

Depth of the water column in relation to carbon isotope ratios in methane in freshwater sediments

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Methane was collected from the surficial sedimentary layer (0 to about 20 cm) in 45 freshwater lakes in Poland. Sampling was also carried out at various depths of the overlying water column (0.15 to 12 m) between noon and early afternoon, on a seasonal basis, between 1992 and 1996. A positive correlation between the depth of the lake water, the $\delta^{13}\text{C}(\text{CH}_4)$ value (from *ca.* -1.4 to -2.3% per 1 m depth) and the wider $\delta^{13}\text{C}(\text{CH}_4)$ variation over the thermocline are probably due to: the time of sinking of organic particles resulting in more intense acetate fermentation in shallower portions of the lake; the temperature variation; differences in the precursors of methane, the diffusion effect, and an increase of bioavailable DIC (dissolved inorganic carbon) at greater depths. Non-seasonal variation of isotope ratios in methane and the depth-isotope ratio correlation show that the lake system is in dynamic equilibrium on a scale of hours and days. Therefore, earlier models of methanogenesis relating and the atmospheric methane isotopic budget, proposed by other authors and based on sampling of methane from sediments, need to be revised. Moreover, $\delta^{13}\text{C}(\text{CH}_4)$ values higher during seasonal overturn (mixing of benthic and surface waters) than during stagnation, have been observed. This is probably due to the fact that during overturn periods some organic compounds (methane precursors) and methane in the surficial part of sediments, are oxidized with a resalting kinetic isotope effect. It is proposed that oxidation of methane and other organic compounds during seasonal overturn may be responsible for post-depositional lamination observed as pale (autumn overturn) and dark (summer organic-rich unoxic stagnation) millimetres-thick layers in freshwater lake sediments.

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INTRODUCTION

Methane is a ^{13}C -depleted important greenhouse gas and an element of the carbon cycle. Quantitative knowledge of representative isotope ratios of methane derived from individual sources is of critical importance for the isotope mass balance of greenhouse gases (e.g. Craig and Chou, 1982; Stevens and Rust, 1982; Khail and Rasmussen, 1983; Tyler, 1986; Cicerone, 1987; Stevens and Engelkemeir, 1988; Wada, 1990). Biogenic methane is produced by the microbial decomposition of organic matter in water-covered sediments, including paddy fields, peat-bogs, and lakes, and is the most important source of atmospheric methane (Khalil and Rasmussen, 1983; Tyler, 1986; Stevens and Engelkemeir, 1988; Koyama, 1990). Fermentation of acetate [$\text{CH}_3\text{COOH} \Rightarrow \text{CH}_4 + \text{CO}_2$] (Barker, 1936) and the reduction of carbon dioxide [$\text{CO}_2 + 4\text{H}_2 \Rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$] (Takai, 1970) are by far the dominant methanogenic pathways (e.g. Games *et al.*, 1978; Stevens and Engelkemeir,

1988) in freshwater systems. Although other (third) formation-consumption pathways may complicate the picture of methane dynamics (Zindler and Brock, 1978a, b; Weimer and Zeikus, 1978; Patterson and Hespell, 1979; Oremland *et al.*, 1982) they represent very specialized environments and in the context of both freshwater methanogenesis and the global methane budget, these third methanogenic pathways are not believed to play a significant role (e.g. by methyl amines and methanol; see Lovley and Klug, 1983).

From tracer experiment data with anoxic marine sediments, Blair and Carter (1992) estimated that the end member methane produced from acetate in marine sediment had a $\delta^{13}\text{C}$ value of -43% while the methane derived from carbon dioxide had a $\delta^{13}\text{C}$ value of -65% . Similarly, incubation of freshwater paddy soil yielded an end member methane $\delta^{13}\text{C}$ signature of -36% from acetate and -77 to -60% for the $\delta^{13}\text{C}$ of methane produced from carbon dioxide (Sugimoto and Wada, 1993). They found that carbon dioxide produced *in situ* during methanogenesis, e.g., CO_2 from acetate carboxyl carbon, may

be utilized as a carbon source for methanogenesis in sediments. Even if one assumes that the $\delta^{13}\text{C}$ value of methane is governed by the two major pathways, i.e. from acetate and CO_2/H_2 , there is very little information on spatial and temporal variations of methanogenesis in freshwater sediments, particularly in lakes (Woltemate *et al.*, 1984; Whiticar *et al.*, 1986; Jędrysek *et al.*, 1994; Jędrysek, 1997).

At present, there are few isotopic data from which accurate estimates of methane production in lake sediments can be derived. Methane produced deeper in the sediments (2 to 3 m deep in the sediment) and in sediments at greater depths in the water column (to 12 m), as well as methane collected at night (night methane), show strong ^{13}C depletion, up to 18‰, as compared to shallow sedimentary (0 to 0.2 m), shallow water (0.15 m) and daytime methane, respectively (Jędrysek *et al.*, 1994; Jędrysek, 1995, 1998, 1999). However, nearly all other published isotope data are on methane collected from surficial sediments or at shallow depths of the water column and/or during the daytime. It is apparent that the process of methanogenesis in natural freshwater conditions is not fully understood and there is concern that the existing data on sediment methane may not be representative for the systems in question. Therefore, the objectives of this study were to provide data for new isotopic mass balance calculations of atmospheric greenhouse gases and to better spatially describe the role of depth of the water column and seasonal stagnation and seasonal overturn in variations of methanogenesis occurring in freshwater lakes.

MATERIALS AND METHODS

SAMPLING

In general, the main aim in the selection of lakes for sampling was to obtain a wide variety of samples with respect to trophic state, anthropogenic impact, depth and altitude. Names of the lakes sampled and their location are shown in the Fig-

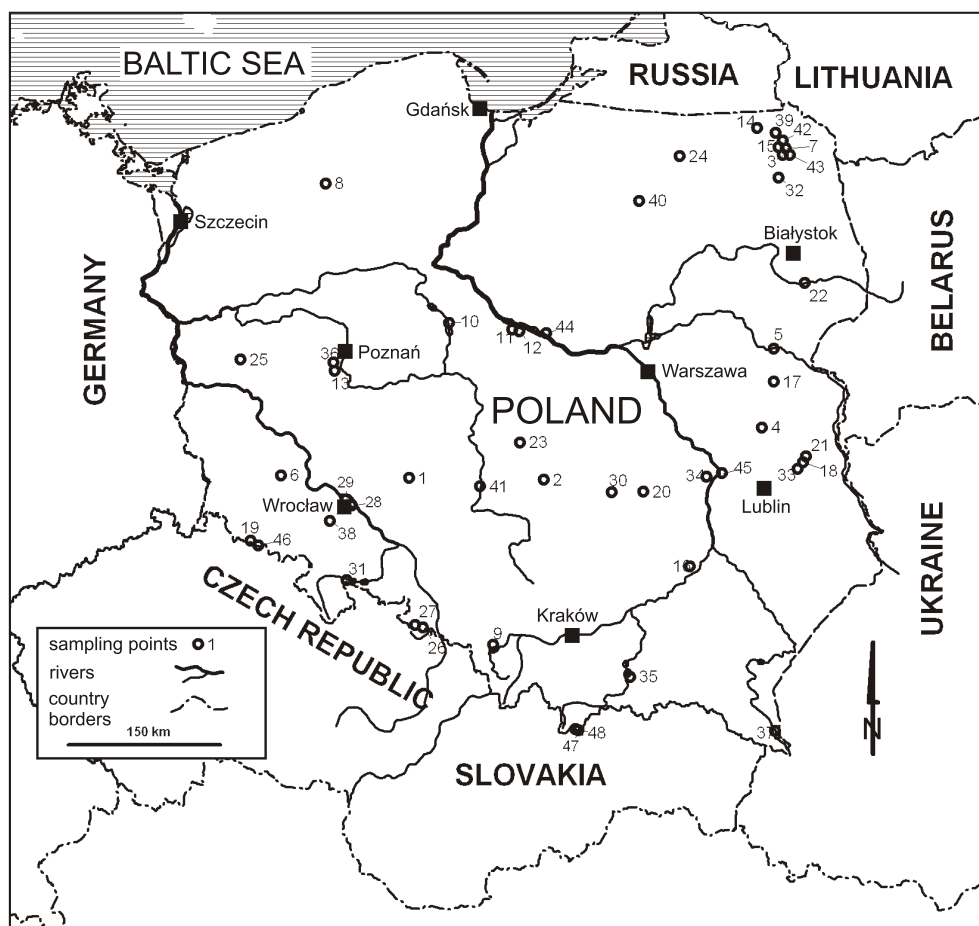


Fig. 1. Sketch showing the locations of lakes, rivers and ponds sampled in Poland

Sampling points are described in Jędrysek (1995, 1997, 1999); 1 — Antonin, 2 — Bełchatów-Słok, 3 — Białe Wigierskie, 4 — Borki village, 5 — Bug River, 6 — Chocianów, 7 — Czarna Hańcza River, 8 — Czarne, 9 — Goczałkowice, 10 — Gopło, 11 — Gościąż, 12 — Gościąż stream, 13 — Góreckie, 14 — Hańcza, 15 — Kamionka River, 16 — Krobielice stream, 17 — Łosice pond, 18 — Łukie, 19 — Mały Staw, 20 — Mniszek stream, 21 — Moszne, 22 — Narew, 23 — Ner River (Dąbie), 24 — Niegocin, 25 — Niesłysz, 26 — Nowa Cerkiew, 27 — Nowa Cerkiew pond, 28 — Odra River (Brochów), 29 — Odra River (Wrocław), 30 — Opoczno pond, 31 — Otmuchów, 32 — Otok, 33 — Piaseczno, 34 — Polesie, 35 — Rożnowskie, 36 — Skrzynka, 37 — Solina, 38 — Sulistrowiczki, 39 — Szurpiły, 40 — Warchały, 41 — Warta River (Osjaków), 42 — Wądołek, 43 — Wigry, 44 — Wisła River (Płock), 45 — Wisła River (Puławy), 46 — Wielki Staw, 47 — Morskie Oko, 48 — Czarny Staw

ure 1, however details of the precise localities and limnological characteristics of the lakes can be found elsewhere (Jędrysek, 1995, 1997, 1999 and *op. cit.*). The methanogenic sediments in these lakes are composed of soft organic-rich sand and mud. The pH measured was similar at both deeper and shallower stations and amounted to about 6. Typical temperatures below the thermocline varied from ~ 4 to $\sim 10^\circ\text{C}$, and above the thermocline the temperature varied from freezing to 27°C (Jędrysek, 1997). Samples have been collected at various distances from the lake bank using boat, or by means of scuba diving (Table 1). Although this paper reports results of samples collected between 1992 and 1996, the majority of samples were collected within an 18-day period in August/September 1993 (Table 1). The surface of the sediment where the methane was sampled was always free of rooted plants.

The interstitial pore waters are saturated with respect to methane, resulting in the formation of gas bubbles. These pore gases were collected for $\delta^{13}\text{C}$ analysis. The bubbles were re-

Table 1

List of samples, sampling details and analytical results: bubble methane collected from recent sediments in lakes, rivers and ponds in Poland

Names of sampled lakes	Date of sampling	Time of sampling	Depth of water [m]	CH ₄ concentration [%]	¹³ C (CH ₄) [‰]
1	2	3	4	5	6
Seasonal stagnation					
Bełchatów-Słok	93.07.24	12:30	-1.1	46.49	-57.45
Bełchatów-Słok	93.07.24	cont.	-2.5	61.68	-61.59
Bełchatów-Słok	93.07.24	cont.	-3	67.56	-58.09
Bełchatów-Słok	93.07.24	cont.	-2.8	72.51	n.a.
Bełchatów-Słok	93.07.24	cont.	-3	79.99	-60.67
Bełchatów-Słok	93.07.24	cont.	-1.8	44.49	-59.26
Bełchatów-Słok	93.07.24	cont.	-2.5	80.37	-69.67
Bełchatów-Słok	93.07.24	15:00	unkn.	55.28	-54.44
Gościąż	93.06.04	13:00	-1	57.75	-62.11
Gościąż	93.06.04	cont.	-3	57.71	-69.03
Gościąż	93.06.04	cont.	-5.5	72.14	-72.73
Gościąż	93.06.04	15:00	-0.5	19.24	-64.19
Gościąż	93.09.07	ca.13:00	-0.3	46.56	-64.37
Gościąż	93.09.07	cont.	-1.3	7.76	-62.71
Gościąż	93.09.07	cont.	-3.2	60.88	-73.24
Gościąż	93.09.07	cont.	-4.4	85.73	n.a.
Gościąż	93.09.07	cont.	-7	77.32	n.a.
Gościąż	93.09.07	cont.	-7.2	79.01	-67.65
Gościąż stream	93.06.04	ca.15:30	-0.3	n.a.	-62.27
Gościąż stream	93.09.07	ca.16:00	-0.1	43.76	n.a.
Gościąż stream	93.09.07	ca.16:00	-0.1	83.55	-67.11
Gościąż stream	93.09.07	ca.16:00	-0.1	43.76	-68.48
Łosice pond	93.08.31	13:30	-0.5	55.86	-65.88
Łukie	92.09.27	15:51	-0.45	72.4	-60.7
Mały Staw	93.08.21	13:00	-1.3	4.05	-68.77
Mały Staw	93.08.21	cont.	-1.7	33.74	-68.71
Mały Staw	93.08.21	cont.	-3.2	53.93	-65.67
Mały Staw	93.08.21	cont.	-4.75	57.65	-64.69
Mały Staw	93.08.21	ca.14:30	-6	71.93	-65.01
Moszne	93.07.17	ca.14:00	-0.7	69.85	-58.42
Moszne	93.08.30	ca.13:00	-0.7	85.73	n.a.
Moszne	93.08.30	ca.15:00	-0.8	81.01	-53.21
Niegocin	93.08.05	11:00	-0.2	61.02	-65.7
Niegocin	93.09.06	cont.	-0.3	54.45	-67.72
Niegocin	93.09.06	cont.	-0.75	47.94	-65.15
Niesłysz	93.07.09	12:00	-1	71.56	n.a.
Niesłysz	93.07.09	12:30	-3	48.3	-62.01
Niesłysz	93.07.09	13:00	-5	58.84	-65.02
N.Cerekiew	92.05.25	cont.	-7	n.a.	-73.8
N.Cerekiew	92.05.25	cont.	-9	n.a.	-76.33
N.Cerekiew	92.11.14	12:00	-4.5	79.41	-68.4
N.Cerekiew	92.11.14	13:30	-10	61.42	-71.79
N.Cerekiew	93.02.07	13:30	-6	68.29	-74.0

1	2	3	4	5	6
N.Cerekiew	93.02.07	13:40	-8	59.53	n.a.
N.Cerekiew	93.03.13	13:30	-7	72.91	-73.78
N.Cerekiew	93.03.13	13:40	-8	n.a.	-72.57
N.Cerekiew	93.03.13	13:55	-9	46.89	-72.43
N.Cerekiew	93.05.29	cont.	0	n.a.	-50.17
N.Cerekiew	93.05.29	cont.	-0.1	27.49	-52.04
N.Cerekiew	93.05.29	cont.	-0.2	26.87	-52.57
N.Cerekiew	93.05.29	cont.	-0.25	59.35	-51.01
N.Cerekiew	93.05.29	cont.	-0.35	n.a.	-63.4
N.Cerekiew	93.05.29	cont.	-6.6	n.a.	-65.25
N.Cerekiew	93.05.29	cont.	-7.5	83.44	-69.83
N.Cerekiew	93.05.29	cont.	-10	69.02	-73.97
N.Cerekiew	93.05.29	15:15	-10.5	66.8	-74.33
N.Cerekiew	93.06.10	cont.	-6	65.82	-73.48
N.Cerekiew	93.06.10	cont.	-9	65.97	-72.53
N.Cerekiew	93.06.16	13:00	-4	75.19	n.a.
N.Cerekiew	93.07.03	14:10	3	63.42	-64.44
N.Cerekiew	93.07.03	14:30	-6	78.32	-69.1
N.Cerekiew	93.07.03	15:00	-9	74.11	-70.65
N.Cerekiew	93.07.03	15:30	-11	71.13	-72.43
N.Cerekiew	93.07.28	16:00	-10.5	80.93	-71.33
N.Cerekiew	93.08.23	14:00	-1	46.96	n.a.
N.Cerekiew	93.08.23	cont.	-2.1	60.3	n.a.
N.Cerekiew	93.08.23	cont.	-4.2	59.24	n.a.
N.Cerekiew	93.08.23	cont.	-6	58.59	n.a.
N.Cerekiew	93.08.23	15:30	-7.5	74.07	n.a.
N.Cerekiew	94.06.24	13:30	-0.4	34.14	n.a.
N.Cerekiew	94.06.24	cont.	-2.9	56.99	-60.48
N.Cerekiew	94.06.24	cont.	-2.9	72.87	-59.22
N.Cerekiew	94.06.24	cont.	-4.4	62.11	-63.08
N.Cerekiew	94.06.24	cont.	-4.4	74.32	-64.44
N.Cerekiew	94.06.24	15:30	-6.7	70.98	-67.49
N.Cerekiew	94.08.01	14:00	-0.6	46.27	-56.53
N.Cerekiew	94.08.01	cont.	-2.9	68.8	-59.99
N.Cerekiew	94.08.01	cont.	-7	35.44	-74.73
N.Cerekiew	95.02.25	13:30	-0.3	37.41	-53.14
N.Cerekiew	95.02.25	cont.	-1	29.96	n.a.
N.Cerekiew	95.02.25	cont.	-3.1	67.35	-62.75
N.Cerekiew	95.02.25	cont.	-4.2	69.67	n.a.
N.Cerekiew	95.07.02	13:30	-0.5	56.01	n.a.
N.Cerekiew	95.07.02	cont.	-2.8	70.62	-60.58
N.Cerekiew	95.07.02	14:00	-4.2	74.04	-60.71
N.Cerekiew pond	93.06.16	14:00	-0.4	60.22	-60.69
Piaseczno	93.07.17	12:00	-0.5	31.66	-63.81
Piaseczno	93.07.17	cont.	-1	18.55	-60.2
Piaseczno	93.07.17	cont.	-1.3	47.58	-60.93
Piaseczno	93.07.17	cont.	-2	54.05	-62.88
Piaseczno	93.07.17	cont.	-3	49.69	-63.3
Piaseczno	93.07.17	ca.14:15	-4	40.06	-68.88
Piaseczno	93.08.29	12:25	-0.5	68.4	-52.23
Piaseczno	93.08.30	13:15	-0.5	43.11	-51.5
Piaseczno	94.02.12	noon	-1	11.39	n.a.

Tab.1 continued

1	2	3	4	5	6
Piaseczno	94.02.12	noon	-2.4	21.89	-66.85
Piaseczno	94.02.12	noon	-4	47.33	-67.6
Piaseczno	94.02.12	noon	-5.5	11.24	-66.25
Piaseczno	94.02.13	14:10	-1	59.21	-55.58
Piaseczno	94.02.13	14:10	-1	49.47	-58
Skrzynka	-	noon	-1.7	60.73	-67.24
Sulistrowiczki	93.08.20	13:30	-0.5	55.25	-57.89
Sulistrowiczki	94.07.04	12:00	-0.15	67.46	-50.26
Sulistrowiczki	94.07.04	15:03	-0.15	70.62	-52.4
Sulistrowiczki	94.07.04	12:00	-0.75	64.62	-56.7
Sulistrowiczki	94.07.04	15:03	-0.75	51.61	-55.26
Szurpiły	93.09.05	15:00	-0.9	58.22	-62.92
Szurpiły	93.09.05	cont.	-1.5	33.11	-73.16
Szurpiły	93.09.05	cont.	-2	66.4	-65.49
Szurpiły	93.09.05	cont.	-3.5	46.85	n.a.
Szurpiły	93.09.05	cont.	-4.7	47.07	-71.06
Szurpiły	93.09.05	ca.16:00	-7	47.32	-75.61
Warchały	93.09.06	after-noon	-0.8	64.19	-64.55
Wądołek	93.09.02	cont.	-1.5	73.49	n.a.
Wądołek	93.09.02	cont.	-4	78.21	n.a.
Wądołek	93.09.02	cont.	-5	79.92	-63.93
Wigry	93.09.03	12:10	-0.8	b.d.	n.a.
Wigry	93.09.03	cont.	-0.9	b.d.	n.a.
Wigry	93.09.03	13:00	-0.2	3.55	n.a.
Wigry	93.09.03	cont.	-1.1	58.48	-66.12
Wigry	93.09.03	13.3	-1.5	32.83	n.a.
Wigry	93.09.03	13.3	-1.5	43.58	n.a.
Wigry	93.09.03	13:43	-0.6	74.21	-63.09
Wigry	93.09.03	13:41	-1	58.08	-67.14
Wigry	93.09.03	14:30	-0.3	79.65	-61.23
Wigry	93.09.03	cont.	-1	89	-58.52
Wigry	93.09.03	cont.	-1.5	87.7	n.a.
Wigry	93.09.03	14:40	-0.4	23.23	n.a.
Wigry	93.09.03	15:08	-0.4	15.24	-78.27
Wigry	93.09.03	cont.	-0.8	39.59	n.a.
Wigry	93.09.03	cont.	-1.7	24.54	n.a.
Wigry	93.09.03	cont.	-3	32.28	-69.29
Wigry	93.09.03	cont.	-4	71.85	-70.09
average			3.03	56.51	64.40
Seasonal overturn					
Białe Wigierskie	93.09.02	14:00	-0.6	44.35	-63.5
Białe Wigierskie	93.09.02	cont.	-1	78.73	-58.53
Białe Wigierskie	93.09.02	cont.	-1.5	76.36	-65.57
Białe Wigierskie	93.09.02	cont.	-3.1	82.64	-62.21
Białe Wigierskie	93.09.02	cont.	-4.5	64.55	-64.17
Białe Wigierskie	93.09.02	cont.	-5.2	69.49	-62.12
Białe Wigierskie	93.09.02	cont.	-6.3	60.37	-64.11
Białe Wigierskie	93.09.02	16:00	-7.4	69.59	-65.08
Borki vill. stream	93.08.31	mid-day	-0.3	48.27	-54.9
Bug River	93.08.31	ca.23:00	-0.4	71.23	-59.4
Cz.Hańcza River	93.09.01	12:00	-0.2	11.93	n.a.
Czarne	93.09.25	13:00	-0.3	43	-51.21

Tab.1 continued

1	2	3	4	5	6
Czarne	93.09.25	cont.	-1	66.51	-59.6
Czarne	93.09.25	cont.	-3	55.35	-60.62
Czarne	93.0.25	cont.	-4.2	46.2	-70.18
Czarne	93.09.25	16:00	-5.5	9.79	-53.38
Goczałkowice	93.08.23	17:00	-0.5	8.77	-55.08
Góreckie	93.05.21	18:00	-2	47.87	-58.9
Góreckie	93.05.22	13:00	-0.8	86.42	-35.55
Góreckie	93.05.22	cont.	-2.5	n.a.	-67.9
Góreckie	93.05.22	cont.	-2.8	49.8	n.a.
Góreckie	93.05.22	cont.	-2.8	65.17	-70.19
Góreckie	93.05.22	15:00	-4.15	n.a.	-69.99
Góreckie	93.09.08	13:00	-0.4	29.08	-63.15
Góreckie	93.09.08	cont.	-1.2	38.68	n.a.
Góreckie	93.09.08	cont.	-2.1	35.95	-62.73
Góreckie	93.09.08	cont.	-3.5	46.49	-62.93
Góreckie	93.09.08	cont.	-4.5	60.1	-66.63
Góreckie	93.09.08	cont.	-5.4	65.57	-62.14
Góreckie	93.09.08	cont.	-6.5	n.a.	-62.97
Góreckie	93.09.08	cont.	-7.4	66.44	-60.73
Góreckie	93.09.08	cont.	-8.5	64	-63.63
Góreckie	93.09.08	ca.16:00	-0.4	38.13	-65.92
Góreckie	93.09.08	cont.	-1.1	61.64	n.a.
Hańcza	93.09.04	12:00	-1	51.45	-56.96
Hańcza	93.09.04	cont.	-3.4	54.88	-54.62
Hańcza	93.09.04	cont.	-4.5	44.43	-64.02
Hańcza	93.09.04	17:00	-0.3	47.58	-60.52
Hańcza	93.09.04	cont.	-1.2	29.41	n.a.
Kamionka river	93.09.01	16:30	-0.15	26.38	-52.9
Kamionka river	93.09.01	cont.	-0.15	30.06	-56.21
Kamionka river	93.09.01	cont.	-0.15	2.58	-57.23
Kamionka river	93.09.01	cont.	-0.15	6.03	-51.8
Kamionka river	93.09.01	cont.	-0.15	6.46	-60.6
Kamionka river	93.09.01	cont.	-0.15	14.21	-60.26
Kamionka river	93.09.01	cont.	-0.15	1.68	-62.7
Kamionka river	93.09.01	cont.	-0.15	10.33	-50.76
Kamionka river	93.09.01	cont.	-0.15	5.17	-56.02
Kamionka river	93.09.01	cont.	-0.2	60.58	-57.46
Kamionka river	93.09.01	cont.	-0.15	b.d.	n.a.
Kamionka river	93.09.01	cont.	-0.15	14.81	-51.76
Kamionka river	93.09.01	cont.	-0.15	41.64	-58.82
Kamionka river	93.09.01	cont.	-0.15	n.a.	-48.47
Kamionka river	93.09.01	19:50	-0.15	n.a.	-59.63
Krobelice stream	93.04.11	14:00	-0.5	1.34	n.a.
Moszne	92.09.27	ca.14:00	-0.4	46.89	-55.62
Moszne	93.05.01	ca.14:00	-0.8	55.5	-59.04
Moszne	93.11.14	ca.14:00	-0.6	71.63	-56.18
Narew	93.08.31	ca.23:00	-0.9	57.17	-58.14
Ner (Dąbie)	93.06.03	17:00	-0.8	78.1	-53.24
N.Cerekiew	92.05.01	15:00	unkn.	14.88	-46.49
N.Cerekiew	93.10.29	13:00	0	27.2	-48.93
N.Cerekiew	93.10.29	cont.	-3.0	59.28	-67.38
N.Cerekiew	93.10.29	cont.	-4.5	74.98	-64.36

Tab.1 continued

1	2	3	4	5	6
N.Cerekiew	93.10.29	cont.	-6.0	56.3	-67.93
N.Cerekiew	93.10.29	14:00	-8.2	68.8	-65.61
N.Cerekiew	94.03.07	13:30	-0.7	14.91	-52.78
N.Cerekiew	94.03.07	cont.	-2.0	67.67	-58.58
N.Cerekiew	94.03.07	cont.	-4.2	68	-65.45
N.Cerekiew	94.03.07	15:00	-11	78.54	-66.92
N.Cerekiew	94.06.05	13:30	-0.7	20.07	-48.65
N.Cerekiew	94.06.05	cont.	-2.2	77.38	-57.14
N.Cerekiew	94.06.05	cont.	-4.5	56.95	-62.12
N.Cerekiew	94.06.05	cont.	-4.5	73.34	-61.82
N.Cerekiew	94.06.05	cont.	-7.0	74.29	-63.99
N.Cerekiew	94.06.05	15:30	-10.7	73.81	-63.99
N.Cerekiew	94.06.09	14:00	-4.4	n.a.	-62.16
N.Cerekiew	95.05.20	13:30	-0.35	36.5	n.a.
N.Cerekiew	95.05.20	cont.	-0.4	46.02	n.a.
N.Cerekiew	95.05.20	cont.	-2.8	75.74	-60.67
N.Cerekiew	95.05.20	14:30	-4.0	74.51	-67.9
Odra (Brochów)	93.08.22	noon	-0.4	1.5	n.a.
Odra (Brochów)	93.08.22	noon	-0.4	25.05	-55.01
Odra (Wrocław)	92.08.25	noon	-1.0	n.a.	-58.85
Odra (Wrocław)	93.12.16	noon	-1.0	3.55	-49.95
Piaseczno	92.09.26	unkn.	-1.0	35.15	-61.13
Piaseczno	92.09.26	14:00	-1.5	n.a.	-60.5
Piaseczno	92.09.26	cont.	-3.0	44.6	-64.67
Piaseczno	92.09.26	cont.	-3.0	n.a.	-58.12
Piaseczno	92.09.26	16:00	-4.25	3.72	-63.92
Piaseczno	92.09.26	15:20	-10.0	2.05	-61.39
Piaseczno	92.09.26	17:00	-0.7	n.a.	-57.89
Piaseczno	92.09.26	17:00	-0.7	n.a.	-57.09
Piaseczno	92.09.26	23:00	-0.7	n.a.	-60.23
Piaseczno	92.09.27	11:40	-0.7	n.a.	-61.38
Piaseczno	92.09.27	18:40	-0.7	n.a.	-58.16
Piaseczno	93.03.21	noon	-0.8	44.78	-58.69
Piaseczno	93.03.21	noon	-0.8	57.57	-62.26
Piaseczno	93.11.13	noon	-1.4	45.98	-58.99
Piaseczno	93.11.13	noon	-1.8	45.83	-63.09
Piaseczno	93.11.13	noon	-3.5	31.62	-61.85
Piaseczno	93.11.14	noon	-2.1	48.08	-57.48
Rożnowskie	93.08.26	ca.22:00	-0.5	39.95	-54.24
Rożnowskie	93.08.26	cont.	-0.9	43.29	-60.19
Rożnowskie	93.09.26	ca.23:00	-0.5	38.64	n.a.
Skrzynka	93.05.23	noon	-2	65.38	-61.11
Skrzynka	93.05.23	noon	-2.5	61.75	-65.9
Solina	93.08.27	15:00	-1.6	11.17	n.a.
Solina	93.08.27	cont.	-3	6.37	-54.44
Solina	93.08.27	cont.	-3	34.75	-57.46
Solina	93.08.27	cont.	-6.2	71.23	-66.52
Solina	93.08.27	cont.	-8.2	64.04	-65.75
Solina (Chrewt)	93.08.28	ca.12:00	-0.2	40.06	-54.58
Solina (dam)	93.08.28	ca.15:00	-1.2	50.27	-58.62
Wisła (Płock)	93.09.07	ca.14:00	-0.5	90.53	-60.64
average			-2.30	45.67	-59.70

Sampling points are described in Jedrysek (1995, 1997, 1999; Fig. 1); n.a. — not analyzed

leased by hand-agitation of the sediment and were trapped in an inverted funnel connected to an inverted glass bottle that was initially filled with gas-free water. Gases were collected from a sediment interval from the surface to a depth of about 20 cm. The depth of water overlying the sediments varied according to location (Table 1). The collection of each sample of gases usually took no more than 2 minutes. Not all of the gas-free water initially in the collection bottle was displaced. The bottle was sealed with rubber and double metal caps. A bactericidal solution (HgCl₂) was added to each bottle immediately after sampling. After returning to the laboratory, the sample bottles were stored inverted, in a refrigerator at 3–4°C. These sampling and storing methods have no influence on δ¹³C values and CH₄ concentration (Jędrysek, 1997).

ANALYTICAL TECHNIQUES

The chemical compositions of the sediment gases, including the concentrations of CO₂ and CH₄, were determined by gas chromatography with a thermal conductivity detector (“*Elwro gas chromatograf 504*”) with uncertainty of CH₄ concentration measurements of ±1%. The gases were prepared for IR-MS (isotope ratio-mass spectrometry) analysis as follows. The methane in the sample was separated from other hydrogen-and-carbon containing gases by cryogenic purification using molecular sieves, a dry ice/ethanol mixture, and liquid nitrogen. The methane was passed twice through a copper oxide furnace (850–900°C), where it was completely combusted to H₂O and CO₂, which were then separated cryogenically. Carbon isotope analyses were performed on a modified *MI-1305* mass spectrometer with a home-made inlet (Halas, 1979) and detection system (Halas and Skorzyński, 1980) and *Finnigan-Mat CH7* mass spectrometer. All δ¹³C measurements are expressed relative to PDB standard and are precise to 0.05‰. The δ value is defined as $[(R_{sp} - R_{st})/R_{st}] \times 1000$ and expressed in [‰], where R is ¹³C/¹²C isotope ratio in the sample (sp) and the standard (st). The overall accuracy of the isotopic preparation of samples and standard methane was better than 0.25‰.

RESULTS

The results reported in the Table 1 represent samples of stagnation and seasonal overturn periods. The stagnation period in lakes is defined here as the period when distinct thermocline and no visual signs of vertical mixing of water have been observed during scuba diving for sampling. Seasonal overturn in lakes is understood here as the process of vertical transport (mixing) of water usually resulting from thermally controlled variations in the density of the water. Although the situation in the riverbed is not equal to that in the lake during seasonal overturn, methane sampled from rivers and streams can be considered as more similar to that relating to the seasonal overturn (Table 1), due to a permanent state of turbulence in river waters, than to that relating to seasonal stagnation in lakes.

The results are shown in Figures 2–5. Shallow-water gas bubbles reveal much wider variations in CH₄ concentration (from near 0 to about 98%) than the deep-water bubbles where methane comprises more than half of the gas content (Fig. 2).

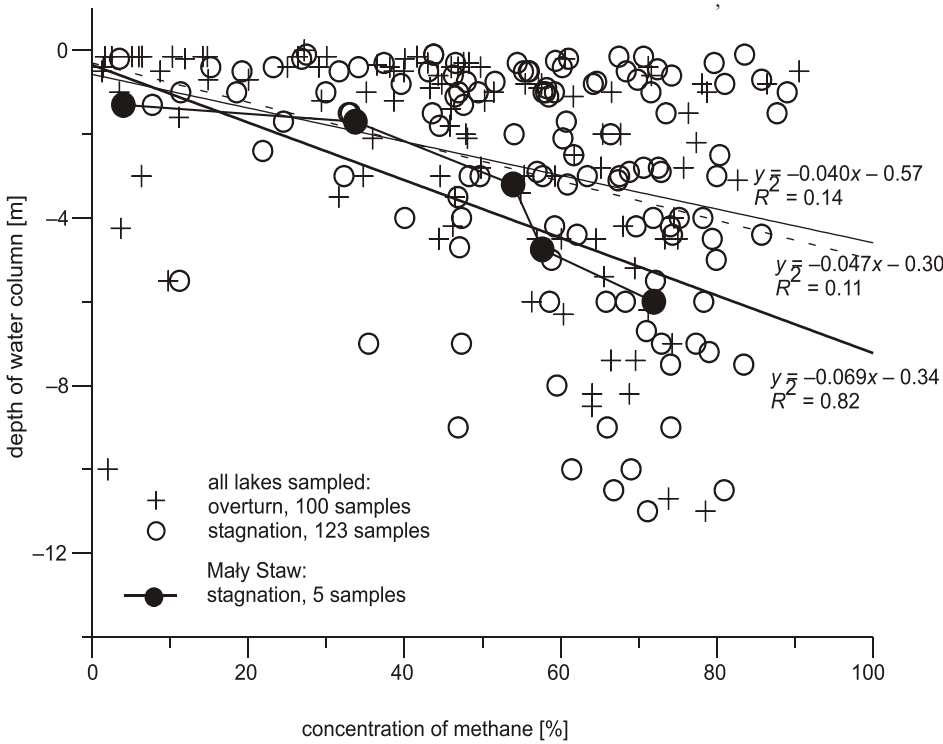


Fig. 2. Concentration of methane in bubbles of gases sampled at various depths in freshwater lake sediments

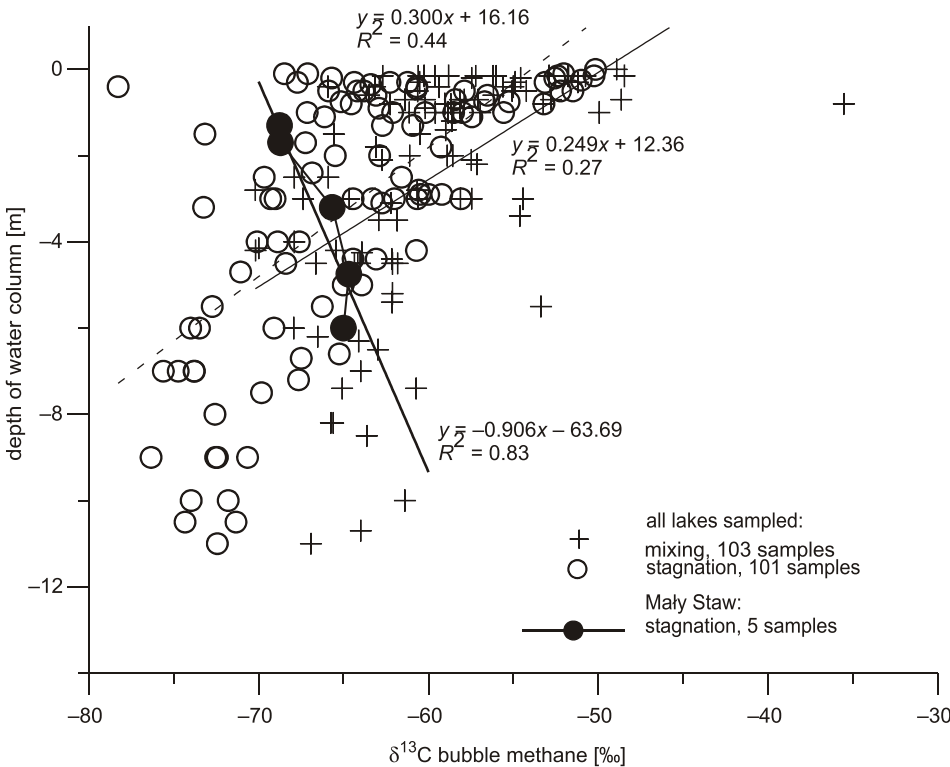


Fig. 3. Carbon isotope ratios in methane from bubble gases sampled, at various depths of the overlying water column, from freshwater lake sediments

Likewise, the average concentration of methane and carbon isotope ratios of methane during seasonal overturn show somewhat lower and higher values respectively ($\text{CH}_4 = 45.67\%$ and $\delta^{13}\text{C} = -59.7\%$, at an average depth of the water column of -2.30 m), as compared to those of seasonal stagnation ($\text{CH}_4 = 56.51\%$ and $\delta^{13}\text{C} = -64.40\%$, at an average depth of the water column of 3.03 m).

Bearing in mind that these average results above are not directly comparable as the average depth of the water column for all samples collected in these two seasons were slightly different (by 0.73 m). However, the higher $\delta^{13}\text{C}$ (CH_4) values observed during seasonal overturn (mixing of benthic and surface waters), as compared to the $\delta^{13}\text{C}$ (CH_4) values observed during stagnation, do not correspond to variations in the CH_4 concentration (CH_4 ; Fig. 4). The different average sampling depth cannot explain the seasonal differences in average CH_4 and $\delta^{13}\text{C}$ values, as the increase in the depth of the water column is accompanied by a higher gradient of increase in CH_4 and decrease in $\delta^{13}\text{C}$ (CH_4) values (Figs. 2 and 3) as compared to that resulting from the 0.73 m difference in the depth of the water column (see Discussion). From Figure 5, one may subdivide all samples into two groups: (1) at shallower samples, representing bubbles collected at shallow depths above the thermocline, and (2) those sampled from greater depths, below the thermocline.

DISCUSSION

POTENTIAL MECHANISMS OF METHANOGENESIS

Preliminary observations have shown a gradual decrease of $\delta^{13}\text{C}$ values in methane from sediments above the thermocline at about 4.5 m (Jędrysek *et al.*, 1994). Likewise, this study shows that an in-

crease in water depth down to 12 m correlated with an increase in concentration of bubble methane up to 90% and a decrease of $20 \pm 5\%$ in the methane $\delta^{13}\text{C}$ value. Moreover, methane collected during seasonal overturn in lakes (seasonal mixing of water due to thermally controlled variation water density) usually shows significant enrichment in the ^{13}C isotope, especially below the thermocline (i.e. usually below 4.5 m). Potential explanations for these trends include:

- temperature — thermodynamic isotope effects;
- light;
- isotopic variations in substrates (acetate and DIC from the water column and sediments) — this can result from pressure, photosynthetic and respiration activities, atmosphere-water-sediment exchange (also the role of the mineralogy of the sediment, oxidation or fractional decomposition of organic matter of different origin — usually kinetic isotope effects and precipitation of ^{13}C -depleted carbonates (e.g. Jędrysek and Sachanbinski, 1994; Aloisi *et al.*, 2002);
- oxidation or consumption of other methane/methane precursors in the shallow depth regions;
- methanogenic pathways — a higher contribution from acetic acid fermentation in the shallower parts of the lake, or a higher contribution from the CO_2/H_2 pathway in the deeper parts of the lake. These factors are discussed below.

TEMPERATURE

In the lakes examined, the typical temperatures below the thermocline varied from ~ 4 to $\sim 10^\circ\text{C}$, and above the thermocline the temperature varied from freezing to 27°C . Therefore, there can be expected, due to substantial differences in the bonding energy between the substrates and methane,

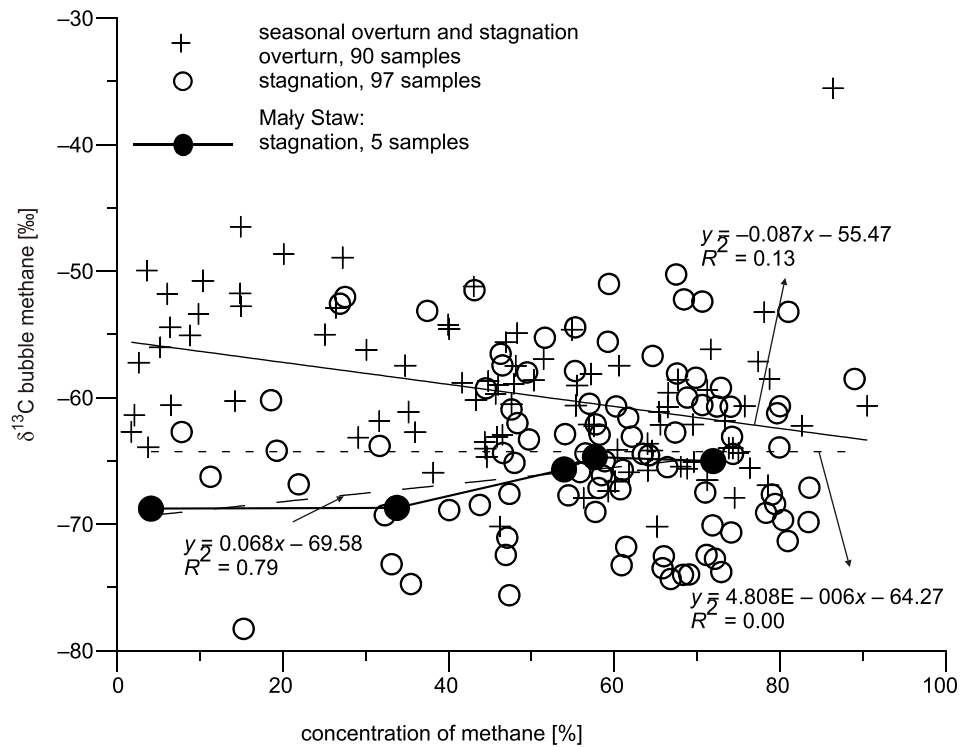


Fig. 4. Carbon isotope ratios and concentration of methane in bubble gases sampled at various depths of the overlying water column

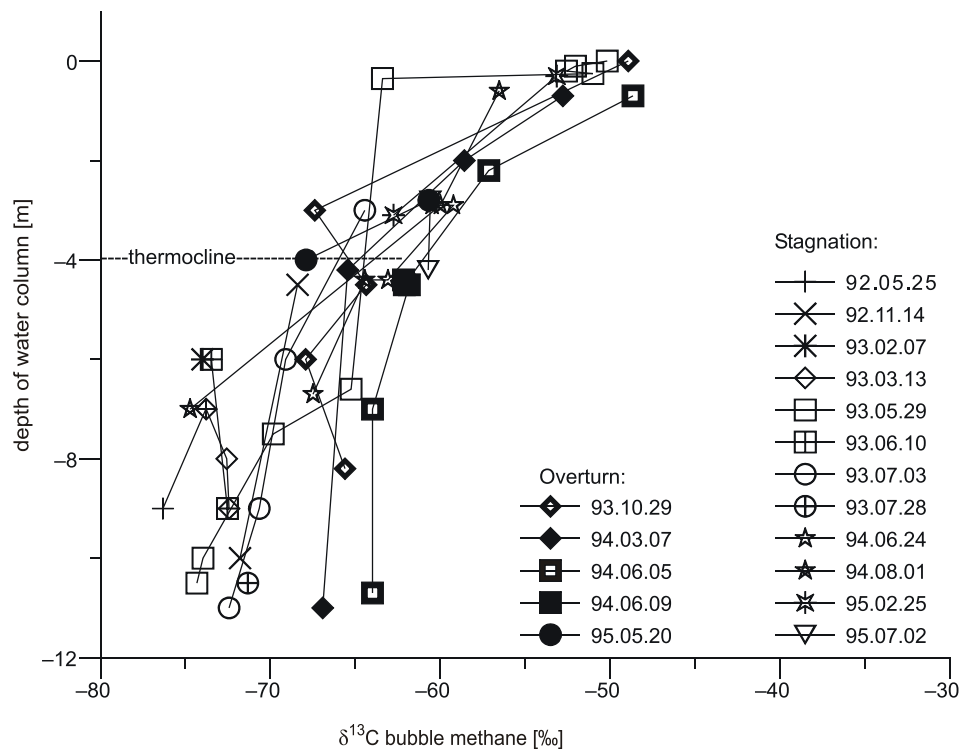


Fig. 5. Carbon isotope ratios in methane from bubble gases sampled at various depths of the overlying water column, and from Nowa Cerekiew freshwater lake sediments

During stagnation the thermocline was always at a depth of about 3.9 m; no thermocline was clearly noted during the seasonal overturn

a large thermodynamic isotope effect expressed as low $\delta^{13}\text{C}(\text{CH}_4)$ values at lower temperatures and consequently strong seasonal variations in the $\delta^{13}\text{C}$ value of methane. However, isotope ratios in methane sampled from the same depth over the thermocline during winter (e.g. 93.03.07 or 95.02.25), do not differ significantly from those in the corresponding spring or summer methane (Fig. 5). This is in agreement with earlier observations that the direct role of temperature, resulting in a thermodynamic isotope effect in the substrate-methane system, is negligible and does not control carbon isotope ratios in freshwater methane (Jędrysek, 1998, 1999). Most probably, this is due to the fact that methane is the product of complex microbial processes which compete for a limited budget of substrates of various origins and metabolize them in variable orders and by various mechanisms. Therefore, kinetic isotope effects probably overwhelm thermodynamic ones.

LIGHT

Given vertical differences in temperature and light penetration, controlling biological activity at various depths, one would expect to see some vertical variation in the concentration of DIC and the $\delta^{13}\text{C}$ of the DIC. These differences would also be expected to be reflected in the carbon isotope signature and the rate of methanogenesis. The largest relative vertical variation in temperature and biological activity, during summer, is concordant with the highest diurnal variation in the methane $\delta^{13}\text{C}$ value in summer (Jędrysek, 1997, 1999). Similarly, seasonal variations of stable hydrogen and carbon isotope ratios were larger in Poland (Jędrysek, 1997) than in North Carolina (Chanton and Martens, 1988) and that was larger than that in the Florida wetlands (Burke *et al.*, 1988). This is probably controlled by seasonal variations in the length of the daylight hours, showing increasing seasonal variations with increasing distance from the equator (Jędrysek, 1997, 1999).

Having dismissed the importance of temperature as a direct controlling factor on sediment methane $\delta^{13}\text{C}$ values, one must consider the effects of solar radiation (sunlight), either directly or indirectly, on methanogenesis in lake sediments (Jędrysek, 1994, 1995). The results from this study show a dramatic decrease in the methane $\delta^{13}\text{C}$ value with increasing depth of the overlying water column, especially during stagnation periods. The average methane $\delta^{13}\text{C}$ value is lower in late August than in early July and the length of the daylight hours decreases dramatically during the same period, supporting the thesis that light plays an important role in controlling the carbon isotope variations in sediment methane (Jędrysek, 1995, 1999). However, light itself cannot penetrate to the sediments, and methanogenesis does not result from the photolysis of organics. Thus, it can be speculated the role of light in methanogenesis and in the variation in methane $\delta^{13}\text{C}$ values must be an indirect one.

ISOTOPE VARIATIONS IN SUBSTRATES

MINERALOGY OF THE SEDIMENTS

The contents of clay minerals and zeolites (e.g. in the Nowa Cerekiew lake) in sediments usually increases with increasing distance from lake bank. The depth of the water column is usually proportional to that distance and these minerals show high sorption potentials for organic compounds. Several studies have shown that about 9 to 40% of the total acetate in sediment porewaters can be removed by equilibrium exchange adsorption to sediment solids (Shaw *et al.*, 1984; Sansone *et al.*, 1987; Michelson *et al.*, 1989). Therefore, the acetate pathway of methanogenesis may be limited and consequently more methane is formed from CO_2 resulting in lower $\delta^{13}\text{C}(\text{CH}_4)$ values at depth (Figs. 3 and 5, see also the section: Decomposition of organic matter during sinking in the water column). Moreover, it can be expected that ^{12}C -enriched acetate is preferentially adsorbed because of its lower vibrational energy. Likewise, in shallow water close to the lake bank, sediments are usually less enriched in methane precursors as they are depleted in organic matter and richer in silicate allochthonous material. If a large part, or nearly all, of carbon dioxide and acetate in the sediments is used as substrates for methanogenesis, the resulting methane will bear a ^{13}C -enriched isotope signature. Moreover, coarse-grained shallow-water sediments are less anaerobic, thus more favorable for oxidation of methane or methane precursors (see section on Oxidation).

RATE OF SEDIMENTATION

Another factor which can enhance the magnitude of the observed effect of the depth of the water column on the $\delta^{13}\text{C}$ value in CH_4 (Figs. 3 and 5), is that fresh organic matter always has more negative $\delta^{13}\text{C}$ values than older matter located at lower levels. The magnitude of this effect in soil and peat in the uppermost *ca.* 20 cm of peat is about 2 to 3‰ (e.g. Dudziak, 1993; Jędrysek and Skrzypek, 2004). Primary production in the zone below the thermocline, which is in general below the euphotic zone, is much less important, or even negligible. Thus, providing that primary production of organic matter is similar at the same horizon (depth) of the water column, the rate of sedimentation of organic carbon should be higher at greater depths, because (over the thermocline) the total primary production in the same lake is directly proportional to the thickness of the water column. Simply, more primary production may form in deep water (large volume) than in shallow water (small volume) in a lake. From this point of view, the water depth below the thermocline should not be considered due to its negligible primary production.

The rate of sedimentation relates to maturation and the age of organic matter in the sediment. It has been shown that resuspension in lake basins may result in a doubling of the total

sedimentation rate in the deepest region (Mieszczankin, 1997). Moreover, with one exception, the Góreckie lake, it was observed as a rule that, at greater water depths, sediments are far less compact and softer than in shallow water. Therefore, if the same depth intervals are considered in sediments (0 to about 25 cm in this study), methane generated from that interval of shallow-water sediment in many cases should correspond to older organic matter as a whole (more compact sediments) than would methane generated in deep-water sediments (less compact sediments). Likewise, sedimentary organic matter in shallower areas, in the euphotic zone, decomposes faster due to higher temperatures (during summer) and more abundant oxidants (O_2 , SO_4^{2-} , *etc.*). All of this can be supported by the observed gradient of the $\delta^{13}C$ depth pattern. The $\delta^{13}C$ pattern dramatically decreases or disappears below the thermocline, especially during seasonal overturn, and two separate ranges of methane $\delta^{13}C$ values are observed: the above-thermocline zone and the below-thermocline zone (Figs. 3 and 5).

PRESSURE AND TEMPERATURE

The generally higher concentration of methane at depth (Fig. 2) can be explained not only by increasing anaerobic conditions but also by a dramatic increase in the solubility of all the major gases except methane. Among these gases, only CO_2 is a precursor of methane. Given the increased solubility of carbon dioxide at greater water depths, one would expect that smaller amounts of gaseous carbon dioxide (bubbles) would be released from sediments in deeper water compared to sediments in shallower water. Besides pressure, the concentration of dissolved CO_2 in the water column depends on the temperature and pH of the water mass. The pH measured in the pore waters of the sediments was similar in all sampling stations and relatively constant (being about 6, regardless of the depth of the sampling stations). Therefore, it can be accepted that in the lakes studied the solubility of carbon dioxide is directly proportional to pressure and inversely proportional to temperature.

When in isotopic equilibrium, at the low temperatures found in lakes studied, carbon dioxide is depleted in ^{13}C compared to bicarbonate by about -8% (Deuser and Degens, 1967). Since any bubbles that escape would be expected to be depleted in ^{13}C , under higher hydrostatic pressure the bioavailable pool of carbon dioxide in deeper water should be larger and more ^{13}C -depleted when compared to shallow depths from where CO_2 bubbles escape faster (Jędrysek, 1997). Accordingly, an abundance of DIC (dissolved inorganic carbon, $CO_2/HCO_3^-/CO_3^{2-}$) at depth may keep the $\delta^{13}C$ of the carbon dioxide at a constant value and promote the CO_2/H_2 pathway of methanogenesis at greater depths. All of this would result in the lower methane $\delta^{13}C$ values observed in the sediments from deeper in the lakes (Figs. 3 and 5). However, the $\delta^{13}C$ gradient dramatically decreases or disappears below the thermocline, especially during seasonal overturn (Fig. 5). This precludes the role of pressure as the most important factor controlling the $\delta^{13}C$ in the bubble methane. Apparently this supports the role of temperature, because from other observations

it is known that the temperature in the sampled sediments was very stable below the thermocline (*ca.* from 4 to 6°C) and very variable above the thermocline (0.0 to 28°C). However, the winter $\delta^{13}C$ pattern has not shown any opposing vertical trends reflecting temperature i.e. lower temperatures did not result in higher $\delta^{13}C$ values of methane in shallow regions of the lakes (Fig. 5), as should be expected. Likewise, the role of temperature is not reflected in correlation with the $\delta^{13}C$ of the methane (Jędrysek, 1997, 1999). Therefore, other factors have to be considered, and the role of photosynthetic activity seems to be the most important.

PHOTOSYNTHESIS AND THE CO_2 ISOTOPE BUDGET

It can be accepted that, in most lakes studied, primary production is the dominant source of organic carbon and thus of methane precursors. Likewise, it can be accepted that all the dissolved CO_2 comprises part of the DIC which in turn is in isotopic equilibrium with that CO_2 and which is the exclusive source of CO_2 for the phytoplankton. Therefore, the carbon isotopic composition of that DIC seems to be crucial here.

The $\delta^{13}C(DIC)$ in surficial water sampled early afternoon, measured in the most frequently sampled Nowa Cerekiew lake, was -4.62% (at 9°C) and -4.42% (at 23°C), (Szynkiewicz and Jędrysek, in prep.). A significant decrease in the DIC $\delta^{13}C$ value with increasing depth of the water column in other lakes has been observed (e.g. max. -4.0% , surface to min. -9.5% , 17 m; Wachniew, 1994; Wachniew and Różański, 1997 or -12.6% , Ogrinc *et al.*, 2002), apparently due to increases in respiration and the decomposition of organic matter and decreases in photosynthesis with depth of the water column. While respiration produces carbon dioxide that is ^{13}C -depleted, photosynthesis tends to preferentially consume the ^{12}C in the water column. This process strongly influences $\delta^{13}C$ values in the DIC and methane formed in the uppermost part of the sediments shows diurnal variations of up to 15‰ (Jędrysek, 1995, 1999). In the deeper parts, where the role of assimilation decreases (less light, lower temperature), and the respiration/photosynthesis rate increases, phytoplankton assimilate then ^{13}C -depleted. Thus, when only some portion of phytoplankton does not migrate vertically within the water column, the entire phytoplankton in deeper parts of the lake would assimilate more ^{12}C and consequently become additionally enriched in the ^{12}C isotope, compared with those in the shallower waters of the lake. This difference is reflected in the $\delta^{13}C$ of the sediment organic matter and carbonates, which are 2 or 3‰ lower in deeper portions of the lakes (Jędrysek, 1997 and in prep.). It can be accepted that in lake systems, photosynthesis takes place only in the water column above the thermocline. This can explain the sudden decrease in the $\delta^{13}C$ depth gradient below the thermocline (Fig. 5, see chapter Rate of sedimentation). This $\delta^{13}C$ difference represents a potential tool for palaeobathymetric reconstructions (Jędrysek, 1997, 1999).

Moreover, in shallow water, CO_2 assimilation is very high but sediments, close to a lake bank, are usually less productive in CO_2 as they are depleted in organic matter and more rich in

silicate allochthonous material. If a large part of carbon dioxide in water column is assimilated, and if nearly all carbon dioxide in the sediments is used as a substrate for methanogenesis, the resulting organic matter (methane precursors) and methane will bear the ^{13}C -enriched isotope signature. Although the carbon dioxide $\delta^{13}\text{C}$ value would be increased as a result of the preferential utilization of ^{12}C during photosynthesis, the overall effect of photosynthesis appears to be negligible, and the $\delta^{13}\text{C}(\text{DIC})$ -depth effect is several times too small to be responsible for the observed $\delta^{13}\text{C}(\text{CH}_4)$ -depth effect. This is based on the observation that there were no differences in the relationship of methane $\delta^{13}\text{C}$ and depth observed between samples collected in the winter, when photosynthetic activity is absent due to the ice cover (causing darkness) and low temperature (max. 4°C), and samples collected in late spring or early summer, when photosynthetic activity above the thermocline is at its maximum (Fig. 5).

ATMOSPHERIC CO_2

The role of atmosphere-hydrosphere exchange in the isotope budget of dissolved inorganic carbon (DIC) cannot be discounted, especially for very shallow depths of the water column. The $\delta^{13}\text{C}$ value of atmospheric carbon dioxide ranges from approximately -7‰ in the early evening to approximately -13‰ in the period from midnight to early morning (Szaran, 1990). In a lake system there is a dynamic equilibrium between the DIC and the reservoir of atmospheric carbon dioxide. The highest rate of exchange of carbon dioxide from the lake surface to the atmosphere takes place at night, reflecting the diurnal variation in photosynthetic-respiration activity. As a result, one would expect that, during the summer months when the photosynthetic activity of the lake vegetation is high, the waters of the lake will absorb ^{13}C -enriched carbon dioxide from the atmosphere during the day and expel isotopically lighter carbon dioxide at night. The DIC, being in an isotopic equilibrium with atmospheric CO_2 , shows higher $\delta^{13}\text{C}$ values. When it is reduced to methane, or assimilated and then turned to methane, the shallow-water methane shows significant enrichment in ^{13}C (Figs. 3 and 5). The important role of photosynthetic activity and atmosphere-water carbon exchange can be supported by the high range of variation in $\delta^{13}\text{C}$ of shallow-water methane as compared to that in deep water (Fig. 3). However, this can be also explained by diurnal variations in temperature (higher temperature activates methanogenesis, also in a diurnal basis; Jędrysek, 1995, 1999) or wider local variations in Eh, when the sediments are more anoxic, proportionally more DIC is reduced and methane shows higher $\delta^{13}\text{C}$ values. An incubation experiment can probably help to explain this problem. Nevertheless, if the model of atmosphere-hydrosphere-sediments exchange of carbon is plausible, CO_2 diffusion isotope effects have to be also considered.

DIFFUSION OF CARBON DIOXIDE IN THE WATER COLUMN — POREWATER SYSTEM

Sorensen *et al.* (1981), Christensen (1984) and Michelson *et al.* (1989) made an implicit assumption that acetate diffusion within the natural environment is negligible, so that all the acetate produced within a given sediment stratum is im-

mediately consumed within that stratum. This cannot be accepted for gaseous CO_2 .

The above-mentioned mechanisms act in the same direction resulting in higher $\delta^{13}\text{C}(\text{CH}_4)$ values in the shallow regions of lakes. The temperature, DIC budget, photosynthetic activity, and respiration are all expected to dramatically decrease with increased depth of the water column. Thus, this requires the assumption that the carbon dioxide dissolved in porewaters will migrate rapidly into the overlying waters, leading to a dynamic equilibrium between the DIC of the porewater and that of the water column. Therefore, the diffusion of carbon dioxide in the sediments and/or the water column might also be partially responsible for the observed depth effect. A quantitative evaluation of isotope gradients produced by diffusional flow is complicated. Dudziak (1993, 1994) studied the $\delta^{13}\text{C}$ values of carbon in soil *versus* depth. The observed profiles of soil carbon dioxide concentration and $\delta^{13}\text{C}$ *versus* depth are non-linear, but a significantly negative correlation between these variables was noted in various soil types and over various depths.

One might argue that the role of isotopic exchange between isotopically lighter DIC and the heavier atmospheric CO_2 is not a plausible driving mechanism for the methane $\delta^{13}\text{C}$ depth pattern since the transport of carbon dioxide between the atmosphere and the site of methane production in the sediments is too slow. The question becomes: how slow is this transport of carbon dioxide in the water column and then diffusion to the sediments? One would expect that more extensive exchange would occur and that there would be more active photosynthetic activity, particularly from phytoplankton, at shallower depths (Wada and Yoshioka, 1995; Yoshioka *et al.*, 1994). Higher primary production at shallow depth consumes isotopically lighter CO_2 , leaving the residual CO_2 pool enriched in ^{13}C . When the concentration of carbon dioxide in the shallow water decreases and the $\delta^{13}\text{C}$ in the residual DIC increases, due to photosynthesis, the diffusion rate of carbon dioxide from the sediments increases. It can be expected that ^{12}C molecules diffuse out from the sediments faster, leaving ^{13}C -enriched CO_2 behind in the sediments, thus resulting in higher $\delta^{13}\text{C}$ values in methane formed at shallower depths. Moreover, it is obvious from this rule that, at greater depths of the lake where $p\text{CO}_2$ is higher, one should expect lower $\delta^{13}\text{C}$ values in CO_2 , and in CH_4 generated from that carbon dioxide.

OXIDATION

It was found that the major contribution of DIC (up to 78%) in lake sediment porewater can be derived from methanogenesis (Ogrinc *et al.*, 2002) and supersaturation with respect to carbonate minerals can be induced by microbial anaerobic oxidation of methane (e.g. Jędrysek, 1997; Aloisi *et al.*, 2002). Likewise, when oxidants such as sulfate (SO_4^{2-}) are present in sediments, acetate (a methane precursor) is consumed by sulfate-reducing organisms (e.g. Scholten *et al.*, 2002; Teske *et al.*, 2003). At the same time, biological oxidation of acetate is assumed to be a first-order process with respect to acetate concentration, and may result in substantial enrichment of heavy isotopes in the remaining acetic acid. Nevertheless, the potential syntrophic linkage between sulfate-reducing and methanogenic bacteria via acetate as a mechanism of $\delta^{13}\text{C}$ variations is

not clear (Miyajima and Wada, 1998). If this acetic acid is subsequently used as a substrate for methanogenesis, the resulting methane will also bear the signature of the ^{13}C enrichment. Likewise, oxidation of methane to carbon dioxide results in significant enrichment of ^{13}C in the reservoir of residual methane (Barker and Fritz, 1981; Coleman *et al.*, 1981; Venkiteswaran and Schiff, 2005), and can proceed in a wide range of temperatures (e.g. Valentine and Reeburgh, 2000; Sloisi *et al.*, 2002; Achouten *et al.*, 2003). If such oxidation occurs in the sedimentary environment, a decrease in methane concentration, and correlations between this concentration and the methane $\delta^{13}\text{C}$ values have to be expected; this is not the case in general (Fig. 4). Also, there are no observations of increased carbon dioxide concentrations that correspond to decreased methane concentrations in the same samples (Jędrysek, 1997). All of this contradicts an important role of oxidation in the DIC- CH_4 system in sediments.

However, an increasing $\delta^{13}\text{C}$ value with increasing depth can be observed in the Mały Staw lake (Fig. 3), or sometimes in Nowa Cerekiew lake (e.g. 93.06.10 and 93.10.29; Fig. 5) where deeper-seated methane was enriched in the heavy carbon isotope as compared with the respective shallow-water methane. These lakes were significantly polluted with SO_4^{2-} which is the main substrate for microbial oxidation of methane and methane precursors, and seasonal mixing was not over. Moreover, the increasing trend in the concentration of methane with increasing depth of the water column in the Mały Staw lake, is similar to that in other lakes (Fig. 2), and low concentrations of methane in that lake corresponds to low $\delta^{13}\text{C}$ values (Fig. 4). This might lead to the conclusion that in temperate lake environments, the oxidation of methane is in general not likely to be the controlling factor in the sediment methane concentration and in the $\delta^{13}\text{C}$ value. This can be supported by the fact that there are no regular patterns or correlations in the data on methane concentration and methane $\delta^{13}\text{C}$ values (Fig. 4), and carbon dioxide or/and methane concentration versus $\delta^{13}\text{C}(\text{CH}_4)$ values in all the lakes studied (Jędrysek, 1997).

During seasonal overturn, a large part of methane can be oxidised due to the supply of large amounts of sulphate, this being the substrate for the microbial oxidation of methane. It was observed that methane oxidation is distinctly seasonal, with the highest activity in late summer or early autumn (Jędrysek, 1997), when the turnover time of methane dissolved in the water column is usually shorter than half a day and about 74% (annual average) of dissolved methane is oxidised (Utsumi *et al.*, 1998). Therefore, during seasonal overturn, when the oxidation is extremely efficient, a light calcite-rich lamina may be formed. Consequently, in general, one pair of laminae should represent an annual cycle of sedimentation starting from the late spring to mid-summer (dark lamina — seasonal high primary production due to phytoplankton blooms, sedimentation and the subsequent formation of anoxic conditions at the bottom) and finishing in autumn to spring (light lamina — seasonal overturn resulting in oxidation of organic compounds and methane and rapid precipitation of calcite). Moreover, it can be expected that, at the end of summer, when, despite oxidation, methanogenesis is still very active, methanogenic removal of CO_2 from sediments promotes precipitation of calcite and leads to enrichment of the remaining DIC, and thus of methane, in

^{13}C . Both oxidation of methane (methane precursors) and additional removal of CO_2 , are consistent with the elevated $\delta^{13}\text{C}$ values in deep-water methane observed during autumn seasonal overturns (Figs. 3 and 5).

METHANOGENIC PATHWAYS — DECOMPOSITION OF ORGANIC MATTER DURING SINKING IN THE WATER COLUMN

It was observed that, in the spring, 65% of methane in lakes is produced due to acetate fermentation while, during autumn, 90% of methane results from CO_2 reduction (Lojen *et al.*, 1999), but the CO_2 -organic compounds- CH_4 system is very complex from a carbon isotope budget point of view (e.g. Hornibrook *et al.*, 1997, 2000). Simple, low molecular weight compounds such as nonstructural carbohydrates and proteinaceous materials are generally more easily degraded than complex polymeric compounds such as the lignin of woody and emergent aquatic plants (Moore, 1969; Wetzzel, 1975; Koyama *et al.*, 1979; Heal and Ineson, 1984; Koyama, 1990). Bell (1969) incubated flooded soil anaerobically and found that glucose and peptone were degraded to methane and carbon dioxide much more rapidly than cellulose, although the total volumes of methane and carbon dioxide eventually produced from these three substrates were roughly the same. Similarly, algal material decomposes to methane and carbon dioxide about 10 times more rapidly than lignocellulose (Benner *et al.*, 1984). The primary production of plankton in the lakes in this study can be relatively high and may vary from 50 to 1000 $\text{mg C}_{\text{ass}} \text{ per m}^2 \text{ per day}$ (where C_{ass} represents organic carbon assimilated due to photosynthesis). In the euphotic zone above the thermocline, almost all the newly produced and the dead organic matter may undergo decomposition during its descent (even several weeks) through the water column. In general, the pool of acetate in sediments is very limited and acetate concentration in sediments decreases within several days if acetate is consumed rapidly (Michelson *et al.*, 1989; Sugimoto and Wada, 1993). Due to low temperatures, the organic matter below the thermocline is apparently more recalcitrant. However, it is more decomposed (especially acetate precursors) during prolonged sinking, and the speed of sinking may slow down in the thermocline zone where colder water has a higher density and viscosity, and vertical thermal currents may occur. Likewise, the organic matter sediment over the thermocline is decomposed by another microbial consortium which can involve other (unknown to the author) pathways of decomposition of isotopically diverse specific group compounds. Anyway, it can be postulated that, in the deeper portions of the lakes, the organic matter that reaches the sediment has undergone more decomposition during the process of settling to the bottom. As a result, it is more refractory or recalcitrant than the material that accumulates in shallower water, with lower amounts of acetate precursors. Therefore, the nature of the organic materials in these deeper sediments and the colder temperatures may lead to less intense acetate fermentation, resulting in the observed relationship between methane $\delta^{13}\text{C}$ values and water column depth. This means that given a deep enough water column, much of the organic matter produced in the photic zone above the thermocline will eventually decompose. However, in shallow waters, the production exceeds the consumption (decomposi-

tion), resulting in the deposition of less decomposed organic matter in the sediments. This process may promote acetic acid fermentation and consequently increase the methane $\delta^{13}\text{C}$ value in the shallower parts of the lake. This can be supported by the variable (above and below the thermocline) gradient of the $\delta^{13}\text{C}$ depth-related pattern (Figs. 3 and 5).

CONCLUSIONS

1. The observed depth-related gradient of $\delta^{13}\text{C}$ values in freshwater bubble methane vary between -1.4 to -2.3‰ per -1 m. The $\delta^{13}\text{C}$ pattern dramatically decreases or disappears below the thermocline, especially during seasonal overturn.

2. The magnitude of variations in the methane $\delta^{13}\text{C}$ values at different depths, is similar or larger than that reported in the literature on seasonal, spatial and diurnal variations in wetlands and lakes. Thus, such historical data may need to be reconsidered for its implications regarding the isotopic mass balance of this greenhouse gas. Likewise, some conclusions on methanogenesis, proposed by other authors and based on sampling of methane from sediments, perhaps need to be revised.

3. The depth of the water column pattern is probably due to combined factors resulting in kinetic isotope effects, acting in the same direction:

a. Decomposition of easily-degraded organic matter as it settles through the water column. The organic matter in deeper water is more recalcitrant than in shallow water, apparently leading

to more intense acetate fermentation in shallower portions of the lake and resulting in higher $\delta^{13}\text{C}$ values of the methane;

b. More active carbon dioxide exchange among the porewaters, water column, and atmosphere at shallow depths results in higher $\delta^{13}\text{C}(\text{CH}_4)$ values due to quantitative and qualitative differences in the methane precursors at different depths;

c. Limited diffusion of isotopically depleted carbon-bearing gases from deeper depths may result in higher $\delta^{13}\text{C}(\text{CH}_4)$ values.

4. Poor summer-winter seasonal variation of isotope ratios in methane above the thermocline together with a negative depth-isotope ratio correlation prove that the lake system is in dynamic equilibrium. Below the thermocline, temporal $\delta^{13}\text{C}(\text{CH}_4)$ variations are largely dependant on seasonal mixing of water. Further studies will be needed on this point.

5. Some oxidation of methane and especially its precursors may occur during seasonal overturn of benthic and surface waters. This effect is marked in the deeper parts of lakes which are anaerobic during stagnation periods.

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