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EBULLITIVE FLUX OF EARLY-DIAGENETIC METHANE FROM RECENT FRESHWATER SEDIMENTS IN LAKE NOWA CEREKIEW (SW POLAND)

Mariusz Orion JĘDRYSEK

Laboratory of Isotope Geology and Biogeochemistry, University of Wrocław, Cybulskiego 30,
50-205 Wrocław, Poland. e-mail: morion@ii.uni.wroc.pl

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Abstract: Observations concerning ebullition of methane from freshwater lake sediments, at depths of 2.8 m and 4.2 m, and occasionally at of 4.5, 5.5 and 11 m have been carried out. A closed type, artificial lake Nowa Cerekiew (SW Poland) about 30 years old, with organic rich sediments 25 cm thick, was selected for this study. Collection of ebulliting gases has been carried out using bottom-situated funnel-shape collectors with connected flasks (exchanged by scubadiving). The observations have been carried out continuously between 1992 to 1996, including winters when the lake was covered by ice.

Concentration of methane in ebullition varied from 9.06% (winter) to 76.82% (early summer). Ebullition (expressed as the mean diurnal production of carbon trapped into the collectors in the form of bubbles of methane naturally released from 1 m^3 of the most productive 25 cm uppermost layer of the sediments $((C\text{-}CH_4)\times day^{-1}\times m^{-3})$) varied from about 100 mg $(C\text{-}CH_4)\times day^{-1}\times m^{-3}$) to near zero during winter. In contrast to the deeper sampling station (4.2 m), the ebullitive methane from the shallower depth (2.8 m) showed substantial seasonal variation in the $\delta^{13}C(CH_4)$ value, from -63.12‰ during winter to -52.46‰ during summer. The global freshwater lake ebullitive CH_4 flux has been roughly estimated at about 5×10^8 $g(C\text{-}CH_4)\times y^{-1}$.

The observed enhanced ebullitive CH_4 flux during summer and the higher $\delta^{13}C(CH_4)$ value during early summer are apparently a result of: (i) efficient decomposition of the fresh organic matter, deposited into the anoxic zone on the sediment surface, and consequently a relatively more enhanced acetic acid pathway and, (ii) increased bacterial activity at higher temperature. The lower $\delta^{13}C(CH_4)$ value in the deeper sampling station during summer may be a result of: (i) longer time for the organic matter to sink to greater depth and consequently there is greater decomposition of easily degradable compounds which are the main precursors of acetate, (ii) perhaps an increase of bioavailable DIC, due to elevated pressures and lower temperatures at greater depths, enhancing the CO_2 pathway, and (iii) limited diffusion of isotopically depleted carbon-bearing compounds from greater depths.

Abstrakt: Przeprowadzono obserwacje ebullicji (naturalnej ucieczki gazu z osadu, w formie bąbli) metanu z jeziornych osadów słodkowodnych. Zbierano gaz na głębokościach 2.8 m i 4.2 m, a w pojedynczych przypadkach na głębokości 4.5 m, 5.5 m i 11 m. Obiektem badań było sztuczne jezioro wypełniające nieczynny, od ok. 30 lat, kamieniołom trzeciorzędowych bazaltów. Miąższość osadów wynosi ok. 25 cm. Gaz zbierano używając specjalnie skonstruowanych do tego celu kolektorów stacjonarnych usadowionych na dnie. Poboru prób dokonywano nurkując. Badania przeprowadzano nieprzerwanie w latach 1992–1996, także zimą, gdy jezioro było zamarznięte.

Stężenie metanu wahało się w granicach od 9.06% (zimą) do 76.82% (wczesne lato). Ebullicje metanu (wyrażone jako średnia dobowa ucieczka węgla, w formie bąbli metanu, z 1m^3 osadu $((C\text{-}CH_4)\times doba^{-1}\times m^{-3})$) wahały się od ok. 100 mg $(C\text{-}CH_4)\times doba^{-1}\times m^{-3}$ (latem) do niemal 0 (zimą). W przeciwieństwie do głębszej strefy (4.2 m), metan z mniejszej głębokości (2.8 m) wykazywał wahania sezonowe wartości $\delta^{13}C(CH_4)$, od -63.12‰ (zimą) do -52.46‰ (latem). W oparciu o uzyskane wyniki globalną ebullicję metanu oszacowano na rząd około $5\times 10^8 g(C\text{-}CH_4)\times rok^{-1}$.

Intensywniejsza ebullicja CH_4 latem i wyższe wartości $\delta^{13}C(CH_4)$ mogły być wynikiem: (1) większej sedymentacji świeżej materii organicznej latem i częściowego rozkładu materii organicznej (prekursorów kwasu octowego) w czasie sedymentacji jeszcze w kolumnie wodnej (dłuższy czas opadania cząsteczek organicznych na większe głębokości) co umożliwiło intensywniejszą fermentację octową w osadach płytszej strefy zbiornika; (2) zwiększonej aktywności mikrobiologicznej (bakterii metanowych) w warunkach wyższej temperatury w osadach płytszych. Niższe wartości $\delta^{13}C(CH_4)$ mogły być spowodowane (1) dłuższym czasem opadania obumarłych cząstek planktonu na większe głębokości co umożliwiało zaawansowany rozkład składników grupowych materii organicznej, które są substratami fermentacji octowej; (ii) wzrostem stężenia węgla nieorganicznego w warunkach wyższego ciśnienia i niższej temperatury – wzrost produkcji metanu w wyniku redukcji CO_2; (3) wolniejszej dyfuzji izotopowo lekkiego metanu, z większej głębokości.

Key words: ebullition, methane, sediments, lake, diagenesis

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INTRODUCTION

The atmospheric methane (CH_4) mixing ratio has increased over the past 200 years and, until recently, the annual average rate was about 1% (Craig & Chou, 1982; Khalil & Rasmussen, 1984; Wada, 1990). Recent monitoring revealed that the atmospheric methane concentration increased at rates of 1 to 1.9% per year from 1979 to 1982 (Khalil & Rasmussen, 1983) but later the rate of increase appeared to have slowed somewhat to 0.78% per year between May 1983 to April 1985 (Steele *et al.*, 1987). The mixing ratio has increased by 11% from 1.52 ppm (1978) to 1.684 ppm in 1987 (Blake & Rowland, 1988). This increase is a cause of considerable concern because CH_4 plays an important role in atmospheric chemistry and radiative forcing (e.g. Craig & Chou, 1982; Khalil & Rasmussen, 1983; Steele *et al.*, 1987) as well as being a sequester of ozone-reactive chlorine atoms (Cicerone, 1987) and source of energy. Therefore, considerable attention has been directed towards quantifying tropospheric methane sources and their isotopic composition, and preparing mass flux and isotopic budget (Stevens & Rust, 1982; Stevens & Engelkemeir, 1988; Tyler, 1986; Wada, 1990).

It is generally agreed that microbial decomposition of organic matter in water-covered sediments (including paddy fields, peat-bogs and lakes), are the most efficient sources of atmospheric methane. In natural freshwater systems, fermentation of acetate (Barker, 1936), $CH_3COOH \rightarrow CH_4 + CO_2$, and reduction of carbon dioxide (Takai, 1970), $CO_2 + 4H_2 \rightarrow CH_4 + H_2O$, are by far the dominant methanogenic pathways. Factors such as salinity (De Laune *et al.*, 1983), fertilization of paddy soil (Wada, 1990), soil redox potential (Cicerone *et al.*, 1983; Svenson & Rossewall, 1984), substrate and volatile end-product concentration (De Laune *et al.*, 1986), wind speed (Sebacher *et al.*, 1983), atmospheric pressure (Matson & Likens, 1990), moisture content or water level (Harriss *et al.*, 1982; Svenson & Rosswall, 1984), temperature (Baker-Blocker *et al.*, 1977; Svenson & Rosswall, 1984; Sebacher *et al.*, 1986), nutrient and organic content of surface soils and their thickness (Harriss & Sebacher, 1981), plant type and its physiological state (ventilation rate, age, height; Dacey & Klug, 1979; Dacey, 1981; Cicerone *et al.*, 1983; Sebacher *et al.*, 1985), primary production (Whiting & Chanton, 1993), depth of water column and depth in the sediments (Jędrysek *et al.*, 1993, 1994, 1996), light (King, 1990), and diurnal cycle and DIC migration in the water column – porewater system (Jędrysek, 1994, 1995, 1996) have been reported to affect methanogenic pathways and methane flux from natural wetlands. Therefore, seasonal variation in the ebullition of methane should be observed very well with respect to changes in the environment due to seasonal variations. In fact, annual variations of ebullition has been described earlier, but the sampling technique and experimental procedure, compared to those presented here, were different and involved different conditions (e.g. Rudd & Hamilton, 1978; Cicerone & Shetter 1981; De Laune *et al.*, 1983; Martens *et al.*, 1986; Burke *et al.*, 1988; Chanton & Martens, 1988; Crill *et al.*, 1988; Ford & Naiman, 1988; Naiman *et al.*, 1991; Duchemin *et al.*, 1995). Nonetheless, seasonal variations in methane flux and isotopic composition of methane fluxes are still not well documented with respect to a given type of freshwater environment. This is particularly true of seasonal variation with respect to depth of water column, thickness and character of sediments, trophic level of freshwater system, water chemistry etc. (Jędrysek, 1996).

The objective of this almost four years study was to:

– quantitatively assess naturally released bubble methane flux (ebullition) from a particular volume of sediments on a seasonal basis (this involves the first direct measurements of seasonal variation in ebullitive total emission of CH_4 from euthrophic lake sediment-water interface, when observations were conducted during winter while the reservoir was covered by ice);

– determine if there is any variation in ebullition with respect to the depth of water column;

– determine if any seasonal variation in the mechanism of methanogenesis occurs as a function of the depth of the water column and temperature – hence, carbon isotope analysis of the methane was carried out. The isotope data also help to control sampling technique and confirm that the technique applied is reliable (has not involved any oxidation or diffusion of ebullitive methane collected);

– determine if seasonal variations in eutrophic lakes of temperate climate exist when the system is not governed by seasonal variation of river transport and the sediments are free from macrophytes.

MATERIALS AND METHODS

STUDY AREA

An artificial lake near Nowa Cerekiew (50.1°N, 17.9°E) at the Moravian Gate, Southern Poland was selected for this study (Fig. 1). The area of Lake Nowa Cerekiew is about 0.03 km^2 and the maximum depth is 12 meters. The lake is usually covered by ice from the middle of December to the end of March (or even middle of April in 1996). The temperature of the water varies from the freezing point (about 0°C) to 27°C on the surface, and from about 4°C to 10°C below the thermocline. In general, the thermocline occurs at a depth of about 4.5 to 5.0 m below the lake surface interface. Unfortunately, the author does not have a good record of the temperature in the sampling stations. Seasonal mixing occurs twice a year, usually between the end of May to the beginning of June and in the end of September.

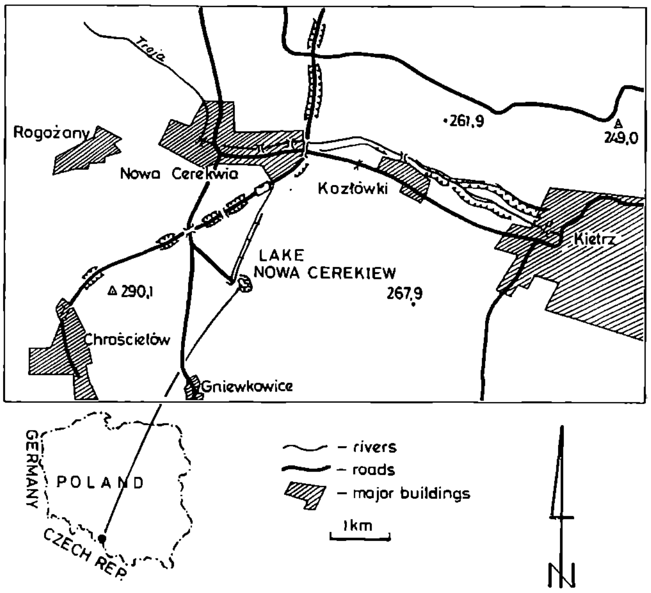

Fig. 1. Location of the study area (SW Poland)

This lake fills the quarry of Tertiary basalts, which was abandoned ca. 30 years ago. The present level of water table was achieved within about 5 years. It is known from stable isotope and hydrogeological studies (E. Konarska – personal comm.), that the lake water has no connection to any source of water other than the surficial feeding of shallow groundwater level and rainwater. Evaporation is probably the principal water sink from the lake (no surficial outflow) but a ground outflow via fractures in the basalt cannot be excluded.

The primary production of plankton in Lake Nowa Cerekiew is relatively high and may reach about 500–1000 mg C_{ass} x m^{-2} x day^{-1} (Jędrysek *et al.* – in preparation). The average thickness of sediments, including sampling stations, is about 0.25 m. In this lake, two distinct periods of mixing of surface water with benthic water occur – during the late spring and during early autumn. The dissolved oxygen and sulfate concentration in the water of the lake which was examined, varied from near zero to several mg/l and from near zero to 20 mg/l, respectively. Both values, in general, decreased as the depth of the water column increased, especially in the bottom regions (E. Konarska – personal comm.).

Several factors were crucial in the selection of the Lake Nowa Cerekiew, for the observations reported, in particular the following:

– The lake is situated on the top of a local hill (c.a. 280 m over sea level), and it was filled initially by shallow ground waters and supplemented by local rain water, without any stream or river transporting in sediments. The basalts, where the lake is located, are covered by about a 5 m layer of glacial sediments, such as sands and clays, free from organic matter. Macrophytes occurred occasionally in some places but only to a maximum depth of about 1.5 m. Thus, the organic matter in the deeper-water sediments is nearly exclusively a product of the water column primary production.

– In Lake Nowa Cerekiew, the thickness (c.a. 0.25 m) and age (not more than 30 years) of the sediments are very well known. It is well known that the dominant production of methane occurs in the uppermost (0 to about 0.5 m) and the youngest levels (usually less than 100 years) of freshwater lake sediments – production from deeper and older sediments appears to be negligible (Jędrysek *et al.*, 1994, 1996). Thus, based on the measurements, carried out in natural conditions, production of methane from the most productive part(s) of the sediments may be estimated.

– Highly eutrophic conditions in the lake makes apparently oxidation of methane negligible, as was shown using carbon isotope analysis (see “Discussion”).

– No human activity causing disturbance to the sediments and water occurred in this lake. This is due to difficult access to the area of the sampling stations, poor transparency of water, unattractive conditions and numerous submerged dead trees and bushes making dangerous any swimming and scubadiving (since 20 years ago, when two swimmers died, swimming has been prohibited there).

– Many other scientific observations have been carried out in this lake.

SAMPLING AND FIELD OBSERVATIONS

The magnitude of ebullition was measured by collecting naturally released gas bubbles from sediments in which no submerged macrophytes were present. The released bubbles were trapped to an inverted funnel-shaped collector, situated about 15 cm over the surface of the sediments and supported by three adjustable pillars. The diameter of the collector was 30 cm, and a scaled volume glass flask in an inverted position was connected to the top of the funnel. A butyl rubber O-ring and a metal clamp covering the flask was used to firmly join the flask to the collector. Bubbles were directed by the funnel into the flask, initially filled with water. Flasks containing sampled gas were collected by scubadiving, without any disturbance to the sediments, and afterwards new flasks were mounted on the top of the collectors. All the underwater work was carried out mostly alone (in order to limit any sediment or water disturbance) by the author of this paper. The pressure in the flasks containing gas, was equilibrated close to the atmospheric pressure by releasing a part of the water from the flask when the gas expanded while ascending to the surface (pressure decreased). The flasks were sealed with a butyl rubber cap and an aluminum seal. Some water remained in the flasks. Afterwards, the volume of gas was measured and the samples were immediately treated with $HgCl_2$ for future gas chromatography and isotope ratio analysis. Flasks with samples were stored in a refrigerator (3–4°C) in the inverted position.

Initially, one permanent sampling station at a depth of 4.2 m was selected. The other collector has been located first at the depth 5.5 m (permanently below the thermocline) and afterwards moved to the depth 11.0 m and then to 4.5 m. However, very little bubble methane from ebullition was collected below the thermocline (Figs 1–3). Finally, the second collector was located at a depth of 2.8 m, resulting finally in two sampling stations, at depths 4.2 m and 2.8 m. The stations were about 5 m apart. Similarity in parameters

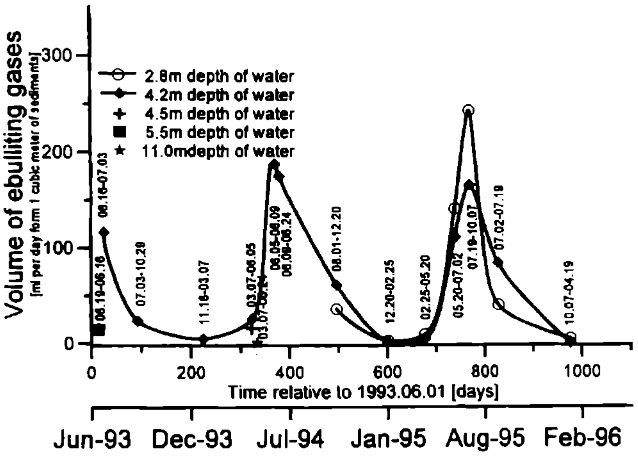

Fig. 2. Seasonal variation in the total volume of gases trapped from ebullition, expressed as average volume [milliliters] of gases ebulliting from 1 cubic meter of sediments per day (Lake Nowa Cerekiew, SW Poland). Labels show dates corresponding to intervals when the gas was collected. Each point represents the mid-point of the starting and ending dates of collection

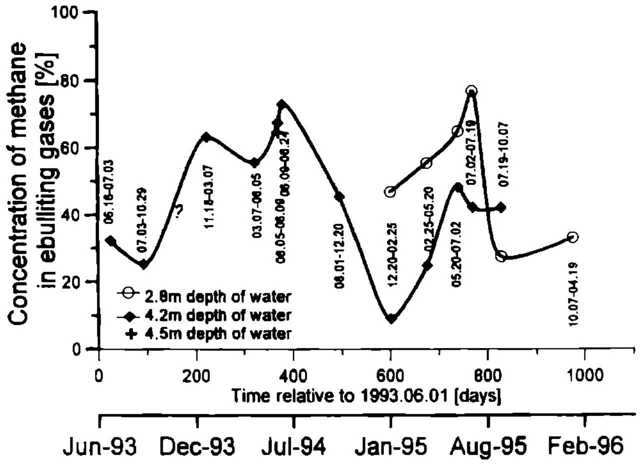

Fig. 3. Methane concentration in the collected bubbles at various depths 2.8 m, 4.2 m and 4.5 m (Lake Nowa Cerekiew, SW Poland). Other gases were mostly nitrogen, carbon-dioxide and trace amounts of oxygen. Methane was collected continuously between 1994 and 1996. Labels show dates corresponding to intervals when the gas was collected. Each point represents the mid-point of the starting and ending dates of collection

of the sediments (mineralogy, thickness, etc.) were crucial in selecting the sampling stations. Moreover, the presence of several firmly lodged trunks of dead trees submerged in the water over or nearby the collectors was important to prevent any artifacts caused by potential fishing or swimming (although no fishing and swimming are performed in this area). Sampling at depths of 4.2 m and 2.8 m have began in 1993.06.16 and 1994.12.20, respectively. The last collection of gas was done on April 19, 1996.

ANALYTICAL TECHNIQUES

The molecular composition of sample gases was analyzed using a TCD gas chromatograph 504.

Using molecular sieves, dry-ice-ethanol mixture, and liquid nitrogen, the methane in the sample gases was cryogenically purified from other hydrogen and carbon containing gases. The methane with hydrogen-and-carbon-free gases was passed through copper oxide (850–900°C) twice. The products obtained, H_2O and CO_2, were separated cryogenically. The carbon isotope analysis was made by a modified MI-1305 mass spectrometer with home-made inlet (Hałas, 1979) and detection systems (Hałas & Skorzyński, 1980) with a precision of 0.05 per mil, and expressed as $\delta^{13}C$ value *versus* PDB standard, by the comparison of working CO_2 gas with CO_2 prepared from NBS 19 and NBS 22 standards. Reproducibility of isotope preparations was about 0.2‰.

RESULTS

As the thickness of sediments is 0.25 m, all the data regarding volume of sediments were recalculated from the data measured for that 0.25 m of the sediments. The intensity of ebullition of gases from sediments, concentration of methane in those gases and consequently the methane flux, varies seasonally. In general, all these values are the highest during the late spring and summer and the lowest during winter.

The volume of gas ebullition from 1 cubic meter of sediments per day, varied from about 250 ml during summer to less than 0.01 ml during winter in/or below the thermocline (Fig. 1). The methane concentration in the collected bubbles varied from 9.06% (4.2 m collector, winter 1994.12.20 to 95.02.25) to 76.82% (2.8 m collector, early summer 1995.07.02 to 1995.07.19), (Fig. 3). Other gases were mostly nitrogen, carbon-dioxide (maximum about 5.9% – this is the same sample for which the lowest CH_4 concentration was detected), and trace amounts, if any, of oxygen.

Variation in the annual production of ebulliting methane (ebullition, Fig. 4) is expressed here as $(C\text{-}CH_4)\times day^{-1}\times m^{-3}$, i.e. the mean diurnal production of carbon trapped into the collectors in the form of methane ebulliting from $1m^3$ from 25 cm the uppermost layer of the sediments (hard basalt rock below). The observed ebullition varied over three orders of magnitude from about 100 mg $(C\text{-}CH_4)\times day^{-1}\times m^{-3}$ (May 20 to July 02 when the first phytoplankton bloom occurred) at a depth of 2.8 m to the lowest value measured of 0.076 mg $(C\text{-}CH_4)\times day^{-1}\times m^{-3}$ (94.12.20–95.02.25) at a depth of 4.2 m (Fig. 4). However, several orders lower ebullition, than the lowest one measured, was observed between 95.10.07–96.04.19, during exceptionally strong and long winter. Between 95.10.07–96.04.19 the collected volume of gas was as small as about 0.5 ml. It is too little to be precisely measured by us using GC technique and isotope analysis.

Methane from the shallower depth (2.8 m) showed substantial seasonal variation in the $\delta^{13}C(CH_4)$ value (Fig. 5)

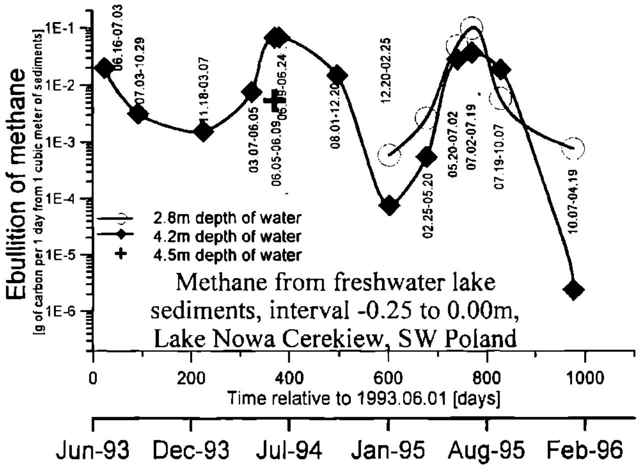

Fig. 4. Variation in the annual production of ebulliting methane expressed as the mean diurnal production of carbon trapped into the collectors in the form of methane ebulliting from 1m^3 of the 25 cm uppermost layer of the sediments ((C-CH$_4$)×day^{-1}×m^{-3}). Labels show dates corresponding to intervals when the gas was collected. Each point represents the mid-point of the starting and ending dates of collection. Lake Nowa Cerekiew, SW Poland

from -63.12‰ during winter to -52.46‰ during summer. Although the isotope data for the methane from the deeper station (4.2 m) are not complete, they clearly do not show any regular pattern on the seasonal basis. No correlation in the concentration of methane and the δ^{13}C(CH$_4$) value (Fig. 6), but slight correlation in the concentration and ebullitive flux (Fig. 7) have been observed.

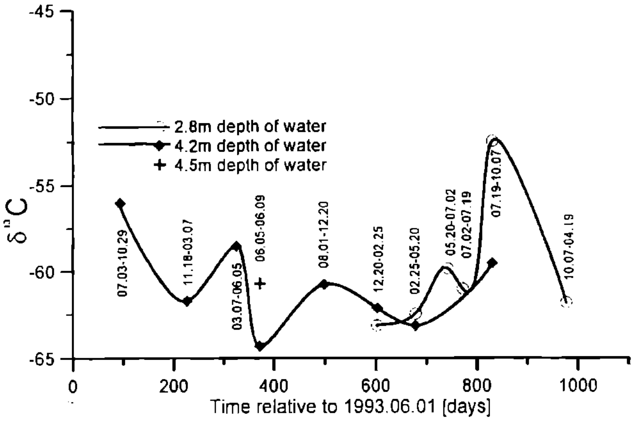

Fig. 5. Seasonal variations in δ^{13}C(CH$_4$) of the ebulliting methane. Lake Nowa Cerekiew, SW Poland. Labels show dates corresponding to intervals when the gas was collected. Each point represents the mid-point of the starting and ending dates of collection

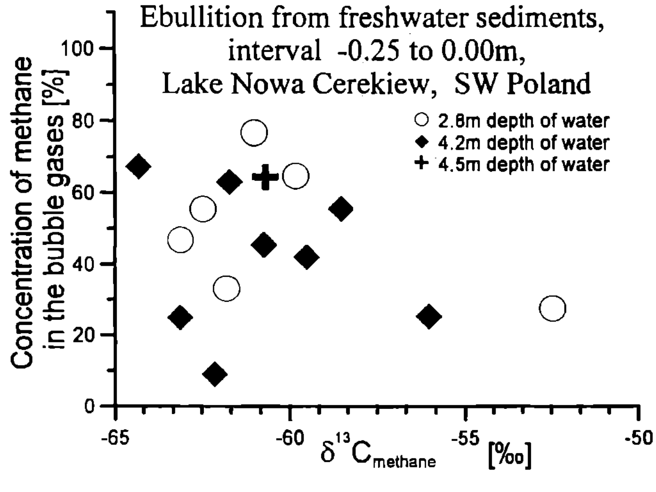

Fig. 6. Concentration of methane in the ebulliting gases *versus* δ^{13}C(CH$_4$) values of that methane. Lake Nowa Cerekiew, SW Poland

DISCUSSION

COMPARISON WITH THE RESULTS OF OTHER SELECTED OBSERVATIONS OF CH$_4$ FLUX

Most measurements of CH$_4$ flux from freshwater sediments concern subtropical or tropical climates, however some data for colder climates are available as well (e.g. Rudd & Hamilton, 1978; Cicerone & Shetter, 1981; De Laune *et al.*, 1983; Martens *et al.*, 1986; Sebacher *et al.*, 1986; Kelly & Chynoweth, 1981; Burke *et al.*, 1988; Chanton & Martens, 1988; Crill *et al.*, 1988; Ford & Naiman, 1988; Naiman *et al.*, 1991; Duchemin *et al.*, 1995). The open water methane flux from Lago Calado, an Amazon foodplain lake, averaged 20.25 mg (C-CH$_4$)×day^{-1}×m^{-2}) (Crill *et al.*, 1988) and is very close to the summer data from Lake Nowa Cerekiew, despite the fact that the climates are totally different. Likewise, the data, obtained in Lake Nowa Cerekiew for spring and summer, are in reasonable agree-

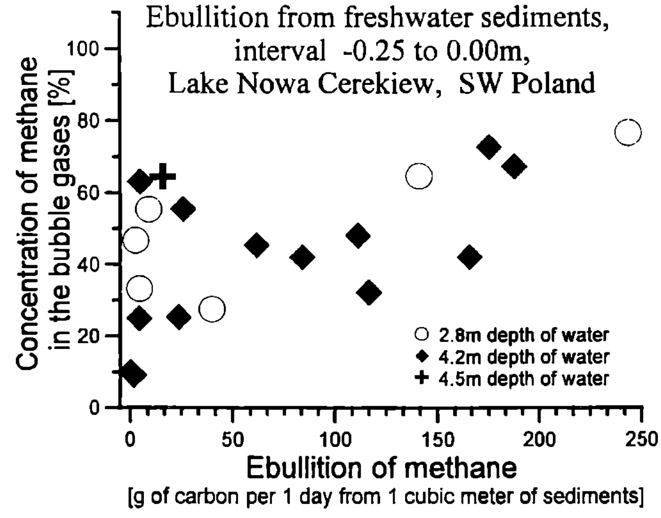

Fig. 7. Correlation in the concentration and ebullitive flux system

ment with the Cicerone & Shetter (1981) and Koyama (1990) estimates for freshwater sediments, about 98.25 mg (C-CH_4)×day^{-1}×m^{-2}) and 145.2 mg (C-CH_4)×day^{-1}×m^{-2}), respectively. The data presented here are somewhat lower than the values, 108.75 mg (Chanton & Martens, 1988) for North Carolina (about 34.8°N) tidal freshwater estuary during low tide, 330 mg for Michigan farm ponds (Baker-Blocker *et al.*, 1977), 275.25 mg for Michigan, Wisconsin and Ontario lakes (Kelly & Chynoweth, 1987). On the other hand measurements carried out in hydroelectric reservoirs in Northern Québec (53 to 54°N) during ice-free sampling periods, gave lower CH_4 emission fluxes between 5 and 10 mg (C-CH_4)×day^{-1}×m^{-2}), (Duchemin *et al.*, 1995). One may conclude that generally the climate basis, does not directly determine the measured CH_4 flux from freshwater sediments.

While comparing the numbers presented here to any other data, one should keep in mind that:

– the data presented here concern ebullitive flux from a certain volume of sediments (0.00 to -0.25 m) – all the other reports data concerning production from the surface, regardless of the thickness of sediments. As was demonstrated earlier, with the exception of the coldest seasons, productivity of methane decreases substantially with increasing depth of sediments (Jędrysek *et al.*, 1994, 1996);

– the observation times included winter when the lake was covered by ice;

– phytoplankton is the almost exclusive source of organic matter for the lake Nowa Cerekiew sediments;

– data presented here involve in general greater depths of the water column than in other studies, which is important for methanogensis (Jędrysek *et al.*, 1994, 1996).

POSSIBLE REASONS FOR THE SEASONAL VARIATION IN THE CH_4 EBULLITIVE FLUX AND IN THE $\delta^{13}C(CH_4)$ VALUE

From Figs. 1, 2 and 3 one may conclude that the rate of methanogenesis is at least two orders of magnitude lower during winter than during the late Spring and Summer. In contrast to the methane from the deeper station (4.2 m), methane from the shallower depth (2.8 m) showed substantial seasonal variation in the $\delta^{13}C(CH_4)$ value from -63.12‰ during winter to -52.46‰ during summer (Fig. 5). The roughly 11‰ variation is somewhat higher than the seasonal variations (6 to 10‰) reported by Chanton & Martens (1988). The concentrations of methane and $\delta^{13}C(CH_4)$ are not correlated (Fig. 6), what suggests that different factors may control these two parameters.

Possibly, several reasons should be considered as responsible for this pattern of behaviour, in terms of the seasonal variation in: the oxidation of methane; the mechanism of methanogenesis; the temperature; the sedimentation rate of the primary production; the carbon budget governed by respiration/assimilation rate, etc. This problem is discussed below.

Oxidation

Coleman *et al.* (1981) demonstrated that partial consumption of methane under aerobic conditions concentrated D and ^{13}C isotopes in the residual methane. Likewise, the oxidation of methane can significantly shift the carbon isotopic ratios positively in the residual methane (Barker & Fritz, 1981; Coleman *et al.*, 1981). However, most probably oxidation could not affect much the results concerning bubble methane flux, however it would be difficult to insist that oxidation has not affected methane collected via the trap to the bottles. On the other hand however, there is no evidence that oxidation influenced significantly the results and it is difficult to judge how effective the oxidation was. Some facts allow to suggest that oxidation should be considered as a secondary importance factor. Oxidation of methane can significantly shift the carbon isotopic ratios positively in the residual methane. If so, the oxidation effect could concern especially the sample 2.8 m (1995.07.19–10.07) because, in that sample, the highest $\delta^{13}C(CH_4)$ value is accompanied by a low (but not the lowest) concentration of methane. However, even in the case of the sample where the $\delta^{13}C(CH_4)$ is the highest and the concentration is low, the flux seems reasonable and the $\delta^{13}C(CH_4)$ is reasonable too. It is due to the fact that concentration of methane varied within the range of less than one order, while the flux varied within the range of three orders (in the case of this sample, the flux was high). It practically means that oxidation of methane, if occurred, could be considered as negligible.

Therefore, perhaps with one exception, oxidation seems to be in general less important when other factors are considered, especially a change in the ratios of methanogenic pathways. In the case of the remaining, but dominant part of samples, the situation is clear. The $\delta^{13}C(CH_4)$ value of methane collected in the collectors corresponds very well to the bubble methane collected by agitation of sediments at the same depth and time (Jędrysek *et al.* – in preparation). If oxidation of methane in the trap was an important factor decreasing methane concentration, a correlation in the $\delta^{13}C(CH_4)$ – CH_4 concentration should be observed, and the $\delta^{13}C(CH_4)$ values should be substantially higher than the $\delta^{13}C(CH_4)$ values representing bubble methane collected by agitation of sediments close to the sampling stations. Both are not the case. It may be explained by the facts that: (1) concentrations of potential oxidants of methane were negligible in the bottom region where the traps were situated and; (2) construction of the trap disabled efficient diffusion. Moreover, experiments carried out by Conrad *et al.* (1995) showed that even under conditions of hypersaline microbial mats, no aerobic CH_4 oxidation occurs, and probably no methanotrophic bacteria occur, although both O_2 and CH_4 are available. It suggests that oxidation of methane not always occurs, even under aerobic conditions. Finally, the seasonal variation of methane flux and depth variation seem quite reasonable and the data are comparable (or lower – but not higher) to other results obtained using similar or other techniques sampling (e.g. Rudd & Hamilton, 1978; Cicerone & Shetter, 1981; De Laune *et al.*, 1983; Martens *et al.*, 1986; Sebacher *et al.*, 1986; Kelly & Chynoweth, 1981; Burke *et al.*, 1988; Chanton & Martens, 1988; Crill *et al.*, 1988; Ford & Naiman, 1988; Naiman *et al.*, 1991; Duchemin *et al.*, 1995).

Accordingly, it was proved earlier (e.g. Chanton & Martens 1988) that no isotopic fractionation occurs during the transport of methane from the sediments to the atmosphere *via* ebullition. The solubility of methane in water is extremely low at pressures close to atmospheric pressure (Yamamoto *et al.*, 1976), and the diffusion coefficient (D_0) is $0.95\times10^{-5}cm^2sec^{-1}$ (Lerman, 1988), thus any loss of methane from bubbles ascending into the collector could be neglected. Finally, the concentrations of methane and $\delta^{13}C(CH_4)$ values are not correlated (Fig. 6), but slight correlation in the concentration and ebullitive flux has been observed (Fig. 7). It supports the thesis that different factors may control parameters and finally confirms that oxidation and diffusion of methane plays a negligible role, at least in the context of the monitoring technique applied.

Mechanism of methanogenesis

Variation in the production mechanisms have been discussed widely in the literature (e.g. Martens *et al.*, 1986; Chanton & Martens, 1988; Kelly *et al.*, 1992). The factor limiting acetate fermentation is the production rate of acetate, while the CO_2/H_2 production of CH_4 may be controlled by H_2 transfer (Conrad & Babbel, 1989). If hydrogen is produced in substantial amounts by bacteria and dissociation of water, and likewise the CO_2 concentration in water increases, it may enhance methanogenesis via the CO_2/H_2 reduction pathway in the uppermost horizons of sediments. The different mechanisms of biogenic methane production and variations in the abundance of substrates should result in a wide range of ebullition of methane.

Carignan & Lean (1991) reported that the degradation of planktonic matter could account for more than 80% of the annual water column production of CH_4 and DIC in a temperate climate lake. Thus, almost all newly produced and dead organic matter might be oxidized and decomposed in the euphotic zone over the thermocline during its downward descent. However, in the shallow parts of the lake, a substantial portion of less decomposed sinking organic matter, may sediment in the anaerobic zone of the sediment surface. Due to the fact that relatively simple, low-molecular weight compounds which are dominant precursors of methane, are more easily degraded than the complex polymeric compounds such as the lignin of woody and emergent aquatic plants (Moore, 1969; Wetzel, 1975; Koyama *et al.*, 1979; Heal & Ineson, 1984; Bell, 1969; Banner *et al.*, 1984), methane production should decrease along with sediment maturation. The time required for sinking of organic particles to the anoxic bottom is proportional to the depth of the water column. The matter which has been descending for a shorter time at a shallower depths is apparently less decomposed. It may promote acetic acid fermentation and consequently increase methanogenesis and the $\delta^{13}C(CH_4)$ value in shallower parts of the lake (Jędrysek *et al.*, 1993, 1994, 1996) – especially during the most active primary production. In fact, the highest ebullitive fluxes and the highest concentrations of methane were observed at the very end of spring and early summer, when the planktonic bloom occurred, and despite that the temperature had not yet reached the maximum (Figs. 1–3). This is in agreement with other observations, namely that acetate concentration in sediments decreases substantially while methanogenesis proceeds (Michelson *et al.*, 1989), which results in substantial decrease of $\delta^{13}C(CH_4)$ values (Sugimoto & Wada, 1993) downcore in sediments (Jędrysek *et al.*, 1994, 1996).

A substantial decrease in $\delta^{13}C(DIC)$ value and in HCO_3^- concentration in lake water is observed during summer (e.g. Takahashi *et al.*, 1990; Wachniew, 1994). In temperate climates, during cold seasons or below the thermocline, assimilation does not proceed or it is vanishingly low, although respiration is much less limited. Consequently, the concentration of DIC increases, enhancing methanogenesis through the CO_2 pathway. A similar model was proposed to explain diurnal variation in $\delta^{13}C(CH_4)$ values (Jędrysek, 1994, 1995).

Temperature

Several orders of magnitude seasonal variation in the ebullitive CH_4 flux, from about 100 $mg(C\text{-}CH_4)\times day^{-1}\times m^{-3}$ to probably less than 0.01 $mg\ (C\text{-}CH_4)\times day^{-1}\times m^{-3}$, suggests that temperature is the crucial factor controlling methanogenesis, but the mechanism of this process is not clear.

At higher temperatures in summer, the rate of decomposition of organic matter is higher and solubility of carbon-bearing compounds is lower than during colder seasons. Furthermore, the abundance of oxygen and other potentially important electron acceptors supporting the decomposition of organic mater also depends on the rates of microbial activities that are, in turn, largely controlled by temperature. Therefore, porewaters during the summer season are supersaturated with respect to methane precursors. This is in agreement with the fact that methane collected between 94.12.20 and 95.02. 25 in the deeper station (4.2 m), where the temperature was 4°C, was isotopically by 1‰ heavier than the methane collected in the shallower station where the temperature was 1.7°C. Accordingly, during summer and early autumn (95.07.19–10.07), when the temperature at the deeper station (still over the thermocline) was lower (max. 20°C) than in the shallower one (max. 27°C in the end of August), the methane from the latter was enriched by 7.1‰ in the ^{13}C isotope. Apparently, at lower temperature carbon isotope effect during production of methane due to the $CO_2 \rightarrow CH_4$ and $CH_3COOH \rightarrow CH_4$ pathways, should be higher. Thus, one might expect that methane in colder sediment (over the thermocline during winter and below the thermocline during summer), should be more depleted than the methane from the relatively warmer sediments (during winter below the thermocline and during summer over the thermocline). However, this is in contrast to another observation, when methane collected between 94.06.05 and 94.06.09 in the deeper station (of 4.5 m) just below thermocline, where the temperature was about 4°C, was isotopically about 3.6‰ heavier than the methane collected in the shallower station of 4.2 m, just over thermocline where the temperature was about 15°C (Fig. 4 and 5). Besides this, King *et al.* (1987) observed no variation in fractionation factors for the production of methane in laboratory cultures as a function of temperature. Thus, the differences in $\delta^{13}C(CH_4)$ values with respect to the depth and seasons must have another origin. Potentially, the variation in methanogenic pathways could be the direct reason and the temperature could act indirectly. Perhaps the lower temperature is the halting factor for the acetic acid pathway, as only the summer to early autumn methane (the highest temperature in the sediments) showed a distinctly higher $\delta^{13}C(CH_4)$ value of -52.46‰, suggesting an enhanced $CH_3COOH \rightarrow CH_4$ pathway (Fig. 5).

The deeper station is situated in general over the thermocline but water there was usually somewhat colder than in the upper station. Moreover, in the lower station, the thermocline zone sometimes appeared resulting in dramatic variations of temperature and consequently influencing methanogenesis (directly or indirectly) and additionally causing movement of poregases and porewater due to thermal shrinking/expansion of the sediment compounds. Consequently, in the thermocline zone the chemistry of the porewater might be varying frequently. Similar effect should be observed during seasonal mixing. Likewise, in the lower temperature of winter the density and viscosity of porewater and lake water increase, hence apparently the magnitude of diffusion and ebullition of gases decrease. Further studies will be required on this point.

Depth of water column

Another factor controlling the isotope ratio of methane could be the variations in the DIC (bioavailable pool) and of the $CO_2/HCO_3/CO_3$ ratio, which depends on temperature, pressure and pH. The pH measured was similar at the deeper and shallower station sediments (about 6). The typical temperatures below the thermocline varied from ~4 to ~10°C, and over the thermocline the temperature varied from the freezing point to 27°C. In the deeper water column, where the pressure is higher, the concentration of CO_2 may be higher, and moreover relatively smaller amounts of CO_2, which is depleted in the ^{13}C isotope, escape from the sediments at greater depths compared to those from shallower depths of the water column. Thus, in the deeper water sediments potentially more methane may be produced from CO_2 reduction (additionally depleted in the ^{13}C isotope) than at shallower depths.

GLOBAL EBULLITIVE CH_4 FLUX FROM FRESHWATER SEDIMENTS

It is understandable that samples for isotopic analysis and flux determination could not be collected at any time and place, and be considered as being generally representative. However, bubbles collected during winter at temperate or colder climates would be negligible from the point of view of isotope mass balance of atmospheric methane. Therefore, one may proceed with very rough calculations. The total surface of freshwater lakes on the Earth is about 855000 km^2 (Lerman *et al.*, 1995) and those not producing ebullitive methane are negligible compared to the error bias of the estimations all the data. However, most sediments below the thermocline produce very few bubble methane (Jędrysek *et al.*, 1994, 1996). On average, only about 10% of a lake sediment surface is situated over thermocline. Hence, the surface of active freshwater lake sediment methanogenesis could be assumed to be of the order of 1×10^5 km^2. If we extrapolate the mean freshwater CH_4 fluxes for freshwater sediments during a year as 5 $mg(C\text{-}CH_4)\times day^{-1}\times m^{-2}$), we obtain a value for the ebullitive global freshwater lake CH_4 flux of the order of about 5×10^8 $g(C\text{-}CH_4)\times year^{-1}$ (this is probably the lowest limit). Many more observations and new strategies for sampling, are required at this point.

CONCLUSIONS

1. In eutrophic lakes of temperate climate, production of methane varies seasonally, by about three orders of magnitude. The highest value measured here was 100 mg of carbon ebulliting in the form of methane from one cubic meter of sediments per day $((C\text{-}CH_4)\times day^{-1}\times m^{-3})$ during the early summer to near zero during winter;

2. Temperature is the dominant factor indirectly governing this biogeochemical rhythm.

3. The most important factors of enhanced ebullitive CH_4 flux during early summer are: (i) an increase of the primary production and consequently decomposition of fresh organic matter sedimented into the anoxic zone of the sediment surface (relatively more enhance the acetic acid pathway); (ii) an increase in bacterial activity at higher temperatures, (iii) apparent accumulation of methane and methane precursors during winter;

4. During the sinking of organic matter downward, partial decomposition of easily degradable compounds of organic matter which are precursors of acetate, may result in a decrease of the acetic acid pathway and consequently a decrease in the $\delta^{13}C(CH_4)$ value, while depth of the water column decreases;

5. The limited diffusion of isotopically depleted CO_2 from greater depths and the increase of bioavailable DIC due to higher pressures and lower temperatures at greater depths, may enhance the CO_2 pathway resulting in a decrease of the $\delta^{13}C(CH_4)$ value.

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Streszczenie

STRUMIEŃ EBULICJI WCZESNODIAGENETYCZNEGO METANU ZE WSPÓŁCZESNYCH OSADÓW SŁODKOWODNYCH JEZIORA NOWA CEREKIEW (SW POLSKA)

Mariusz O. Jędrysek

Wyniki obserwacji produkcji metanu w osadach słodkowodnych, przedstawione w niniejszej pracy, dotyczą obiegu węgla w układzie litosfera–biosfera–hydrosfera–atmosfera. Głównym produktem wczesnodiagenetycznego rozkładu materii organicznej w osadach anoksycznych jest metan. Powstaje on w wyniku redukcji dwutlenku węgla (Takai, 1970) i fermentacji octowej (Berker, 1936). Inne drogi wczesnodiagenetycznej metanogenezy nie są istotne z punktu widzenia badań izotopowych (Lovley & Klug, 1983). Metan powstały w wyniku redukcji CO_2 jest silnie zubożony w izotop ^{13}C w stosunku do metanu powstałego z CH_3COOH (Blair & Carter, 1992; Sugimoto & Wada, 1994). Proces utleniania metanu prowadzi do wzbogacenia pozostałego metanu w izotop ^{13}C (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 dążenie do zmian w metodach gospodarki w niektórych krajach, w celu zmniejszenie 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. Takie obliczenia powinny być także poparte bezpośrednimi obserwacjami wielkości emisji metanu z poszczególnych źródeł. Obserwacje te były głównym celem opisanych badań.

Z drugiej strony, proces utleniania metanu sprzyja powstawaniu węglanów wczesnodiagentycznych silnie zubożonych w

izotop ^{13}C. W ten sposób powstaje, w profilach osadów, zapis izotopowy o warunkach panujących w zbiorniku. Ma to istotne znaczenie w interpretacjach paleośrodowiskowych. Poznanie wielkości produkcji metanu, procesów jego utleniania i mechanizmów rządzących zmiennością składu izotopowego metanu powstającego w wyniku procesów wczesnodiagenetycznych ma więc istotne znaczenie dla izotopowego bilansu mas gazów efektu cieplarnianego oraz dla badań paleośrodowiskowych.

Przeprowadzono obserwacje ebullicji (naturalnej ucieczki gazu z osadu, w formie bąbli) metanu z jeziornych osadów słodkowodnych. Zbierano gaz na głębokościach 2.8 m i 4.2 m, a w pojedynczych przypadkach na głębokości 4.5 m, 5.5 m i 11 m. Obiektem badań było sztuczne jezioro wypełniające nieczynny, od ok. 30 lat, kamieniołom trzeciorzędowych bazaltów. Miąższość osadów wynosi ok. 25 cm. Głównym ich składnikiem jest materia organiczna, minerały ilaste, węglany i alofany. Gaz zbierano używając specjalnie skonstruowanych do tego celu kolektorów stacjonarnych usadowionych na dnie. Poboru prób dokonywano nurkując. Badania przeprowadzano nieprzerwanie w latach 1992–1996.

Stężenie metanu wahało się w granicach od 9.06% (zimą) do 76.82% (wczesne lato). Ebullicje metanu (wyrażone jako średnia dobowa ucieczka węgla, w formie bąbli metanu, z 1m^3 osadu ((C-CH$_4$)×doba^{-1}×m^{-3})) wahały się od ok. 100 mg(C-CH$_4$)×doba^{-1}× m^{-3} (latem) do niemal 0 (zimą). W przeciwieństwie do głębszej strefy (4.2 m), metan z mniejszej głębokości (2.8 m) wykazywał wahania sezonowe wartości δ^{13}C(CH$_4$), od -63.12‰ (zimą) do -52.46‰ (latem). W oparciu o uzyskane wyniki globalną ebullicję metanu oszacowano na rząd około 5×10^{8}g (C-CH$_4$)×rok^{-1}.

Intensywniejsza ebullicja CH$_4$ latem i wyższe wartości δ^{13}C (CH$_4$) mogły być wynikiem: (1) większej sedymentacji świeżej materii organicznej latem i częściowego rozkładu materii organicznej (prekursorów kwasu octowego) w czasie sedymentacji jeszcze w kolumnie wodnej (dłuższy czas opadania cząsteczek organicznych na większe głębokości) co umożliwiło intensywniejszą fermentację octową w osadach płytszej strefy zbiornika; (2) zwiększonej aktywności mikrobiologicznej (bakterii metanowych) w warunkach wyższej temperatury w osadach płytszych. Ponadto, wyższe wartości δ^{13}C(CH$_4$) mogły być następstwem niewielkiego utleniania metanu. Niższe wartości δ^{13}C(CH$_4$) mogły być spowodowane zmniejszoną produkcją metanu w wyniku fermentacji octowej; (ii) wzrostem stężenia węgla nieorganicznego w warunkach wyższego ciśnienia i niższej temperatury – wzrost produkcji metanu w wyniku redukcji CO$_2$; (3) wolniejszej dyfuzji izotopowo lekkiego metanu, z większej głębokości.