_4		Soil organic carbon		
Location	Plot	Type	Submerged period (days)	concentration (%)	$\delta^{13}C$ (‰)	concentration (%)	$\delta^{13}C$ (‰)	Soil C/N
HKD1	−1	W	61	23.4	−53.8	2.4	−27.0	12.5
	−2	W	61	27.9	−55.7	1.9	−27.2	12.1
	−3	W	61	14.7	−49.9	1.6	−26.7	12.1
	−4	W	61	10.2	−57.0	3.2	−26.6	12.4
HKD2	−1	S	56	11.0	−53.9	3.5	−27.7	16.4
HKD3	−1	S	62	8.7	−52.0	1.6	−26.6	13.2
	−2	S	62	20.4	−52.7	2.6	−26.8	13.3
HKD4	−1	W	62	23.5	−53.4	1.5	−26.8	10.7
	−2	W	62	16.4	−51.2	1.7	−26.7	10.3
	−3	W	62	55.4	−55.3	1.9	−26.9	11.0
IWT	−1	W	63	27.9	−54.3	6.9	−21.2	13.7
MYG	−1	C	63	5.9	−54.9	1.4	−25.1	12.5
	−2	C	63	5.0	n.a.	1.9	n.a.	12.7
	−3	C	63	6.8	−56.0	1.7	−25.1	12.0
CB	−1	W	69	10.3	−54.9	1.7	−26.1	10.9
	−2	W	69	40.4	−59.4	1.6	−25.7	11.0
	−3	W	69	39.3	−56.7	2.8	−25.5	10.4
MT	−1	C	77	12.4	−59.6	1.5	−24.6	11.7
	−2	C	77	7.0	n.a.	1.9	n.a.	9.3
	−3	C	77	9.5	−56.5	1.8	−27.2	9.6
MIE	−1	W	76	10.1	−55.7	1.9	−27.2	13.2
HRM	−1	W	45	13.7	−51.1	1.8	−25.8	11.2
	−2	W	45	32.1	−49.8	1.6	−25.9	11.6
	−3	W	45	33.5	n.a.	1.5	n.a.	11.3
FKK	−1	S	22	7.1	−58.7	2.6	−26.6	10.7
	−2	W	22	6.2	n.a.	2.5	n.a.	10.4
	−3	W	22	13.1	−60.7	2.8	−26.6	10.1
KGS	−1	C	89	18.8	−53.9	1.1	−26.0	11.7
	−2	C	89	19.8	−55.6	1.2	−24.5	11.4
	−3	C	27	5.4	−68.3	1.8	−24.9	13.3
OKW	−1	W	119	50.6	−53.4	0.8	−23.7	10.1
	−2	W	119	72.2	−47.5	1.0	−22.3	10.3
	−3	W	119	53.4	−53.8	0.8	−25.1	9.6

Letters in the column for the type of main organic source indicate the following: W, whole rice plant except grain (about 0.6 kg dry weight/m^2/year); C, compost heap (0.6—2.0 kg dry weight/m^2/year); and S, only rice stubble remaining after harvest (about 0.1 kg dry weight/m^2/year). n.a. stands for "not analyzed." Abbreviation of locastions: see Fig. 1.

$\delta^{13}C$ attained a maximum. After then, the CH_4 concentration reached a second peak before drainage.

Although CH_4 concentration seems to vary seasonally, it does not clearly correlate to the seasonal variation of $\delta^{13}C$. The correlation between the $\delta^{13}C(CH_4)$ and the CH_4 concentration is weak, if any ($r^2 = 0.02$ for Yokohama and 0.15 for the nationwide survey). Neither does the $\delta^{13}C(CH_4)$ indicate a clear correlation with the estimated extent of bubble accumulation in the paddies. However, the significant correlation between $\delta^{13}C(CH_4)$ and CH_4 concentration was observed for these data obtained at the 60—70th day (Fig. 4). The $\delta^{13}C$ value became higher with decreasing CH_4 concentration.

At the nationwide locations, $\delta^{13}C(CH_4)$ values appear to follow Yokohama in a similar manner (Fig. 5). The nationwide survey supports the observed increase in $\delta^{13}C(CH_4)$ after about 30th day of flooding irrespective of the types of supplied organic manure. It shows that the

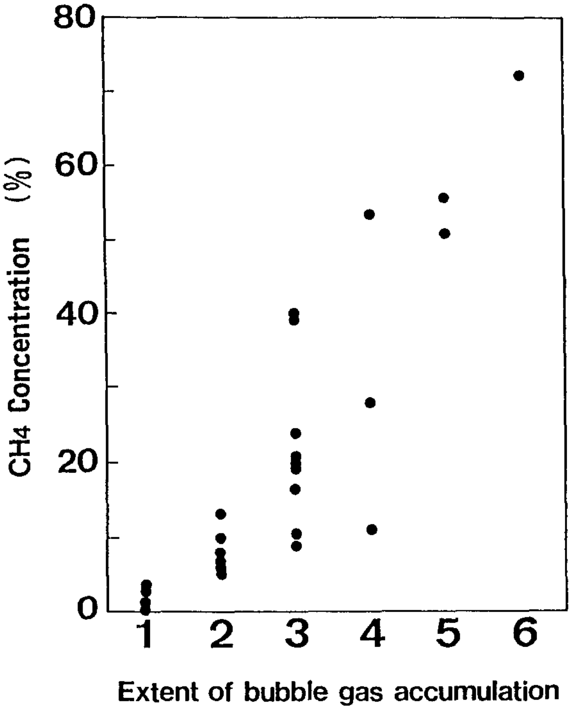

Fig. 2: Plots of CH_4 concentration (% V/V) in bubble versus extent of bubble gas accumulation in submerged soils. The extent was estimated by area of paddy field to collect 50 ml of bubble gas for the nationwide bubble samples (see sampling methods section of text).

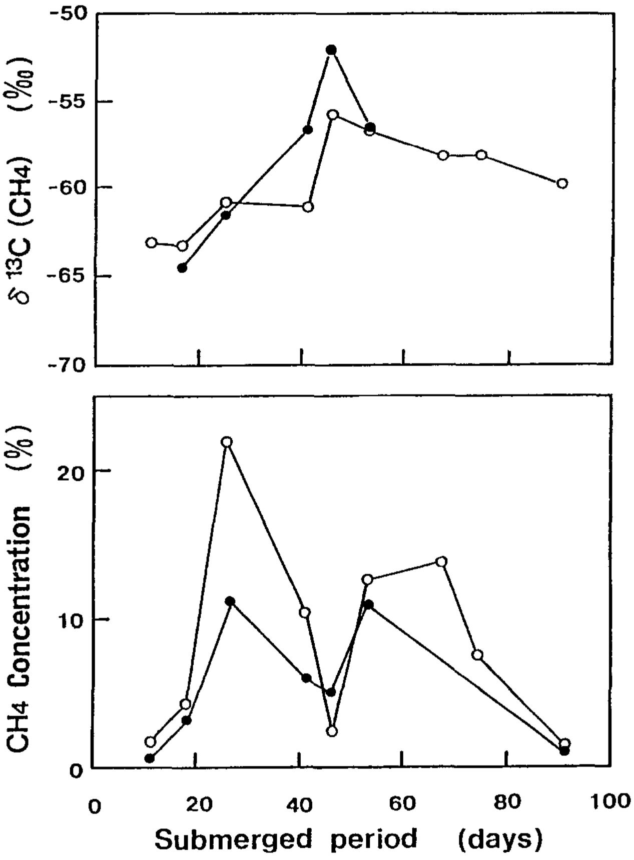

Fig. 3: Temporal variation of CH_4 concentration (bottom) and its $\delta^{13}C$ value (top) along with submerged period at the Yokohama paddy field. The drainage of paddy water was started from about 80th day after flooding. Open and closed circles correspond to the two sites of the paddy field, respectively.

Japanese paddy fields are similar to one another in terms of $\delta^{13}C(CH_4)$ variation in spite of their difference in kind and quantity of suplied organic matter, although rather high CH_4 concentrations with high $\delta_{13}C$ values were somethimes obtained from W-type paddy fields where readily decomposable organic matter was applied. The present study gives an overall average of −55.9 ± 4.2‰ for bubble CH_4 from the 13 locations.

At the Yokohama paddy, the $\delta^{13}C$ for soil organic carbon did not change at both sites throughout the cultivation period. At site 1, the average $\delta^{13}C$ was −23.9 ± 0.2‰ (8 samples), while it was −24.3 ± 0.1‰ at site 2 (5 samples). However, soil $\delta^{13}C$ at different locations

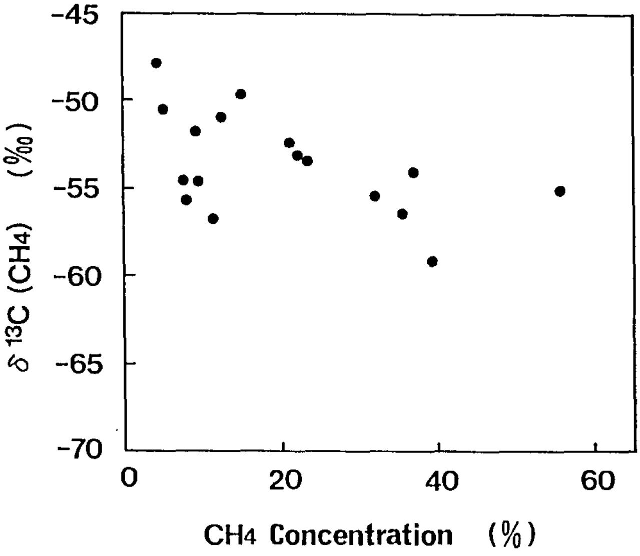

Fig. 4: Relation between $\delta^{13}C(CH_4)$ and CH_4 concentration for bubbles from the nationwide paddy fields. They were collected during the 60—70th days after flooding.

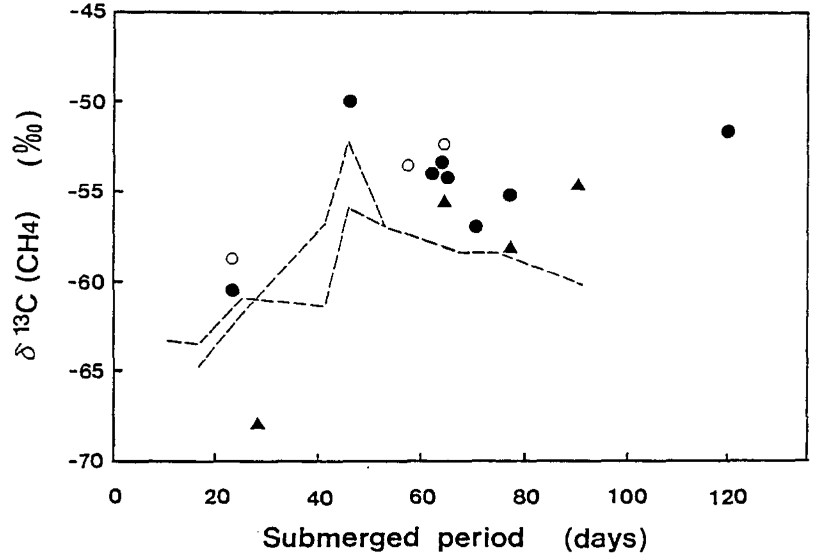

Fig. 5: Plots of $\delta^{13}C(CH_4)$ value in bubble gases versus submerged period. Dashed lines indicate the seasonal variation of $\delta^{13}C$ (CH_4) at Yokohama paddy field (cf., Fig. 3).

varied greatly. In the nationwide survey, the 33 paddy fields showed a large variation in $\delta^{13}C$ for their soil organic carbon. The lowest $\delta^{13}C$ was −27.7‰ at HKD2 and the highest −21.2‰ at IWT, and the nationwide average was −25.7 ± 1.6‰.

Discussion

Rate of CH_4 production and $\delta^{13}C(CH_4)$

The CH_4 emission rate was not measured in the present study. The concentration in bubbles is likely to be related to the rate since the solubility of CH_4 is low and methanogenesis must play an important role in the formation of bubbles in the submerged anoxic layers. From our semi-quantitative observation, it appeared that, when more gas was formed, CH_4 concentration in bubbles was higher (Fig. 2). Yamane & Sato (1970) reported the same relation for submerged soils of rice field at Kashimadai, Miyagi Prefecture, Japan.

The CH_4 concentration of W-type paddy fields was 26.7 ± 15.1% (average submerged period at the time of sampling was 64.6 ± 25.8 days at 8 locations), while C-type paddies gave the average concentration of 10.5 ± 6.3% (47.2 ± 23.3 days at 4 locations) and S-type paddies 10.9 ± 3.8% (46.7 ± 17.6 days at 3 locations) (Table 3). Yielding the highest CH_4 concentration among the three types, W-type paddy is likely to generate the largest quantity of CH_4. This agrees with Yagi & Minami (1990) who report a significant increase in the CH_4 emission rate by application of rice straw and with Tsutsuki & Ponnamperuma (1987) who showed the enhancement of CH_4 formation by application of readily decomposable organic matter but not of compost.

The bubble CH_4 concentrations from two sites of the Yokohama paddy field showed a peak at about the 25th day and another at the 50—70th

Table 3. $\delta^{13}C$ value and its concentration for bubble methane from the 15 paddy fields in Japan.

	Numbers of location	Methane $\delta^{13}C$ (‰)	Methane concentration (%)
For paddy fields having submerged periods of 22 to 119 days			
W-type fields	8	−54.7 ± 3.2	26.7 ± 15.1
S-type fields	3	−55.0 ± 3.3	10.9 ± 3.8
C-type fields	4	−59.2 ± 6.3	10.5 ± 6.3

day after flooding. Assuming that the CH_4 content reflects its production, these peaks would correspond to maximal production. Though different in details, such seasonal variations in CH_4 production rate were reported by Holzapfel-Pschorn & Seiler (1986) for an Italian rice paddy, by Yagi & Minami (1990) for Japanese paddy fields, and by Cicerone et al. (1983) for a Californian rice paddy.

Possible causes of the observed seasonal variation of $\delta^{13}C(CH_4)$ (Figs 3, 5) would be:

— change in $\delta^{13}C$ value for CH_4 precursor, CO_2 or acetic acid,
— change in the CH_4 production mechanisms,
— influence of aerobic CH_4 oxidation.

Among them, the first is likely to govern the overall trend of the $\delta^{13}C(CH_4)$ variation. Nakamura et al. (1990) showed a $\delta^{13}C$ increase of about 7‰ for CO_2 in the reduced layer of paddy soils at approximately 70th day after flooding due to the progress of dark carbon dioxide fixation and production of CH_4 from CO_2. The dark carbon dioxide fixation was found for the first time by Wood and Werkman in 1935 (Wood et al. 1962), and was also observed in incubation experiments of paddy soil by Takai (1970). The fractionation factor has been determined experimentally as 1.028 by Sorokin (1960). Its effects might gradually raise the observed $\delta^{13}C(CH_4)$ value for the nationwide paddies throughout the entire submerged period. As for the $\delta^{13}C$ change for acetate, very little is known. The $\delta^{13}C$ for acetate in submerged soil and the fractionation associated with its fermentation are also poorly understood. Only Blair et al. (1987), studying acetate samples from the anoxic marine sediment of Cape Lookout Bight, North Carolina, U.S.A., reported the mean $\delta^{13}C$ values for acetate about 5‰ heavier than that for total organic carbon fraction. Detailed investigations of acetate are required.

Some previous work emphasized the second possible cause as the most probable factor governing the seasonal variation of $\delta^{13}C$ for biogenic CH_4 under wet anoxic environments (Whiticar et al. 1986; Martens et al. 1986). As CH_4 from the acetate fermentation is higher in its $\delta^{13}C$ than that from CO_2 reduction, the increase in the $\delta^{13}C(CH_4)$ after the 40 to 50th day as shown in Figures 3 and 5 may be partly due to the higher contribution of acetate fermentation. Takai (1970) showed that acetate gradually accumulates in submerged paddy soils to the maximum at 1—2 months after flooding, while Yamane (1977) gave 2—3 weeks. Moreover the reduction of CO_2 is believed minor in paddy fields, however the actual figure for its estimated contribution varies from 20—30% (Koyama 1963, 1964; Takai 1970) to 30—50% (Schütz et al. 1989). More detailed surveys on acetate and CO_2 dynamics will be required, since our present available data were very limited.

The third possible cause can also be responsible for the seasonal variation, because aerobic bacterial CH_4 oxidation enriches remaining CH_4 in ^{13}C (Zyakun et al. 1981) and because a rice paddy field is a shallow water-soil system where diffusion of atmospheric oxygen into soil system can take place rather easily by physical and biological perturbation, although paddy soils become anoxic within the first week after flooding and remain so throughout submerged period (Yamane 1960; Inubushi et al. 1984). Maximal $\delta^{13}C(CH_4)$ at the 40—45th day after flooding clearly coincided with the low CH_4 concentration (Fig. 3). Furthermore, the $\delta^{13}C(CH_4)$ value at the 60—70th day of the flooding became higher from −56 to −53‰ with decreasing concentration of CH_4 in bubbles (Fig. 4). The progress of oxidation process can thus be emphasized for bubble samples in the paddy fields.

Whatever the cause, the observed variation of the $\delta^{13}C(CH_4)$ must reflect dynamic interactions taking place in the paddy field and more knowledge would enable us to determine their relative importance.

$\delta^{13}C$ (CH_4) values from Japanese rice paddies

Stevens and Engelkemeir (1988) reported $\delta^{13}C$ values of −67‰ for atmospheric CH_4 in the rice paddy area north of Sacramento, California. Tyler et al. (1988) reported $\delta^{13}C$ values between −57 and −63‰ for atmospheric CH_4 in rice paddy fields, Kenya. Wahlen et al. (1989) present $\delta^{13}C(CH_4)$ of −63.2‰ for atmospheric methane in Louisiana paddy fields. For bubble CH_4, Nakamura et al. (1990) reported $\delta^{13}C$ value of −55.1‰ from a paddy soil at Konosu, Japan. The present study gives an overall average of −55.9 ± 4.2‰ for bubble CH_4 from the 13 locations. At first, these results may appear to suggest a higher $\delta^{13}C$ value for the bubble CH_4 than that over paddy fields. A large fraction of CH_4 in paddy soil escaping to the atmosphere goes through rice plants (Schütz et al. 1989; Inubushi et al. 1989). If lighter CH_4 is preferentially transported through such a route, it would explain the discrepancy. However, Chanton et al. (1988) showed that $\delta^{13}C$ for bubble CH_4 in Florida Everglades soils is 5—10‰ lighter than that transported to the atmosphere through plants. Neither does the isotope effect of CH_4 oxidation during ebullition explain the lighter value for atmospheric CH_4, because the process enriches the remaining CH_4 in ^{13}C (Zyakun et al. 1981). If the CH_4 oxidation in bubbles has occurred, the $\delta^{13}C$ value becomes heavier. The oxidation may partly explain the higher $\delta^{13}C$ value for the present paddies. Figure 4 shows that, paddies of common cultivated stage (60—70th day after flooding), higher $\delta^{13}C(CH_4)$ is found for the bubbles of lower CH_4 concentration. The paddies of the common stage were selected to minimize the influence of seasonal variation of $\delta^{13}C(CH_4)$. The relation appears to show that the CH_4 oxidation is likely to occur even for bubble CH_4. Although there are some overlapping values with previous studies, it may seem that the slightly higher $\delta^{13}C$ for Japanese paddies is true to all types of supplied organic matter. Its confirmation, its cause, and similar studies on CH_4 from paddies in other Asian countries would be of urgent importance. Recently we have obtained a rather low $\delta^{13}C(CH_4)$ value of −70‰ from an experimental paddy field applied 0.6 kg dry weight/m^2/year of rice straw (unpublished).

Amount of CH_4 and CO_2 from Japanese paddies

Although the present nationwide survey showed that more understanding is necessary to get a mean $\delta^{13}C(CH_4)$ from Japanese paddies, it would be of interest to estimate roughly the total CH_4 production, using isotope mass balance.

Rice plants plowed into soil after harvest are the most abundant organic matter that would be the source of CH_4, and the average $\delta^{13}C$ value for the rice plant in Japan is about −25.5‰ (Samejima 1985; Nakamura et al. 1990). Nakamura et al. (1990) also gave the $\delta^{13}C$ of −26.7‰ for compost heap made from rice straw and showed little difference between $\delta^{13}C$ values for soil and incoming organic matter to the paddies at Konosu. Though every paddy soil has its own $\delta^{13}C$, the average of −25.7 ± 1.6‰ in the present study is very similar to that for the organic matter commonly supplied to Japanese paddies. Therefore, we assume that the average $\delta^{13}C$ for incoming organic matter to Japanese paddies is −25.7‰.

Although the average $\delta^{13}C$ value for CO_2 changes along the cropping period, Nakamura et al. (1990) gave an estimate of −18.5‰ from their study of paddy soils at Konosu, Japan, where a mixture of rice straw and soybean compost was supplied. Because $\delta^{13}C(CH_4)$ also changes, we adopt the simple average and the standard deviation (1σ) as the probable range for CH_4; it would be −60.1‰ to −51.7‰. The residual solid organic matter also should be an additional important pool. However, it appears that the pool can be neglected on isotope mass balance, since $\delta^{13}C$ value of soil organic matter is similar to that of supplied organic matter as stated above. Assuming that all the organic carbon supplied into anaerobic paddies decomposed to yield either CH_4 or CO_2, then isotope mass balance gives that 17 to 22% of organic carbon transforms to CH_4. The lower value is more probable if we take the CH_4 oxidation into consideration.

The total annual input of rice plant remains into Japanese paddy fields in 1987 is 5.4×10^{12} g, estimated by the Production Division, Agriculture

Production Bureau, the Ministry of Agriculture, Forestry, and Fisheries of Japan (pers. comm.). If all of this organic carbon decomposed to yield CH_4 and CO_2, the annual output of CH_4 from Japanese paddies would be 4.7 to 6.0×10^{11} g/year. This figure would be, on one hand, an overestimate in a sense that it assumes a complete decomposition of incoming organic matter to gases under anaerobic conditions. On the other hand, it would be an underestimate in a sense that other sources of organic inputs such as manure and weeds are ignored.

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