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RELEASE OF GASES FROM BOTTOM SEDIMENT OF THE RZESZÓW RESERVOIR, POLAND

Spatial and seasonal variations in gases released from the bottom sediment of shallow, eutrophic reservoir were measured using *in situ* chambers. The major gas released was methane, 40–88% vol. Nitrogen ranged between 10–30% vol. Carbon dioxide did not reach the value higher than 3.4% vol. The rate of gas release tended to decrease at the lower stations of the reservoir. The fluxes of methane, nitrogen and carbon dioxide were closely correlated. In autumn, when the temperature of water decreased, the gas release rate was generally lower.

1. INTRODUCTION

Biogeochemical processes of organic matter decomposition are the main sources of gases released from bottom sediment. The production of methane in aquatic ecosystems was reviewed by numerous authors [1]–[4]. Another biogeochemically important gas is carbon dioxide. As it is greenhouse gas, it has become an important subject in climate change studies. Systematic studies on the chemistry and flux of CO₂ are rather seldom and deal with estuarine and coastal waters [5]–[7]. Most biogeochemical studies of aquatic ecosystems have been concentrated on nutrients. The ammonium released through organic matter decomposition becomes available for nitrification followed by denitrification. The recognition of the gaseous products resulting from these processes is important because of the removal of fixed nitrogen from aquatic ecosystems. Numerous studies, especially on denitrification, have dealt with reservoir sediment [8]–[13]. In the bottom deposits of aquatic ecosystems, many environmental factors such as temperature, organic matter concentration and other influence the gas release rates. That is why revealing these factors and determining the rate and composition of outgoing gases are of significant interest for limnologists.

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The aim of this study was to report spatial and seasonal variations in the gas release data from the bottom sediment of the Rzeszów reservoir. Fluxes of the gases as well as the coefficients of correlation between evaluated gases were calculated.

2. STUDY SITES AND METHODS

The Rzeszów reservoir is a small, shallow man-made lake located on the Wisłok River in the immediate vicinity of the Rzeszów city. It was constructed in 1973. Its retention time was 21 days at the minimum river flow ($Q_{\min} = 1.34 \text{ m}^3 \text{ s}^{-1}$) and 2 days at $Q_{\text{mean}} = 12.4 \text{ m}^3 \text{ s}^{-1}$. Originally the reservoir had an average depth of $\sim 1.5 \text{ m}$ (maximum depth of 6 m), area of 1.18 km^2 and volume of $1.8 \cdot 10^6 \text{ m}^3$. After twenty years of exploitation, water depth decreased considerably, and a fast growth of aquatic plants started on the previously open surface water. Consequently, the reservoir has mostly silted up [14]. As a result of excessive silting, the total volume of the reservoir decreased by $\sim 30\%$ (to $1.2 \cdot 10^6 \text{ m}^3$) after 9 years and by $\sim 60\%$ (to $\sim 0.5 \cdot 10^6 \text{ m}^3$) after the next 5 years. In the 8 years that followed, further filling up of the reservoir and its gradual transformation into land took place [8]. The first dredging began in 1985 and then continued in 1986. However, it did not bring expected results. The rubble input was larger than the amount of the dredged material. In 1995, the reconstruction of the reservoir and its dredging started anew. The volume of the modernized reservoir (in 1995) was slightly less than $1.0 \cdot 10^6 \text{ m}^3$. After next seven years from 1996 to 2002 the reservoir was suffered its fate without any preservation or reclamation. The reservoir watershed ($\sim 2050 \text{ km}^2$) is an area of high economic activity both industrial and agricultural.

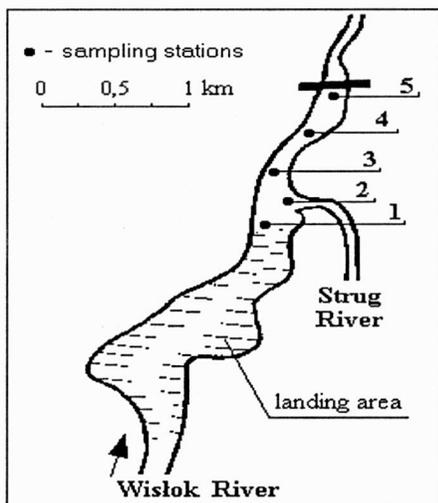


Fig. 1. Sampling stations

To evaluate the composition of released gases and the rates of their release from bottom sediment the reservoir was investigated from spring to autumn over the period

of two following years. The observations were carried out in five series at sites located on the reservoir (figure 1) with a water depth from 0.5 m to 1.0 m.

The gas bubbles outgoing from the sediment were trapped and analysed. The metal chamber for collecting gases was used [15]. It was installed by means of a special anchor pipe. The chamber enclosed 21.5 dm³ of water and had a surface area of 0.073 m². After the system was closed and filled with water the chamber was left in place for the time intervals measured. Exposure time varied from several hours to a few days, depending on the rate of gas release and oxygen consumption. Before the gases were sampled, the total volume of the accumulated gases in the burette was recorded. Gas samples were collected with Hamilton's gas-tight syringes and were analysed using a Philips gas chromatograph (model PU-4410/19) equipped with a thermal conductivity detector (TCD) and two glass columns: one packed with a molecular sieve, 5 A, to separate nitrogen and oxygen, and the other packed with Porapak Q to separate nitrogen, methane, and carbon dioxide [15].

3. RESULTS AND DISCUSSION

The rates of gas release (CH₄, CO₂, N₂ and O₂) were measured by gas chromatographic headspace analysis with time under *in situ* temperature conditions. The volume composition of the gases released from the bottom sediment of the Rzeszów reservoir is shown in table 1.

Table 1

Mean volume composition of gases

Series/station	O ₂ (vol. %)	N ₂ (vol. %)	CH ₄ (vol. %)	CO ₂ (vol. %)
Series I				
Stat. 1	3.6	23.5	70.6	2.3
Stat. 2	4.1	25.8	68.7	2.5
Stat. 3	2.9	20.7	74.0	1.4
Stat. 4	3.0	30.2	65.3	1.5
Stat. 5	3.5	56.5	39.2	0.8
Series II				
Stat. 1	2.2	14.5	80.0	3.4
Stat. 2	6.4	34.9	57.2	1.5
Stat. 3	1.8	20.2	76.1	1.9
Stat. 4	3.5	33.1	62.2	1.2
Stat. 5	4.6	52.6	42.3	0.6
Series III				
Stat. 1	3.09	19	76	2.14
Stat. 2	1.56	13	84	1.85
Series IV				
Stat. 1	0.6	17	81	1.71
Stat. 2	0.6	12	84	3.04
Series V				
Stat. 1	1.0	12	83	3.26
Stat. 2	0.2	10	88	2.30

The released gas was mostly methane. Its share made up 88% of the total gas volume, but occasionally nitrogen was abundant as well (up to 56%). The composition of the gases released from the bottom sediment was similar to that of the gases in Lake Beloe or Lake B. Plenski [16]. Similarly to these lakes, in our reservoir there were no favourable conditions for carbon dioxide formation. The volume of this gas was usually less than a few per cent. The presence of oxygen in the gas headspace was a special feature. The oxygen content in the total volume of the gas did not exceed 6.6%, and was usually much lower. According to the available hypotheses, the oxygen finds two ways into gas bubbling: one from the water and the other from the upper layer of the sediment. In our experiment, a small content of the oxygen in a newly formed gas headspace was due to a physical stripping of the dissolved oxygen. Because the experiment was carried out in a dark chamber, oxygen production from the upper layer of the sediment due to benthic algal activity was excluded. This explains that the oxygen in the gas headspace comes not from the sediment, but from the water. This is in disagreement with the results reported by MATRINOVA [16], but agrees with her further observations of anaerobic conditions of near-bottom water layers [17]. The acceptance of that statement (exclusion of oxygen as the gas released from the sediment) allowed us to analyse the spatial and seasonal effects for methane, nitrogen and carbon dioxide. The rates of the gas release from the bottom of the Rzeszów reservoir calculated from the volumes of the gases released over the time of the experiment are shown in table 2.

Table 2

The rates of gas release from the bottom sediments of the Rzeszów reservoir

Series/station	O ₂ (cm ³ m ⁻² h ⁻¹)	N ₂ (cm ³ m ⁻² h ⁻¹)	CH ₄ (cm ³ m ⁻² h ⁻¹)	CO ₂ (cm ³ m ⁻² h ⁻¹)
Series I				
Stat. 1	4.68	28.9	89	3.09
Stat. 2	2.97	17.5	44	2.03
Stat. 3	2.48	16.0	60	0.83
Stat. 4	1.48	13.6	34	0.75
Stat. 5	0.59	8.39	7.1	0.11
Series II				
Stat. 1	6.60	37.0	202	7.95
Stat. 2	5.54	31.7	55	1.32
Stat. 3	1.25	12.2	49	1.27
Stat. 4	1.20	11.5	22	0.43
Stat. 5	1.06	8.78	7.2	0.07
Series III				
Stat. 1	0.85	5.35	21	0.71
Stat. 2	0.66	5.25	36	0.81
Series IV				
Stat. 1	0.34	10.1	60	1.77
Stat. 2	0.42	7.47	56	2.17
Series V				
Stat. 1	2.30	29.2	173	7.34
Stat. 2	0.18	9.62	87	2.65

The spatial differences in the rates of gas release between 5 stations for II series are shown in figure 2.

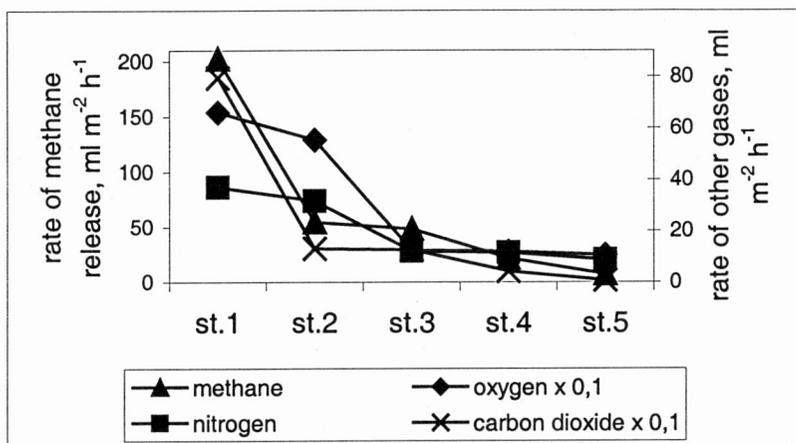


Fig. 2. Spatial differences in gas release between stations

For the gases analysed a decrease in the release rate downwards the reservoir was observed. This phenomenon can be explained by the differences in the structure of the sediment. In the upper part of the reservoir, the abundance of fresh sediment was conducive to gas formation and release. The upper sediment layer swell as a result of gas expansion and gas bubbling and sediment flotation was observed. The lower stations were characterised by the sediment of compact structure. Seasonal differences in the average rates of gas release are shown in figure 3. Seasonal variability in gas release rate proves that temperature significantly affected biological reactions and was the principal determinant of carbon and nitrogen mineralization rates.

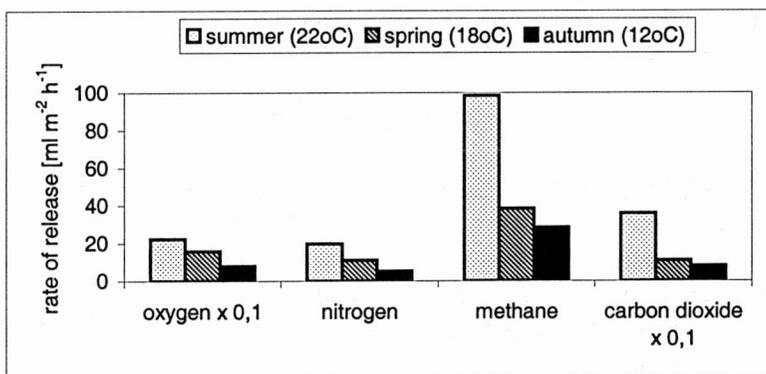


Fig. 3. Seasonal differences in average rates of gas release in the Rzeszów reservoir

When interpreting the data on the gas composition of the sediment it was assumed that sediment was supersaturated with methane and nitrogen. When methane-rich bubbles are released from sediment they strip the sediment of other dissolved gases. The content of carbon dioxide was below saturation, which is in agreement with MARTINOVA'S [18] observations.

High correlations between the gases tested were observed (table 3). A high positive correlation between methane and carbon dioxide in spite of the low concentration of carbon dioxide indicates that there is no reduction of carbon dioxide to methane. A positive correlation between oxygen and nitrogen confirmed the origin of the former.

Table 3

Correlation coefficients for the gases evaluated	
$n = 16$	R
O ₂ -N ₂	0.93
O ₂ -CH ₄	0.58
O ₂ -CO ₂	0.54
N ₂ -CH ₄	0.76
N ₂ -CO ₂	0.73
CH ₄ -CO ₂	0.99

The abundance of nitrogen in the gas released from the sediment results from denitrification. There are two sources of nitrate in the bottom sediment: diffusion from water and nitrification in sediments. Anaerobic conditions in the upper layer of the sediment and accessibility of organic matter caused that in the Rzeszów reservoir (similar to the lakes investigated by MARTINOVA [17]) the main source of nitrate was nitrification in the sediment. Gas solubility in water is an important factor affecting bubble composition. It should be stressed that the solubility of carbon dioxide is higher by an order of magnitude than that of nitrogen and methane. Hence the solubility of methane and nitrogen cannot be the main reason for the differences in the gas composition.

4. CONCLUSIONS

Seasonal differences in the rates of methane, nitrogen and carbon dioxide release prove that temperature may significantly affect the processes and therefore can be a principal determinant of carbon and nitrogen mineralization rates. Spatial differences in the release rates of methane, nitrogen, carbon dioxide and oxygen depend on the structure of the sediment. Gas solubility in water can be an important factor affecting bubble composition and should be taken into account when calculating gas release rates. Our experiments proved that the use of *in situ* chambers reflected natu-

ral conditions, allowing quicker and easier measurements of gas release compared to *in vitro* method with sediment cores.

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UWALNIANIE GAZÓW Z OSADÓW DENNYCH RZESZOWSKIEGO ZBIORNIKA ZAPOROWEGO

Przeanalizowano czasowe i przestrzenne zmiany gazów wydzielanych z osadów dennych płytkiego, eutroficznego zbiornika zaporowego przy użyciu reaktorów w warunkach *in situ*. Większość wydzielonego gazu stanowił metan, 40–88% obj. Azot mieścił się w przedziale 10–30% obj., dwutlenek węgla nie przekroczył 3.4% obj. Szybkość wydzielania gazów była mniejsza w niższych partiach zbiornika. Przepływy metanu, azotu oraz dwutlenku węgla były ściśle skorelowane. Stwierdzono również zmniejszenie szybkości wydzielania gazów wraz z sezonową obniżką temperatury.