Environment Protection Engineering

Vol. 37 2011 No. 3

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METHANE EMISSION FROM THE NIELISZ RESERVOIR

The results of measurements conducted in 2010 of methane emission from the surface of the Nielisz Reservoir on the River Wieprz have been presented. This is a lowland reservoir located in the forested areas of the South-Eastern Poland (The Central Roztocze). The content and isotopic composition of methane in the upper (1 cm) layer of the bottom sediment have also been examined. The methane flux ranged from 15.98 to 383.85 $\text{mmol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$, while concentrations of the gas in pore water ranged from 133.33 to 1265.45 $\mu\text{mol}\cdot\text{dm}^{-3}$, and the value of $\delta^{13}\text{C-CH}_4$ was within the range –8.05 and –56.22‰. The fractionation coefficients ($\alpha_\text{C}\text{CH}_4\text{-CO}_2$) between methane and $\sum\text{CO}_2$ equalled approximately 1.05. The results of investigations suggest that methane in the sediment of the Nielisz Reservoir is produced by acetate fermentation. Levels of emission of this gas to the atmosphere can be compared with the values reported for large tropical reservoirs.

1. INTRODUCTION

The global warming of recent years has stimulated research on greenhouse gases emission to the atmosphere from both aquatic and terrestrial environments [1–6]. The main causal agents underpinning enhancement of the greenhouse effect are considered to be CO_2 and CH_4 as emitted excessively by human civilisation. Although methane remains in the air much more briefly than CO_2, its potential for causing global warming while it remains is 23 times higher [7]. Over the last 300 years, the atmospheric concentration of methane has more than doubled [8]. It has been estimated that about 7% of the carbon gases emitted from anthropogenic sources originate in dam reservoirs [9], while over 40% of methane emissions to the atmosphere derive from natural wetlands or croplands kept periodically underwater [10].

Emission of greenhouse gases from dam reservoirs reflects decomposition of flooded terrestrial biomass, biomass produced in the reservoir and organic matter in various states of decomposition introduced into the body of water via tributaries. Bio-

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genic CH_4 is formed by the two main processes of acetate fermentation and CO_2 reduction. CO_2 and CH_4 are produced by hydrolytic decomposition:

$$CH_3COOH \rightarrow CO_2 + CH_4$$

Acetate can also be oxidized to CO_2 and H_2O, the former then being reduced metabolically to CH_4, wherein hydrogen serves as the source of electrons [9]:

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$$

The application of stable carbon isotope analysis to CH_4 ($\delta^{13}C_{CH_4}$) and also to co-existing CO_2 ($\delta^{13}C_{CO_2}$) may yield a quite precise determination of the mechanism underpinning methane formation in sediments [11–14]. Thus the main purpose of this study was to determine the flow of methane into the atmosphere from the Nielisz Reservoir, as well as and the mechanism underpinning its formation in sediments.

2. METHODS AND MATERIALS

Study site description. The Nielisz Reservoir was put into operation in 2008. It is located in Eastern Poland (Lubelskie Voivodship, Zamość District, Nielisz Community), along the middle reaches of the Wieprz River at its confluence with the Por River.

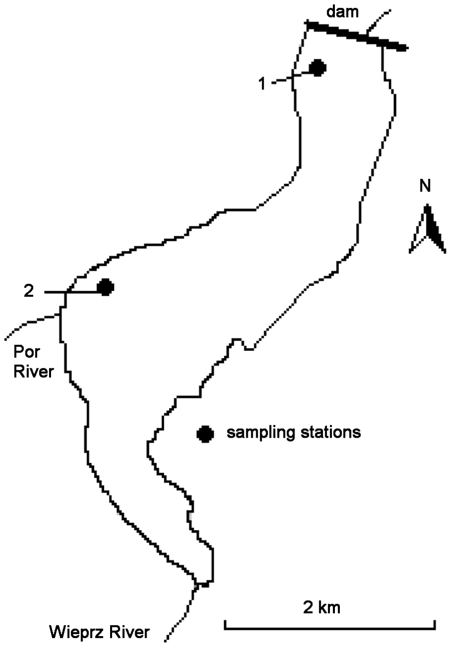

Fig. 1. Locations of the sampling stations in the Nielisz Reservoir; morphometric properties of the reservoir: volume – 19.5 mln m^3, area – 10.6 km^2, mean depth – 2 m, maximum depth – 4 m

Surrounded by coniferous forests, the reservoir has at its dam end a hydroelectric power plant of the capacity of 362 kW. Basic tasks of this body of water include: protection against flooding, reduced fluctuations in water level during the breeding season for birds, energy supply, recreation and amateur fishing. The locations of the sampling stations for the reservoir studied are shown in Fig. 1. Station 1 was located near the dam, while station 2 was situated near the place where the Por River flows into the Nielisz Reservoir.

Sampling and methods. Gas samples were taken from the studied reservoir in June, July and September 2010 (Table 1). The CO_2 and CH_4 fluxes were measured using a static chamber method, specifically a stainless steel chamber (of 0.3 m × 0.3 m × 0.16 m) equipped with a dry battery-driven fan and a small vent stopped by a silicon septum for sampling. Five gas samples from the chamber air headspace were withdrawn manually into gastight syringes 0, 10, 20, 30 and 40 min after deployment. All samples were transported to the laboratory and analysed for gas concentrations within 4 h. Gas fluxes were calculated from a linear regression of time dependences of gas concentration within the chamber, and expressed in $\mu mol \cdot m^{-2} \cdot d^{-1}$. Positive changes indicated emissions of gas from the reservoir.

Simultaneously with the methane emission study, sediment cores were taken from the stations using a gravity sediment corer (by KC Kajak, Denmark). Sampled cores together with overlying water were transported to the laboratory immediately.

Although sediment cores are normally processed for sediment gases in helium filled glove bags, the failure to measure sediment nitrogen ensured that cores were processed in the open within a few hours of collection. Pore water from the top 1 cm layer of sediment was recovered to gastight glass vials, using a modified pore water squeezer [15]. Immediately after collection, the samples of water in vials were acidified using 6 M HCl (final concentration ca. 50 mM) to quantitatively convert all carbonate anions into CO_2 [16]. The gas concentrations in the overlying and pore water were analyzed using the headspace equilibration technique. Gases were extracted from the water in glass gastight vials, a known volume of water being replaced with helium. Water was equilibrated in the vials with added helium by means of 5 min of vigorous shaking. The gas phase was immediately analyzed for the concentrations and isotopic composition of CH_4 and CO_2.

The CH_4 and CO_2 concentrations in gas samples were analyzed using a Pye Unicam gas chromatograph (model PU-4410/19) equipped with a flame ionization detector (FID) and a stainless steel column packed with a Haye Sep Q, 80/100 Mesh, 6 ft long and of 2 mm ID. The GC was also equipped with a methanizer to detect low levels of carbon dioxide. The methanizer is packed with a nickel catalyst powder and heated to 380 °C. When the column effluent mixes with the FID hydrogen supply and passes through the methanizer, CO_2 is converted to CH_4. The carrier gas was helium at the flow rate of 30 cm^3/min. The carbon isotopic compositions of CH_4 and CO_2 were determined with an IRMS DELTA^{Plus} Finnigan on line with GC/CIII.

Sediment subsamples were dried and further measured for loss on ignition (LOI) at 550 °C for 4 h. The contents of organic total carbon and total nitrogen were measured using an elemental analyser (Flask 1112, ThermoQuest). The nitrogen ($\delta\,^{15}$N) and carbon ($\delta\,^{13}$C) isotopic compositions were detected using an IRMS DELTA^{Plus} Finnigan coupled with the elemental analyser. Total organic carbon and $\delta\,^{13}$C was measured following the removal of inorganic carbon by contact with the vapour of HCl in a desiccator [17].

Stable carbon and nitrogen isotopic compositions were reported in standard δ notation (δ^{13}C, δ^{15}N) expressed as "per mil": δR (‰) = $(R_a/R_{b(sample)}/\ R_a/R_{b(standard)} - 1] \cdot 10^3$, where R_a/R_b are the $^{13}C/^{12}C$ or $^{15}N/^{14}N$ ratios relative to the PDB and air standards, respectively.

The carbon isotope separation between CH_4 and ΣCO_2 was expressed in δ notation as the fractionation factor ($\alpha_C CH_4$-CO_2): $\alpha = \delta^{13}C_{CO_2} + 1000/\delta^{13}C_{CH_4} + 1000$ [14].

3. RESULTS AND DISCUSSION

Selected parameters characteristic of physical and chemical properties of water and atmospheric air are as shown in Table 1.

Table 1

Main features of air and water

Station	Sampling date	Temperature of air [°C]	Temperature of water [°C]	Oxygen concentration [mg·dm^{-3}]	pH
1	17.06.2010	23	22.5	5.80	8.51
	13.07.2010	29	25.2	9.17	8.93
	21.09.2010	13	15.1	8.87	8.09
2	17.06.2010	22	20.2	7.92	8.46
	13.07.2010	29	26.7	8.21	8.55
	21.09.2010	15	13.5	9.80	8.36

Figure 2 shows time dependences of methane concentration in the static chamber during the research period at the two sampling stations. The largest difference between the initial methane concentration and that recorded in the 40th minute at station 1 was only 7.2 μmol dm^{-3}, while the highest CH_4 concentration was 8.2 μmol dm^{-3}.

A significantly larger amount of methane in air samples collected from the static chamber was observed at sampling station 2 (except in July 2010). In June and September, the differences between the methane concentrations at the beginning and end of the experiment were of ca. 72 and 49 μmol·dm^{-3}, respectively. The highest concentration was 91 μmol·dm^{-3}.

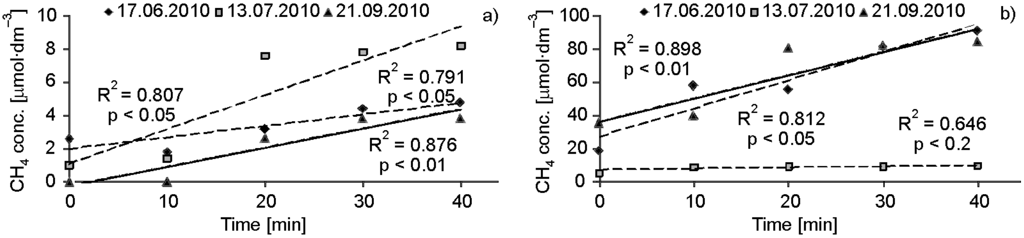

Fig. 2. Time dependences of concentrations of methane in the chamber: a) station 1, b) station 2

In line with regression equations, the change in methane concentration at the time determined the rate of emission of this gas to the atmosphere (Fig. 3). The lowest flow of methane at the water–atmosphere interface was of 15.98 mmol·m^{-2}·d^{-1}, while the highest was of almost 384 mmol·m^{-2}·d^{-1}. In June and September, the methane emissions at station 2 were respectively about 24 and about 12 times higher than at station 1. The exception was in July when the methane flow into the atmosphere was slightly more than twice as high at station 1, but did not exceed the value of 47 mmol·m^{-2}·d^{-1}.

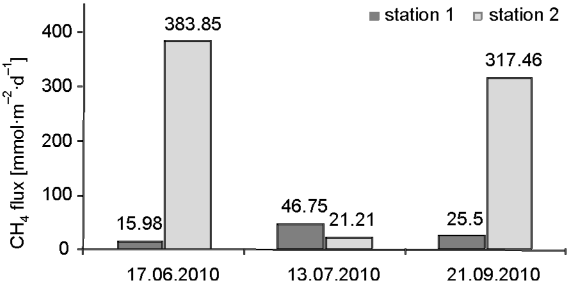

Fig. 3. Fluxes of CH_4 at the water–air interface in the studied reservoir

The average emission of methane from reservoirs of the temperate zone has been estimated to range from 0.6 to 5 mmol·m^{-2}·d^{-1} (1.25 mmol·m^{-2}·d^{-1} on average), while the corresponding figures for tropical reservoirs range from 1.25 to 93.75 mmol·m^{-2}·d^{-1} (18.75 mmol·m^{-2}·d^{-1} on average) [9]. It was, however, found that the methane emission from a tropical reservoir was slightly above 237 mmol·m^{-2}·d^{-1} [18]. As can be seen, the determined flow rates of methane for the Nielisz Reservoir are very high, and comparable with (or even in excess of) emissions from tropical reservoirs. However, it should be noted that the reservoir is relatively "young", with flooded areas of land capable of providing large amounts of labile organic matter and stimulating methanogenesis. Immediately after the flooding of a reservoir area there is a large emission of greenhouse gases, which eventually decreases slightly and then remains relatively constant throughout the life of the waterbody. For example, in the case of Arctic reservoirs, the maximum emission of greenhouse gases occurs from 3 to 5 years after water retention in the reservoir [19]. A positive correlation between temperature and methanogenesis is well documented (cf. e.g. [20, 21]), thus it is surprising that in September (when water and air temperatures were lowest) so high level of methane emissions at station 2 was recorded. Certainly, further research will verify whether the phenomenon in question was a short-lived one or not.

Table 2

Results of analysis of CH_4 and CO_2 in pore water,
as well as of C and N analysis in sediment of The Nielisz Reservoir

Station	Sampling date	Gas concentration [μmol·dm^{-3}]		Isotope ratio			Data of bulk sediment		
		CH_4	$\sum CO_2$	$\delta^{13}C_{CH4}$ [‰]	$\delta^{13}C_{CO2}$ [‰]	$\alpha_C CH_4$-CO_2	$\delta^{13}C$ [‰]	$\delta^{15}N$ [‰]	LOI [%]
1	17.06.2010	1172.73	3066.67	–56.62	–9.90	1.049	–18.60	3.39	8.04
	13.07.2010	1047.27	1233.33	–57.35	–10.29	1.050	–23.54	3.48	1.37
	21.09.2010	1265.45	1973.33	–56.22	–9.41	1.050	–19.98	4.28	6.32
2	17.06.2010	133.33	2133.33	–58.05	–12.27	1.049	–26.53	2.27	13.02
	13.07.2010	300.00	2822.33	–57.03	–11.11	1.049	–25.94	0.39	5.40
	21.09.2010	273.33	2493.33	–56.95	–9.90	1.050	–26.12	1.98	4.29

Methane concentrations in sediment pore water ranged from 133.33 to 1265.45 μmol·dm^{-3} (Table 2), and values about threefold higher were recorded at station 1. Methane concentration in the sediment pore water only correlated very poorly with the content of organic matter and total organic carbon in the surface (0–1 cm) layer of sediment (Figs. 4a, b). A strong dependence of $\delta^{15}N$ on $\delta^{13}C$ in bottom sediment was shown (Figs. 4c, d).

Studies of the isotopic composition of carbon and nitrogen in sediments enable determination of the origin of organic matter (allochtonous and autochthonous matter) deposited in bottom sediments [17, 22]. Depletion of isotope ^{12}C in organic carbon and higher values of $\delta^{15}N$ are characterized by an autochthonous origin of matter [23–25]. Autochthonous organic matter is more easily degradable than the allochtonous one, and it contributes to the formation of anoxic conditions and processes entailing methanogenesis. It is also known that algae decompose to methane and carbon dioxide tenfold more rapidly than lignocellulose does [26]. Figures 4c, d show clearly that the concentration of methane in pore water increases with $\delta^{15}N$ and $\delta^{13}C$ values. Based on these results it may be suggested that the process of methanogenesis is not dependent on the quantity of organic matter but rather on the origin of organic matter in sediments. Autochthonous matter is a better substrate for the methanogenesis than the matter of terrigenous origin. It remains in contrast with the results of Murase and Sugimoto [12] who argue that the amount of deposited organic matter is the dominant factor of methanogenesis in sediments.

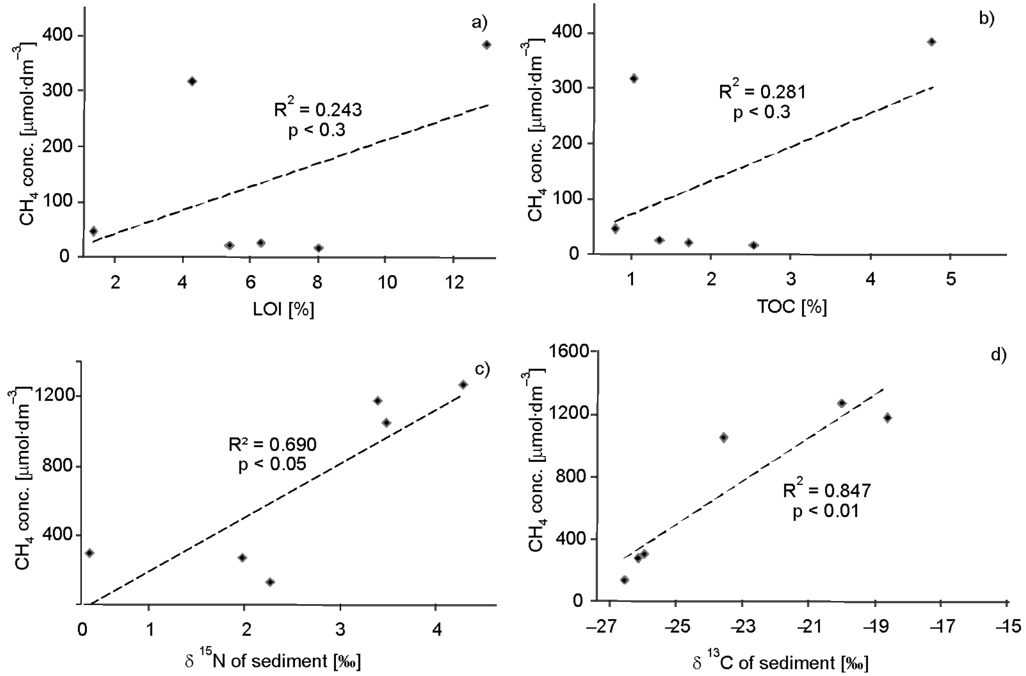

Fig. 4. Dependences of methane concentration on a) loss on ignition, b) total organic carbon content in sediment, c) δ^{15} N value for sediment samples, d) δ^{13} C value for sediment samples

The dependence shown in Fig. 4d can also be explained based on preference for the lighter isotope of carbon among methanotrophic bacteria in the process [14]. This is how increased production of methane will tend to cause depletion of the substrate, with ^{12}C and thus the δ^{13}C value being increased in the sediments.

The values of $\delta^{13}C_{CH_4}$ varied within the range from –58.05‰ to –56.22‰, while the values of $\delta^{13}C_{CO_2}$ changed from –12.27‰ to –9.41‰ (Table 2). The resulting values of $\delta^{13}C_{CH_4}$ are characteristic of freshwater reservoirs [27–29]. Biogenic CH_4 is mainly formed by the acetate fermentation and CO_2 reduction processes. The first mechanism is more common in (sulphate-poor) freshwater environments in which organic matter is readily available [14]. Methane produced by acetate fermentation has a δ^{13}C value within the range from –65‰ to –30‰, while methane formed by CO_2 reduction has δ^{13} values between –110‰ and –60‰ [30].

Figure 5 shows a positive correlation between δ^{13}C-CH_4 values and methane concentration, as well as between δ^{13}C-CH_4 and $\delta^{13}C_{CO_2}$ values. Knowledge of the δ^{13}C carbon dioxide which coexists with methane is helpful in identifying sources of CH_4.

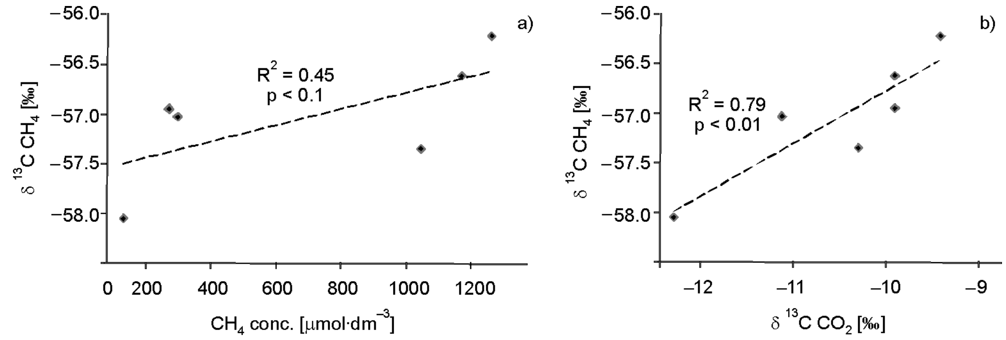

Fig. 5. Dependences of δ^{13} C_{CH4} on methane content (a)
and δ^{13} C_{CO_2} (b) in porewater of the Nielisz Reservoir

Knowing the coefficient of isotopic fractionation ($\alpha_C CH_4$-CO_2), a methanogenesis mechanism can be specified. In marine environments, where methane is usually formed through the reduction of CO_2, $\alpha_C CH_4$-CO_2 values vary in the range 0.05 to 1.1. However, in freshwater ecosystems, where fermentation is dominated by methyl fermentation, the values of $\alpha_C CH_4$-CO_2 range from 1.04 to 1.055 [14]. The $\alpha_C CH_4$-CO_2 values were either 1049 or 1050 for the Nielisz Reservoir. Based on both the δ ^{13}C-CH_4 value and that of the coefficient $\alpha_C CH_4$-CO_2, it can be seen that methane in the reservoir in question is generated from acetate fermentation.

4. SUMMARY

- Methane flows at the water–atmosphere interface were within the range of 15.98–384 mmol·m^{-2}·d^{-1}, and are thus comparable with those found to be typical of tropical reservoirs.
- Concentrations of methane in the sediment pore water ranged from 133.33 to 1265.45 μmol·dm^{-3} and correlated positively with the δ ^{15}N and δ ^{13}C values. It was concluded that the autochthonous organic matter is a better substrate for the methanogenesis than the matter of terrigenous origin.
- δ $^{13}C_{CH_4}$ values reached levels typical of freshwater reservoirs and varied from –58.05‰ to –56.22. Both δ $^{13}C_{CH_4}$ values and $\alpha_C CH_4$-CO_2 coefficient values (~1.05) confirm that methane in the Nielisz Reservoir is formed by acetate fermentation.

ACKNOWLEDGEMENTS

The study was supported by the Polish Ministry of Science, via grant No. N N305 077836.

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