

EARLY-DIAGENETIC METHANE FROM VARIOUS TROPICAL FRESHWATER SEDIMENTS: MOLECULAR AND CARBON ISOTOPE VARIATIONS IN ONE DIAL CYCLE

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Abstract: In the tropical climate of Southern Thailand, on September 5 and 6, 1994, dial emissions of CO₂ and CH₄, and dial variations in bubble CO₂ and CH₄ concentrations and the ¹³C/¹²C ratio in bubble methane were observed in shallow freshwater sediments of a high sulphate concentration pit, a high turbulence canal, and in a pond with a high density of emerged macrophytes. Measurements show that δ¹³CH₄ values are lowest in the night, and highest in the daytime, ranging from a minimum of –63.8‰ at 02:20 (canal) to a maximum of –47.6‰ at 6:45 (pit). High δδ¹³CH₄ values of daytime methane occur when the concentration of CO₂ decreases and acetic acid fermentation becomes relatively more important. Minimum δ¹³CH₄ values are apparently caused by an enhanced CO₂-H₂ methanogenesis pathway. Irregular diurnal variation of the δ¹³CH₄ value in the pond was caused by oxidation and ventillation of sediments by macrophytes and the different lithologies of the sediments in separate sampling stations. Generally, δ¹³CH₄ values in the pit and the pond were about 10‰ higher as compared to values from the canal, suggesting an active acetic acid pathway and oxidation effect in the former two environments. Likewise, the lowest production rate of methane and the lowest δ¹³CH₄ values in the canal suggest an enhanced CO₂ reduction pathway. The maximal δ¹³CH₄ value accompanied by the highest bubble CO₂ concentration is caused by strong oxidation of methane when the production rate of methane in early morning is lowest.

Abstrakt: Badania dotyczyły dobowych zmian w emisji CO₂ i CH₄ z powierzchni wody oraz stężenia CO₂ i CH₄ a także stosunków izotopowych ¹³C/¹²C w bąblach gazowych uwalnianych z osadów słodkowodnych klimatu tropikalnego. Opróbowania przeprowadzono w Południowej Tajlandii, 5 i 6 września 1994, na obszarach płytkowodnych: wkopu wypełnionego wodą o wysokim stężeniu siarczanu, kanału melioracyjnego o silnej turbulencji wody i stawu gęsto zarośniętego roślinami ukorzenionymi. Stwierdzono, że wartość δ¹³CH₄ bąbli gazowych z osadów jest najniższa nocą a najwyższa w ciągu dnia, wahając się w zakresie od –63.8‰ (godz. 02:20, kanał) do –47.6‰ (godz. 6:45 wkop). Wysokie wartości δ¹³CH₄ występują kiedy stężenie CO₂ obniża się powodując proporcjonalnie większy udział fermentacji octowej w produkcji metanu. Niższe wartości δ¹³CH₄ są wynikiem wzmożonej metanogenezy opartej na redukcji CO₂ przez H₂. Nieregularne wahania δ¹³CH₄ w osadach stawu są najprawdopodobniej wynikiem intensywnego, z różnym nasileniem, utleniania metanu, wentylacji osadu przez system korzeniowy roślin i różną litologię w różnych miejscach poboru prób. Generalnie, wartość δ¹³CH₄ była około 10‰ wyższa w osadach wkopu i stawu niż w osadach kanału, co było najprawdopodobniej wynikiem niskiego udziału fermentacji octowej w osadach kanału oraz rezultatem intensywnego utlenieniem w osadach wkopu i stawu. Najwyższa wartość δ¹³CH₄, której towarzyszy najwyższe stężenie CO₂ w osadzie, jest najprawdopodobniej wynikiem silnego utleniania metanu nad ranem (najniższa produkcja metanu).

Key words: freshwater sediments, diagenesis, methane, carbon dioxide, carbon isotopes, greenhouse effect.

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INTRODUCTION

Early diagenesis of organic matter and simultaneous emission of methane are crucial factors governing subsequent generation of hydrocarbons in later stages of diagenesis and burial of the sediments. Thus, information on the mechanisms of early-diagenetic methanogenesis and on the isotope signature of ebulliting (natural bubbling from sediments) methane appear to be very important for hydrocarbon exploration. However, such information is currently limited only to the day-time methanogenesis. On the other hand, methane emission from wetlands to the atmosphere is of concern especially in relation to the greenhouse effect (Craig & Chou, 1982; Khail & Rasmussen, 1983; Cicerone, 1987; Wada, 1990). Information on the exact isotope composition of methane from different emitters is crucial to the calculation of the isotope mass balance of greenhouse gases. Freshwater sediments are considered to be the largest global emitter of methane and the main factors governing isotope composition and production rate of such methane are isotope composition of methane precursors, temperature, mechanism of methanogenesis and methane consumption. Most information on methanogenesis in natural conditions has resulted from day-time sampling of early-diagenetic bacterial methane emitted from wetlands, paddy fields, landfills, waste areas, etc. However, it has been found recently that mechanisms of methanogenesis in temperate climate freshwater systems may vary with diurnal cycle (Jędrysek *et al.*, 1993; Jędrysek, 1994, 1995). Thus, one may infer that current knowledge of the mechanism of methanogenesis in natural freshwater conditions is not extensive enough, and isotope values collected to the present day are not representative of nearly half of the methane emitted from sediments. The aim of this paper is to show that in a variety of different conditions diurnal variation in stable carbon isotope ratios in methane from tropical freshwater sediments may be different due to diurnal variations in the mechanisms of methanogenesis and the oxidation effect (or mechanism of oxidation).

GEOLOGICAL SETTING

Observations on diurnal variation in methanogenesis in sediments were made in the artificial aquifers (pit, canal and pond) in the experimental fields of the Pikurnthong Development Royal Study Center (PDRSC), Narathiwat Province, Southern Thailand (Fig. 1). This part of Thailand is dominantly characterised by three main structural features, dominated by granitoid batholiths, arrayed in NW–SE direction. The Eastern batholith consists of medium to coarse-grained porphyritic biotite granite, adamellite and granodiorite of Triassic and Jurassic age. The other two batholiths are dominated by porphyritic biotite granite, granodiorite, hornblende-adamellite and fine-grained muscovite tourmaline granite, formed in Cretaceous and Tertiary. Moreover, in the southern portion of the area under consideration, adjacent to Malaysia border, some sedimentary sequence comparable to Kanchanaburi Formation has also been observed. It consists mainly of sandstones, shales, cherts, matatuffs,

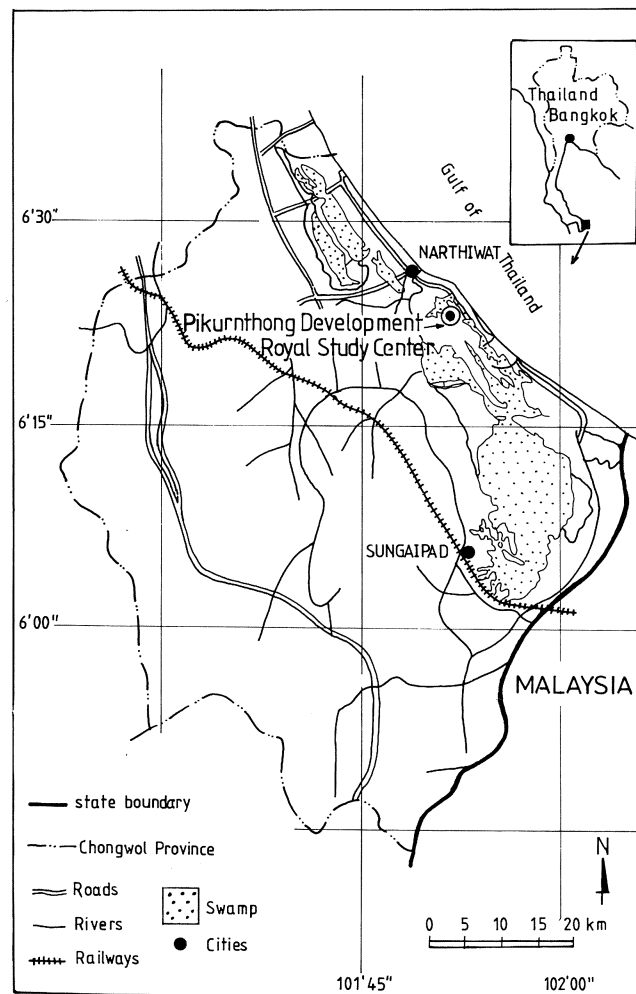


Fig. 1. Location of the study area (S Thailand)

schists, quartzites, black shales and mudstones with limestone lenses. Quaternary deposits covering the whole area are dominantly peats and peat soils, or sandy soils acidified by marine sulphate (Vijarnsorn, 1996; Vijarnsorn & Liengsakul, 1987).

FIELD OBSERVATIONS

Sampling was carried out on September 5 and September 6, 1994. The pit was ca. 50 m² in area, 2 m deep and free from any macrophytes. The water in it was transparent, in so far that the bottom (2m depth) could be seen, and low in suspended and dissolved organic matter. The pit was dug in sulphate-rich soil and the water is rich in sulphate. The canal is a stream isolated from the soil by an impermeable cement cover, ca. 0.5 m deep and about 1.5 m wide, and was free from any macrophytes. Thickness of sediments was about 10 cm. Water in it was highly turbid (maximum flow velocity was about 0.8 m/s) and was fairly rich in suspended soil material. However, it was transparent in so far as the shallow depth 0.5 m had not allowed one to judge the transparency limit. The pit and canal sediments were very homogenous and similar in each station. The pond was c. a. 0.1

km² in area, several metres deep and rich in dissolved organic matter. Water in it showed very poor transparency (the bottom below the depth of 0.15 m could not be seen). About 80% of total surface of the pond was covered by leaves of emerged macrophytes and several trees and bushes grow within 2–3 m of the sampling stations. Sediments in the pond (clay, sand, mud to organic gyttia) were different at each sampling station and the density of emerged and submerged macrophytes varied substantially – all of which could result in variability of the oxidation state in the sediments.

SAMPLING

Carbon dioxide-and-methane-containing gas mixtures (bubbling and diffusing from sediments and water) were collected in floating plastic chambers, for gas chromatography analysis. The volume of a single chamber was about 2 dm³ and the collecting surface was about 350 cm². Each chamber was initially filled with ambient atmosphere. The bottom of the chambers were opened to the underlying water surface and the temperature in the chambers was not controlled. These chambers were situated in the same sampling stations (over the same sediments) throughout the duration of the observations and the first sampling was several hours after the chambers were put on the water surface. About 5 ml of collected gas, from the chambers was transferred by gas-tight syringe to bottles initially filled with 1N HCl solution (bubbled with He to eliminate CO₂ and CH₄) and sealed with a butyl rubber cap and an aluminium seal. Some solution remained in the bottles. Bottles with samples were stored in a refrigerator (3–4°C) in an inverted position.

Bubble methane for ¹³C/¹²C analysis was obtained from submerged sediments by agitation and trapped in an inverted funnel about 20 cm in diameter. The bubbles produced were introduced into a glass bottle filled with the aquifer water. For all sampling, gases were collected from 0 to about 15 cm depth in the sediments. Water depths over the sediments from which the gas was sampled were 2.0, 0.5 and 0.7 m in the pit, canal and the pond respectively. The sampling was done at different stations, 0.5, 0.5 and 1.0 m from the banks of the pit, canal and pond respectively. The stations along the banks were about 2 m apart. The sampling time of bubble gases was usually no longer than 2 minutes. Some water remained in the bottles. The bottles were sealed with a butyl rubber cap and an aluminium seal and the samples were immediately treated with HgCl₂ solution. The bottles were always in inverted position in order to prevent diffusion. Bottles with samples were transported to Poland by air-plane as a personal baggage, to prevent substantial variation of pressure or temperature and reorientation of bottles. Bottles with samples were stored in a refrigerator (3–4°C) in an inverted position. Repeated analysis (after about 6 months) proved that the length of the period over which samples were held before they were analysed did not influence the results. Moreover, it was proven previously that samples collected at the same time from the same depth of water, from the same depths within sediments (0–25 cm) and from reasonably similar sediments but at different sam-

pling stations, gave the same results within analytical error (Jędrysek *et al.*, 1994; Jędrysek, 1994, 1995).

ANALYTICAL TECHNIQUES

CO₂ and CH₄ from floating collectors were determined in the laboratory using gas chromatograph equipped with a FUV detector (HNU system Model 321) set up at Department of Land Development in Bangkok, Thailand, and the bubble gases were analysed by TCD gas chromatograph 504 in the Laboratory of Isotope Geology and Biogeochemistry, University of Wrocław, in Poland.

Using molecular sieves, a dry-ice-ethanol mixture, and liquid nitrogen, the methane in the sample gases was cryogenically purified under vacuum from other hydrogen-and-carbon containing gases. The methane was then passed through a copper oxide furnace (850–900°C) twice. The products obtained, H₂O and CO₂, were separated cryogenically. Isotope preparation was carried out in the Laboratory of Isotope Geology and Biogeochemistry, University of Wrocław, in Poland. Carbon isotope analyses were made on a modified MI-1305 mass spectrometer with a home-made inlet (Hałas, 1979) and detection systems (Hałas & Skrzyński, 1980) at the Mass Spectrometry Laboratory, Maria Curie-Skłodowska University, Lublin, Poland. Precision is 0.05‰, and ratios are expressed as δ¹³C values relative to the PDB standard, using a mass spectrometric comparison of working CO₂ gas with CO₂ prepared from NBS 19 and NBS 22 standards. The reproducibility of isotope preparation was ±0.05 to ±0.2‰.

RESULTS

Carbon dioxide and methane from floating chamber collectors

The observation time, using floating chamber collectors, was probably of too short duration to reveal clear diurnal variation in emission of methane and carbon dioxide from water. The results of analysis of CO₂ and CH₄ concentrations in chamber collectors are shown on Fig. 2 and Table 1. In the pit, a large increase in concentration of methane was observed – from an initial value about 45 ppm one hour after setting up the gas-collecting chamber to about 750 ppm after about 24.5 hours. No constant rate of the increase of concentration of methane suggests that one bubbling event occurred between 14:00 and 18:00 (Fig. 1). In the case of the canal the increase was less remarkable, from about 420 ppm after about 4 hour chamber to about 480 ppm in the end of the experiment – after about 21 hours. In the case of the pond, the initial value after 4.5 h was ca. 200 ppm (more than after the same time in pit) and after about 25 hours of collecting, the concentration of methane was about 600 ppm (less than after the same time in the pit). A similar, progressive increase in carbon dioxide concentration was observed in chambers floating on the water of the pit, the canal and the pond. Concentrations of CO₂ in the chambers varied between 2773 to 11245 ppm. A remarkable decrease in the

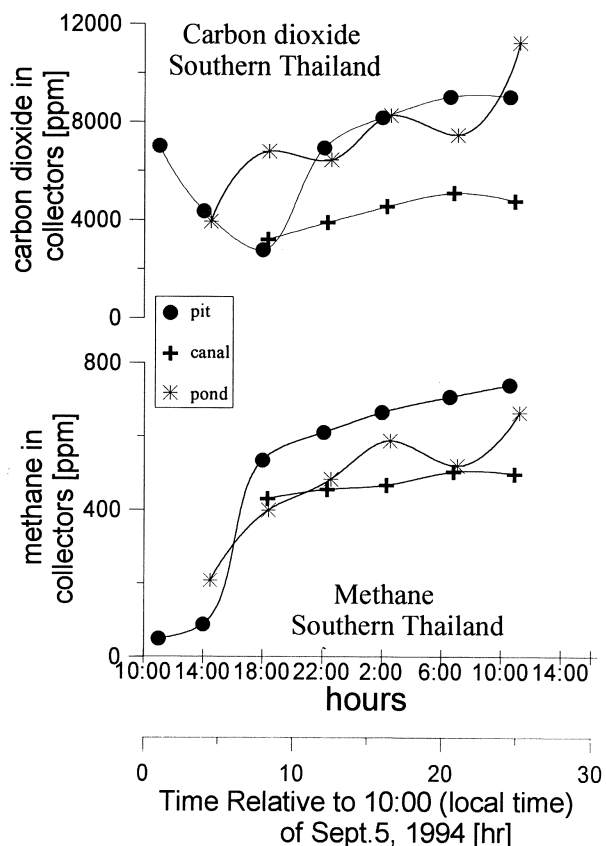


Fig. 2. CO₂ and CH₄ concentrations in chamber collector floating on water surface of pit, canal and pond. See captions for Table 1 for details

CO₂ to a minimum concentration was observed just before sunset. Coincidental decrease both in CO₂ and CH₄ concentrations was observed exclusively in the pond collectors just after sunrise (Fig. 1). Differences in the CO₂/CH₄ ratio, apparently resulted from differences in the production rate of CO₂ and CH₄ and oxidation rate, in the pit, the canal and the pond are shown clearly in Fig. 3. In this figure, two sample points from the pit (11:00 and 14:00) do not fall on the best fit line passing through the remaining pit data.

Bubble carbon dioxide and methane

The concentration of bubble carbon dioxide and methane varied from 0 (water in the bottle was not saturated with respect to CO₂) to 21.14% and from 31.74 to 75.71%, respectively. In general, the concentrations of bubble CO₂ and CH₄ varied independently (Fig. 4). Differences in bubble CO₂ and CH₄ concentrations are clearly different between pit and pond (Fig. 5). In the case of canal, the water in the gas-containing bottle was not saturated with respect to bubble CO₂, so no CO₂ over water saturation limit was observed.

The $\delta^{13}\text{C}$ of bubble methane ranged from -64 to -47‰ (Fig. 6, Table 1) and the canal methane was ¹³C-depleted with respect to pit and pond methane by about 10‰. However, diurnal variation in the $\delta^{13}\text{C}_{\text{CH}_4}$ value in the pit and canal was observed. The bubble methane $\delta^{13}\text{C}$ value was nearly

Table 1

CO₂ and CH₄ concentrations in chamber collectors floating on water surface and bubble CO₂ and CH₄ concentrations and $\delta^{13}\text{C}$ of bubble methane from sediments of pit, canal and pond in the experimental fields of Pikumthong Development Royal Study Center, Narathiwat, Southern Thailand). Sampling was carried out on September 05 and September 06, 1994. b.s – below saturation (due to low concentration of bubble CO₂, water remaining in the bottles containing gas samples was not saturated with respect to CO₂) – hence canal data are not plotted on respective Figures; n.s. – not sampled; lost – sample lost during transport

Sampling		Gases in collectors			Bubble gases			
Sampl. stat.	Date 1994	Time h:m	CH ₄ ppm	CO ₂ ppm	Time h:m	CH ₄ %	CO ₂ %	$\delta^{13}\text{C}_{\text{CH}_4}$ ‰
Pit	5.09	11:00	48	7025	11:01	72.33	10.11	-51.8
Pit	5.09	14:00	87	4362	14:01	70.25	5.36	-51.5
Pit	5.09	18:00	535	2773	18:10	63.06	5.35	-55.0
Pit	5.09	22:05	611	6938	lost	lost	lost	lost
Pit	6.09	2:00	665	8196	2:10	58.26	8.87	-55.6
Pit	6.09	6:35	707	9056	6:45	66.73	21.14	-47.6
Pit	6.09	10:35	739	9044	10:45	75.71	12.98	-52.0
Canal	6.09	n.s.	n.s.	n.s.	14:10	62.84	b.s.	-58.5
Canal	5.09	18:20	430	3200	18:21	58.08	b.s.	-58.1
Canal	5.09	22:20	455	3902	22:21	48.89	b.s.	-58.5
Canal	6.09	2:20	467	4555	2:21	56.05	b.s.	-63.8
Canal	6.09	6:55	503	5107	7:00	72.22	b.s.	-56.6
Canal	6.09	10:55	497	4775	11:00	64.65	b.s.	-55.3
Pond	5.09	n.s.	n.s.	n.s.	11:30	49.88	4.41	-49.3
Pond	5.09	14:30	208	3929	14:31	45.4	3.88	-50.7
Pond	5.09	18:25	399	6793	18:30	36.17	3.21	-50.2
Pond	5.09	22:35	483	6448	22:40	44.06	3.66	-49.1
Pond	6.09	2:20	588	8281	2:35	31.74	3.36	-53.4
Pond	6.09	7:05	520	7481	7:10	38.46	3.55	-54.4
Pond	6.09	11:15	664	11245	11:20	36.46	3.51	-53.6

10‰ lower during night than in the daytime. Methane isotope data do not show regular diurnal variation in the pond. The highest $\delta^{13}\text{C}$ value (-47.6‰) in bubble methane and highest CO₂ concentration was found in the same bubble sample taken in the early morning in the pit.

Similarly, plots $\delta^{13}\text{C}_{\text{CH}_4}$ versus CO₂ concentration (Fig. 7) and $\delta^{13}\text{C}_{\text{CH}_4}$ versus CH₄ concentration (Fig. 8) clearly discriminate between three different CO₂-CH₄ systems of the pit, canal and the pond respectively.

DISCUSSION

In natural freshwater systems, fermentation of acetate (Barker, 1936) and reduction of carbon dioxide (Takai, 1970) are the dominant methanogenic pathways. Other pathways (Zindler & Brock, 1978ab; Weimer & Zeikus, 1978; Patterson & Hespell, 1979; Oremland *et al.*, 1982) which could be considered as a third group of pathways, are negligible from the isotopic point of view (Lovley & Klug, 1983). On the basis of tracer experiments with anoxic ma-

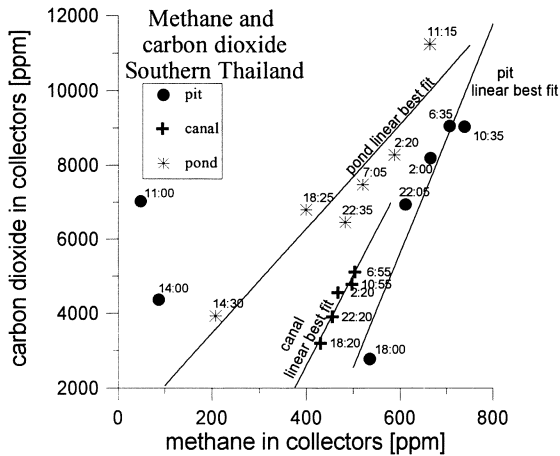


Fig. 3. Correlation of the CO₂ and CH₄ concentrations emitted from water surface of pit, canal and pond into floating chamber collector. See captions for Table 1 for details

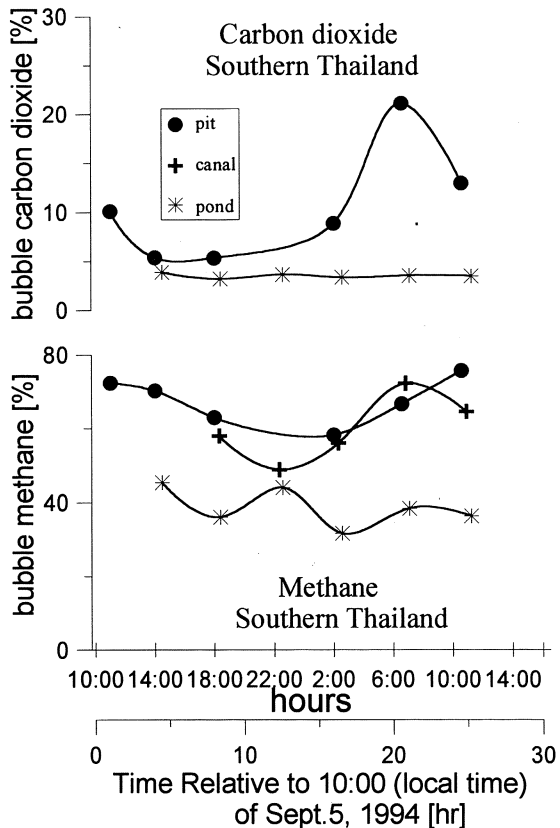


Fig. 4. Bubble CO₂ and CH₄ concentrations in sediment pore-gases of pit, canal and pond. See captions for Table 1 for details

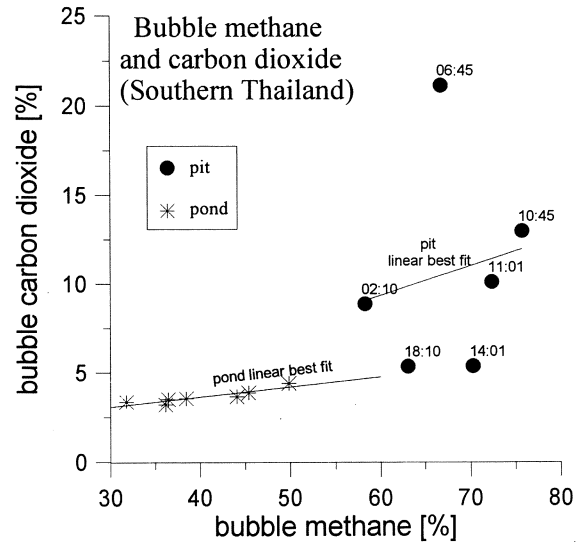


Fig. 5. Correlation of bubble CO₂ and CH₄ concentrations in sediment pore-gases in pit, canal and pond. See captions for Table 1 for details

rine sediments, Blair & Carter (1992) estimated the $\delta^{13}\text{C}$ values of endmember CH₄ to be -43‰ from acetate and -65‰ from CO₂. Similarly, based upon freshwater paddy soil incubation experiments, the endmember $\delta^{13}\text{C}$ of methane produced from acetate dissimilation is -36‰ and the $\delta^{13}\text{C}$ value of CH₄ from CO₂/H₂ was estimated to be -77 to -60‰ (Sugimoto & Wada, 1993). Therefore, we may suggest that smaller $\delta^{13}\text{C}_{\text{CH}_4}$ values were likely to be the result of an enhanced activity of the CO₂-reducing methanogenesis pathway. On the other hand, higher values may be caused by increased importance of the acetic acid pathway as a result of reduction of the ¹²CO₂ pool size and increase in primary production.

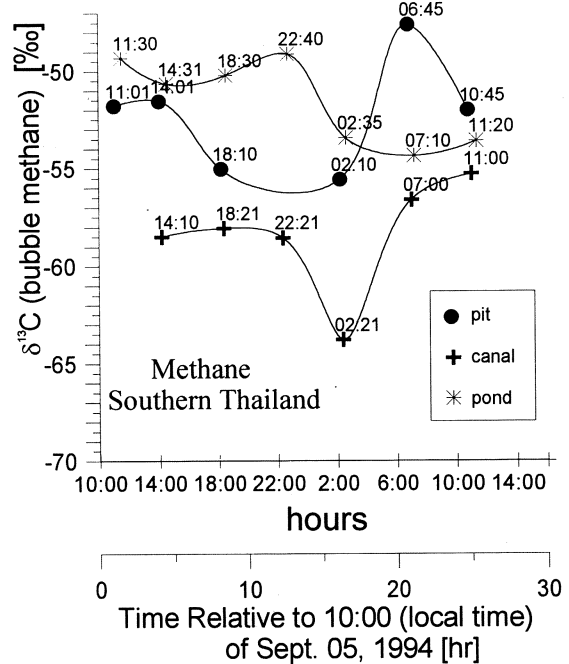


Fig. 6. Dial $\delta^{13}\text{C}$ variations in bubble CH₄ from sediments in pit, canal and pond. See captions for Table 1 for details

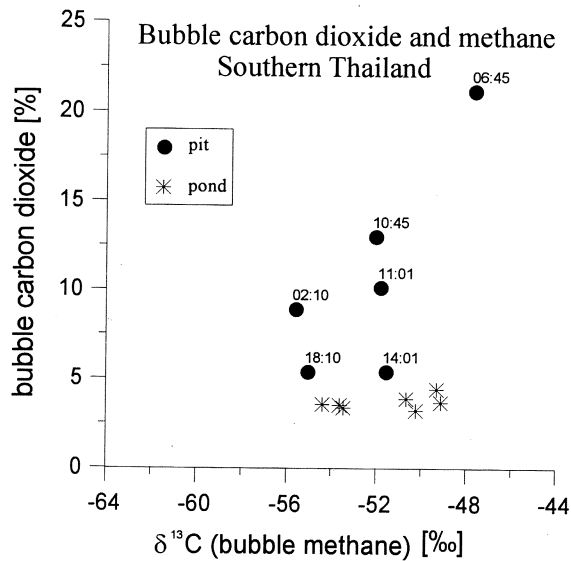


Fig. 7. Correlation of bubble CO₂ concentrations and δ¹³CH₄ of pit, canal and pond. See captions for Table 1 for details

Atmospheric carbon dioxide and its δ¹³C value range from ca. 350 ppm at noon to ca. 550 ppm during the night, and from ca. -7‰ in the early evening to ca. -13‰ during the night, respectively (Szarán, 1990). The δ¹³CO₂ variation is driven directly by photosynthetic and respiration activities. The pattern of 10‰ diurnal variation in δ¹³CH₄ in Thailand shows a significant coincidence with the δ¹³CO₂ change in the atmosphere and the δ¹³C change in methane from temperate climate freshwater sediments (Jędrysek, 1994, 1995). The decrease in the CO₂ concentration in the pit chamber to the minimal value 2773 ppm observed afternoon just before sunset was probably caused by significant absorption of CO₂ from the atmosphere (Fig. 2). However, absorption of the isotopically heaviest atmospheric CO₂ in the daytime, and release of isotopically lighter CO₂ at night, may not be a plausible driving mechanism for the diurnal variation in δ¹³CH₄ if transport of CO₂ between the atmosphere and the methane production locus in the sediments is probably too slow. However, when the concentration of CO₂ in water decreases, the absorption of CO₂ from sediments (perhaps even isotopically heavier due to diffusion isotope effect) could be substantial enough to decrease its concentration in porewaters, and consequently increase δ¹³CH₄ value due to enhanced methanogenesis via acetic acid fermentation. Likewise, photosynthetic-respiration activities in water may influence isotope ratios in DIC. Increased primary production during daytime should have consumed isotopically lighter CO₂, leaving heavier CO₂ in the residual CO₂ pool. This progressive increase in δ¹³CO₂ may increase the δ¹³C value of the methane produced during the daytime in the surficial regions of sediments. In general, atmospheric CO₂ of equatorial regions is depleted in ¹³C isotope compared to temperate climate CO₂ in atmosphere. Therefore, as it may be observed here, methane from tropical freshwater sediments is in general more depleted in heavy carbon isotope than the temperate climate earlydiagenetic methane.

Likewise, during day-time, hydrogen is produced in

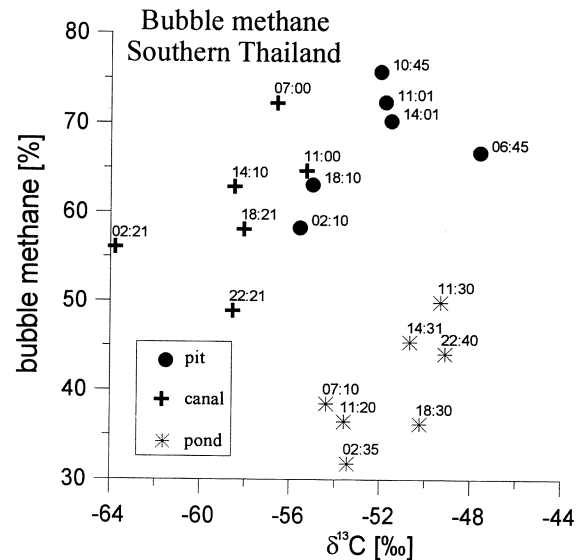


Fig. 8. Correlation of the bubble CH₄ and δ¹³CH₄ in pit, canal and pond. See captions for Table 1 for details

substantial amounts in aquatic system and, similarly, CO₂ concentration decreases and its δ¹³C value increases due to photosynthetic activity. Thus, afternoon methanogenesis via the CO₂/H₂ reduction pathway in the uppermost horizons of sediments may become less active, resulting in a subsequent increase in δ¹³CH₄ (Fig. 6). In fact, concentration of bubble CO₂ is lowest in the afternoon and evening. This fact, in conjunction with the step by step (10:45, 11:00 and 14:00) decrease in pit bubble CO₂ concentration, accompanied by slight increase in δ¹³CH₄ (Fig. 7), supports the thesis that the daytime deficit of CO₂ may increase the δ¹³CH₄.

Another factor increasing the δ¹³CH₄ value could be biological oxidation of methane leaving behind isotopically heavier molecules. Moreover, oxidation of acetate (and probably of its precursors) is assumed to be the first order factor controlling acetate concentration and may result in a substantial enrichment in heavy isotopes in the remaining acetic acid and, consequently, in methane. During this process, the remaining acetic acid or/and methane can significantly shift the hydrogen and carbon isotopic ratios positively in the newly produced and residual methane (Barker & Fritz, 1981; Coleman *et al.*, 1981). This process strongly modulates methane fluxes in aquatic systems (King, 1990); hence, the more positive day-time δ¹³CH₄ values were observed. On the other hand, methane productivity should decrease and the concentration of carbon dioxide in bubble methane should increase as a consequence of methane oxidation and/or that of the methane precursor's. In general, this is not the case, however. Visually judged high productivity during day-time may suggest that the acetic pathway becomes more active as a consequence of increasing primary production and immediate acetate fermentation. However, one pit sample (6:45; Table 1) is exceptional. In this sample, the highest bubble CO₂ concentration (21.14%, 6:45 on Fig. 4, 5 and 6) coupled with the highest δ¹³CH₄ value (-47.6‰, 6:45 on Fig. 6 and 7) may suggest significant oxidation of methane. The oxidation effect is not reflected, however, in the methane concentration (Fig. 4 and

5) probably because only several per cent of methane was oxidised. Thus, the high concentration of CO₂ probably resulted from the cumulation of CO₂ in sediments and water due to respiration during the night. On the other hand, the highest CO₂ concentration and the highest $\delta^{13}\text{C}_{\text{CH}_4}$ value is not resulted by oxidation of any significant portion of acetic acid, because this process should decrease the acetic acid pathway and consequently increase the CO₂ pathway. Finally, oxidation of acetic acid may substantially decrease the production rate of methane but presumably have a lesser influence on $\delta^{13}\text{C}_{\text{CH}_4}$ value. This one sample does not, of course, prove that such oxidation is a regular pattern in the early morning in oxidant-rich aquifers similar to the pit with its enhanced concentration of sulphate in water. When SO₄²⁻ is present, acetate is used by SO₄²⁻ reducers. The fact that pit bubbles show the highest carbon dioxide content and high $\delta^{13}\text{C}_{\text{CH}_4}$ values could not be resulted by enhanced acetic fermentation, but rather supports the thesis on strong oxidation effects in the pit sediments. More intense, acetic acid fermentation caused by higher primary production in the higher water column of the pit (2 m) compared with the canal and pond (0.5 and 0.7 m) is probably negligible because the pit water was extremely poor in living organic matter e.g. algae. During fermentation of fresh organic matter, its remaining part becomes isotopically enriched. Therefore, organic matter sinking in the morning may become significantly enriched in heavy carbon isotope. On the other hand, a decrease in $\delta^{13}\text{C}_{\text{CH}_4}$ values with increasing depth of about -1‰/-1 m of water column (Jędrysek *et al.*, 1994, 1996) suggest that if the pit and canal bubble samples were from the same depth, the difference in carbon isotope ratios would be higher than that observed (Fig. 6) – methane from shallower water should be $\delta^{13}\text{C}$ -enriched.

The canal methane showed low $\delta^{13}\text{C}$, presumably due to low activity in primary production (potential precursor of acetic acid). Consequently, methane was produced mostly by reduction of CO₂. The pond methane showed no regularity in diurnal variation, partly because of inhomogeneity of the sediments that contained the bubble CO₂ and CH₄. Furthermore, high $\delta^{13}\text{C}_{\text{CH}_4}$ values accompanied by the lowest concentration of bubble carbon dioxide (Fig. 7) and methane (Fig. 8) was probably caused by high density of roots of macrophytes emerging and vegetating on the bank of the pond. This would promote ventilation of the sediments with air and result in a decrease in CO₂ and CH₄ and simultaneously in significant ^{13}C enrichment of the residual methane. Moreover, light penetration into the pond water was extremely poor because of very limited transparency and high abundance of macrophytes. This limited primary production in water could be, perhaps, the reason for the significant shift in phase of the minimal $\delta^{13}\text{C}_{\text{CH}_4}$ value from night to early morning and the maximal $\delta^{13}\text{C}_{\text{CH}_4}$ value from the time of sunset to early night.

CONCLUSIONS

1. $\delta^{13}\text{C}_{\text{CH}_4}$ values are lowest in the night and highest in the daytime. High values representing daytime methane occur when the CO₂ pool decreases and acetic acid fermenta-

tion becomes relatively more important. Minimum values are apparently caused by an enhanced CO₂-H₂ methanogenesis pathway.

2. The scale and shape of diurnal emissions of CO₂ and CH₄, and diurnal variations in bubble CO₂ and CH₄ concentration and in the $^{13}\text{C}/^{12}\text{C}$ ratio in bubble methane, strongly depend on physical, chemical and biological conditions, including vegetation.

3. Oxidation may play crucial role in $\delta^{13}\text{C}_{\text{CH}_4}$ values especially when the production rate of methane is low.

4. Remarkable ^{13}C -depletion of methane from tropical freshwater sediments may be important factor which could help to discriminate, origin of hydrocarbon deposits. More studies would be required at this point in the near future.

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Streszczenie

**WCZESNODIAGENETYCZNY METAN
Z RÓŻNYCH OSADÓW SŁODKOWODNYCH
KLIMATU TROPICALNEGO: ZASTOSOWANIE
CHROMATOGRAFII GAZOWEJ I ANALIZY
STOSUNKÓW IZOTOPOWYCH
W OBSERWACJACH CYKLU DOBOWEGO**

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Głównym produktem wczesnodiaogenetycznego rozkładu materii organicznej w osadach anoksycznych jest metan. Powstaje on w wyniku redukcji dwutlenku węgla (Takai, 1970) i fermentacji octowej (Berker, 1936). Inne drogi wczesnodiaogenetycznej metanogenezy nie są istotne z punktu widzenia badań izotopowych (Lovley & Klug, 1983). Metan powstały w wyniku redukcji CO₂ jest silnie zubożony w izotop ¹³C w stosunku do metanu powstałego z CH₃COOH (Blair & Carter, 1992; Sugimoto & Wada, 1994). Proces utleniania metanu prowadzi do wzbogacenia pozostałego metanu w izotop ¹³C (Barker & Fritz, 1981; Coleman *et al.*, 1981).

Metan jest jednym z najważniejszych gazów efektu cieplarnianego a wzrost jego stężenia w atmosferze jest obecnie około 10-cio krotnie szybszy niż wzrost stężenia innych gazów efektu cieplarnianego (np. Craig & Chou, 1982; Khail & Rasmussen, 1983; Cicerone, 1987; Steele *et al.*, 1987; Wada, 1990). Szacuje się, że w około 45% metanu atmosferycznego pochodzi z obszarów kontynentalnych okresowo lub stale pokrytych wodą (pola ryżowe, bagna, jeziora). Izotopowy bilans mas umożliwia znacznie dokładniejsze, niż inne obecnie znane metody, oszacowanie udziału poszczególnych źródeł metanu w bilansie atmosfery Ziemi. Wyniki takich obliczeń mogą w przyszłości istotnie wpłynąć na decyzje w polityce międzynarodowej poprzez wymuszenie na niektórych krajach zmniejszenia emisji metanu do atmosfery. Jednakże, aby dokonać takich obliczeń, konieczne jest zebranie informacji o czasowo-przestrzennej zmienności składu izotopowego metanu pochodzącego z różnych źródeł oraz poznanie przyczyn tych zmienności. Wykazane wcześniej, silne zubożenie w ciężki izotop węgla metanu wczesnodiaogenetycznego powstałego w nocy, w stosunku do metanu powstałego w dzień, pozwala zasugerować, że przyjmowany 45% udział metanu wczesnodiaogenetycznego w ogólnym bilansie metanu atmosfery, jest prawdopodobnie o około połowę mniejszy (Jędrysek, 1995).

Jednocześnie, proces utleniania metanu sprzyja powstawaniu węglanów wczesnodiaogenetycznych silnie zubożonych w izotop ¹³C. W ten sposób powstaje, w profilach osadów, zapis izotopowy o warunkach panujących w zbiorniku. Ma to duże znaczenie we współczesnych interpretacjach paleośrodowiskowych. Poznanie mechanizmów rządzących zmiennością składu izotopowego metanu powstającego w wyniku procesów wczesnodiaogenetycznych ma więc istotne znaczenie dla izotopowego bilansu mas gazów efektu cieplarnianego oraz dla badań paleośrodowiskowych. Ponadto, zaobserwowane niższe wartości $\delta^{13}\text{C}$ metanu z osadów

klimatu tropikalnego niż metanu z osadów klimatu umiarkowanego mogłoby być dobrym wskaźnikiem do badań nad warunkami powstawania i pochodzeniem złóż ropy i gazu.

Przedstawione w tej pracy wyniki badań dotyczyły trzech różnych typów źródeł metanu wczesnodiagenetycznego powstałego w klimacie tropikalnym. Obserwacje i opróbowanie przeprowadzono 5 i 6 września 1994, na polach eksperymentalnych Królewskiego Centrum Rozwoju Badań Pikunthong w okolicach Narathiwat, Pd. Tajlandia (6° szer. geogr. Pn.). W odstępach ok. 4 godzin pobierano próby gazów zbieranych do specjalnie w tym celu skonstruowanych pływających kolektorów (początkowo wypełnionych powietrzem), oraz gazów, których ucieczkę z osadu wymuszano. Wykonano analizy chromatograficzne stężenia CO₂ i CH₄ w atmosferze zawartej w kolektorach i w gazach z osadów oraz analizy izotopowe $\delta^{13}\text{C}$ metanu z osadów ($\delta^{13}\text{CH}_4$).

Badane gazy pochodziły z:

– osadów wkopu – sztucznego zbiornika wykopanego w glebie o wysokim stężeniu siarczanu (obecność SO₄²⁻ powoduje utlenianie metanu i zapobiega jego powstawaniu w szczególności na drodze fermentacji octowej),

– osadów strumienia o silnie natlenionej wodzie płynącej (obecność tlenu w wodzie utrudnia także procesy redukcyjne w osadzie),

– osadów stawu silnie zarośniętego roślinami (rośliny ukorzenione powodują wentylację osadu i w wyniku respiracji dostarczają CO₂),

Zaobserwowano, niezbyt regularne ale wyraźne wahania

dobowe w mierzonych parametrach. Wartość $\delta^{13}\text{CH}_4$ była najniższa w nocy, a najwyższa w dzień: minimum -63.8‰ o godz. 2:20 (kanał) a maksimum -47.6‰ o godz. 6:45 (wkop). W oparciu o te dane (Tab. 1) oraz zależności przedstawione na Fig. 2-8 wysunięto przypuszczenie, że wysokie dzienne wartości $\delta^{13}\text{CH}_4$ są związane ze spadkiem stężenia CO₂ (dyfuzja do kolumny wodnej w wyniku zwiększonej asymilacji fotosyntetycznej planktonu) i wzrostem aktywności procesu fermentacji octowej w wyniku rozkładu świeżo obumarłego planktonu. Minimalne wartości $\delta^{13}\text{CH}_4$ związane są z relatywnie wysoką aktywnością procesu metanogenezy w wyniku reakcji CO₂-H₂, co jest następstwem braku fotosyntezy i wzrostu koncentracji CO₂ w wyniku respiracji. Nieregularności zmian dobowych są związane najprawdopodobniej z procesami utleniania, niehomogenicznością osadów (różny osad w różnych punktach opróbowania warunkuje produkcję i dyfuzję metanu co wywołuje także efekt izotopowy), zróżnicowaniem stopnia ukorzenienia, niepowtarzalnością sposobu wymuszania ebulicji (ucieczki gazów z osadu). Zaobserwowano, że generalnie wartość $\delta^{13}\text{CH}_4$ wkopu i stawu była o około 10‰ wyższa niż wartość $\delta^{13}\text{CH}_4$ strumienia (Ryc. 6). Można to tłumaczyć brakiem fermentacji octowej w osadach strumienia oraz silniejszym utlenianiem metanu w osadach wkopu i stawu. Ponadto, fakt zanotowania najniższych wartości $\delta^{13}\text{CH}_4$ kanału sugeruje intensywną redukcję CO₂ w jego osadach. Najwyższa wartość $\delta^{13}\text{CH}_4$ towarzysząca najwyższej koncentracji CO₂ w gazach osadów wkopu (Fig. 7, godz. 06:45) pozwala wnioskować o zaawansowanym procesie utleniania (związanego z redukcją siarczanu).

