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Quantitative Fluxes of the Greenhouse Gases CH_4 and CO_2 from the Surfaces of Selected Polish Reservoirs

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Abstract: Research carried out in the years 2009–2011 and 2018–2019 sought to determine the magnitudes of fluxes of methane (CH_4) and carbon dioxide (CO_2) from the surfaces of three eutrophic reservoirs in SE Poland. The "static chamber" method was deployed at five or six stations located along the reservoirs, where the water column at its deepest slightly exceeds 2 m. Obtained values for the fluxes of CH_4 varied across a wide (0–2513.48 $\mathrm{mmol \cdot m^{-2} \cdot d^{-1}}$) range, with many of these values therefore exceeding those characteristics for large tropical reservoirs. The reservoirs studied were not found to differ significantly in terms of average CH_4 flux, however. Where obtained values for CO_2 fluxes in the range from −10.96 to 621.69 $\mathrm{mmol \cdot m^{-2} \cdot d^{-1}}$ were concerned, most fell within the range given for temperate-zone reservoirs, while differences between reservoirs were noted for average values in this case.

Keywords: carbon dioxide; methane; greenhouse gases; reservoirs

1. Introduction

Carbon dioxide (CO_2) and methane (CH_4) are the two main greenhouse gases (GHGs), and the atmospheric concentrations of both are increasing steadily, with the result that average air temperatures continue to rise globally [1]. The global warming problem is sufficient to motivate much research worldwide to identify the sources of GHGs in the atmosphere, and to quantify their emissions from environments both aquatic [2–7] and terrestrial [8–11]. Accurate estimates of GHG fluxes to and from the atmosphere are crucial to any understanding of the global carbon budget, as well as to predictions of climate change.

Among the various bodies of water, inland waters play a disproportionate role in the global dynamics of GHGs, and artificial reservoirs all the more so. As water is impounded, areas covered with land vegetation (trees, plants and dead plant organic matter) become flooded and experience decay. Then, once reservoirs are in existence, organic matter is produced via primary production (generating autochthonous matter), while also being augmented from the catchment (allochthonously). The organic material accumulating in these ways is in part deposited in sediments and, where aerobic conditions prevail, this mineralizes, with one of the end products being CO_2. Alongside oxygen, other oxidants like NO_3^-, Mn^{4+}, Fe^{3+}, and SO_4^{2-} may also participate in the mineralization process [12]. In contrast, in anaerobic conditions, organic matter is decomposed by fermentation, with the final products being CH_4 as well as CO_2.

The GHGs produced in reservoirs as organic matter decomposes are emitted to the atmosphere by diffusion from the water surface [3,13], the release of gas bubbles (ebullition) [4,14], advection through the roots of aquatic plants [15,16] and degassing below the dam [17]. The amount of CO_2 and CH_4 transferred to the atmosphere at the water–air interface do not usually equate to those actually produced, as the gases also undergo transformation in the reservoirs themselves (Figure 1). CO_2 is consumed in the course of both methanogenesis (CO_2 reduction) and primary production. The major supply of reservoirs with biogenic compounds and associated high levels of primary production ensure the dominance of photosynthesis over respiration, with amounts of CO_2 left over to be emitted to the atmosphere reduced somewhat as a result [18]. Indeed, where the water–air interface features concentrations of dissolved, free CO_2 below the equilibrium concentration, supplementation from the atmosphere may actually take place. In the case of CH_4, a significant proportion of what is produced in sediments is available to be oxidized. Research on various freshwater ecosystems shows how oxidation by methanotrophs may consume from 50% to over 95% of the CH_4 diffusing out from zones of production [4,19,20]. The main oxidant is O_2, but recent research shows how alternatives present in freshwater sediments may include SO_4^{2-}, NO_3^- or metals such as Mn^{4+} and Fe^{3+} [21–26].

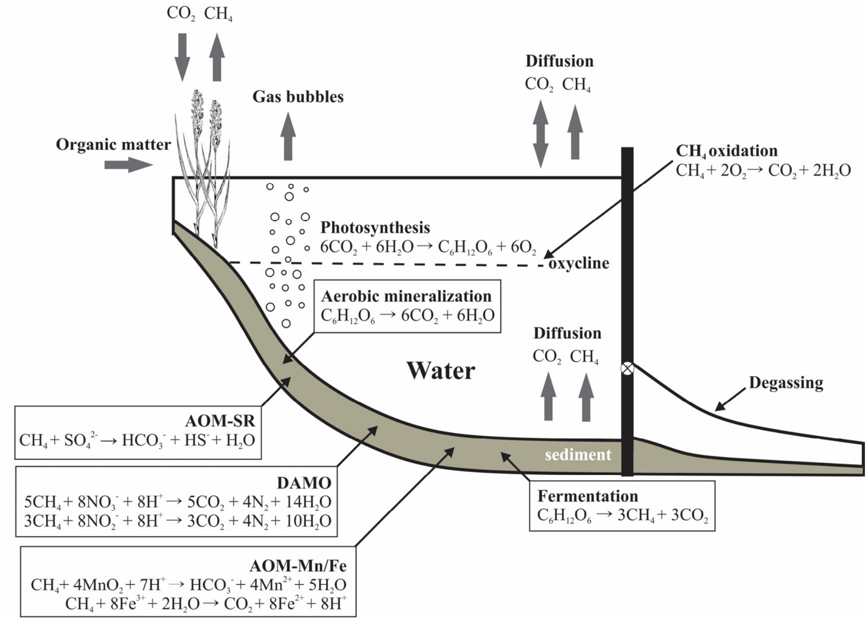


Figure 1. Transformations of CH_4 and CO_2 ongoing in reservoirs, plus transfer to the atmosphere; AOM-SR—anaerobic oxidation of methane coupled to sulfate reduction, DAMO—anaerobic oxidation of methane coupled to nitrate and nitrite reduction and AOM-Mn/Fe—anaerobic oxidation of methane coupled to manganese and iron reduction.

According to preliminary estimates, emissions of GHGs from dam reservoirs account for about 7% of the total from anthropogenic sources [27]. However, these figures may be underestimates given the non-inclusion of releases below dams [28]. Other calculations show that the lakes and reservoirs constituting 2.2% of the Earth's surface emit 0.32 Pg C into the atmosphere annually [29]. Reservoirs used in the generation of HEP (Hydroelectric Power) account for some 20% of the total, and each year emits 48 Tg C as CO_2 and 3 Tg C as CH_4. That represents 16% of emissions from artificial bodies of water, and 4% of global carbon emissions from freshwater ecosystems (natural and artificial taken together) [18].

Despite the relative abundance of data on CH_4 and CO_2 emissions from the world's reservoirs and lakes, research remains a necessity if the role in the global carbon balance is to be assessed more precisely. Current analyses multiply average flux rates for a given gas obtained from local or regional measurements by the overall areas covered by given aquatic systems [30,31]. However, GHG emissions from reservoirs vary markedly, not only between systems located in different climate zones, but also within the same zone, from one reservoir—or even from one measuring station—to another [32]. Indeed, the literature seems especially poor in data on GHG emissions from temperate-zone (and especially European) reservoirs.

The work described here thus sought to determine fluxes of CH_4 and CO_2 from the surfaces of three eutrophic reservoirs located in SE Poland.

2. Materials and Methods

2.1. Research Periods and Sites

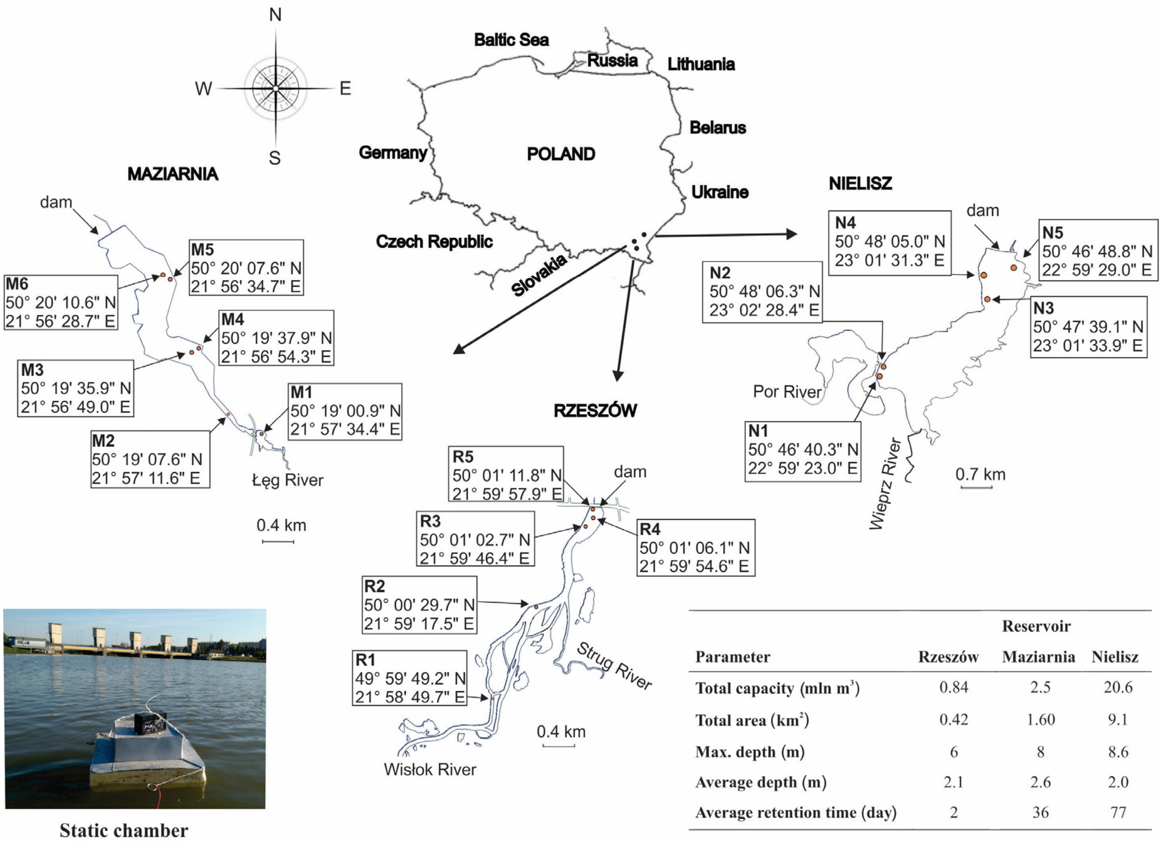
The research was carried out in the years 2009–2011 and 2018–2019, from spring through to autumn. Rzeszów, Maziarnia and Nielisz Reservoirs were the three artificial bodies of water in SE Poland selected for study.

Rzeszów Reservoir was established in 1974, with flood-control and recreational functions, and with a further use in raising the water level for the intake serving the city of Rzeszów. However, the Reservoir's central part has now undergone such far-reaching siltation that areas are well-vegetated and inhabited by birds. The catchment has only limited forest cover, along with a 68% share of agricultural land, while there are built-up urban areas in the Reservoir's immediate vicinity.

Founded in 1988, Maziarnia Reservoir also serves recreational functions, as well as both agriculture and fish farming. The catchment is predominantly arable, with mixed zones of cultivation and meadows accounting for some 70% of the area. A dominant role is played by individual-scale farming on highly fragmented holdings of land.

Nielisz Reservoir, commissioned in 2008, has as its main tasks protection against flooding, the safeguarding of limited fluctuations of the water table during the breeding season for birds, energy generation and use in recreation, leisure and angling. The reservoir is ringed by a strip of coniferous forests, while its dam supports a 362 kW hydropower plant.

In the years 2009–2011 each reservoir was studied at a pair of stations located in the upper part (R2, M4 and N2) and the lower part (R5, M5 and N4). However, the research done in 2018–2019 was of expanded scope, due to the establishment of further stations (R1–R5, M1–M6, and N1–N5). Other than R4, M6 and N5 (where depths were slightly over 2 m), measuring stations were in shallow water of depth around 1 m. Locations of both reservoirs and measuring stations are as shown in Figure 2.



Parameter	Reservoir Rzeszów	Reservoir Maziarnia	Reservoir Nielisz
Total capacity (mln m^3)	0.84	2.5	20.6
Total area (km^2)	0.42	1.60	9.1
Max. depth (m)	6	8	8.6
Average depth (m)	2.1	2.6	2.0
Average retention time (day)	2	36	77

Figure 2. Locations of the reservoirs studied and their measuring stations.

2.2. Measurement of CH_4 and CO_2 Fluxes at the Water–Air Interface

CO_2 and CH_4 fluxes were measured using the "static chamber" method, with a steel chamber of dimensions 0.3 m × 0.3 m × 0.16 m fitted out with a battery-powered windmill and a valve sealed with a silicone septum to allow for gas sampling. Four or five gas samples were collected from the inside of the chamber into gas-tight syringes, at 10 min intervals. Samples transported to the laboratory were kept for no more than 4 h before being analyzed for CH_4 and CO_2 concentrations using a gas chromatograph.

Concentrations of the gases sampled through the 2009–2012 period were determined 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 in length and of 2 mm ID. The GC was also equipped with a methanizer to detect low levels of carbon dioxide. This was 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 is helium supplied at a flow rate of 30 $mL \cdot min^{-1}$.

Where the 2018–2019 research was concerned, use was made of a Shimadzu GC-2010 Plus gas chromatograph equipped with a Barrier Discharge Ionization Detector (BID) and a Shin Carbon ST column (2 m, 1.00 mm ID, Mesh 100/120). Gas samples were injected into the GC apparatus with the detector operating at 250 °C. The carrier gas was helium, supplied at a 50 $mL \cdot min^{-1}$ flow rate.

Gas fluxes, expressed in $mmol \cdot m^{-2} \cdot d^{-1}$, were calculated from a linear regression with gas concentration change within the chamber versus time, having regard to the surface area and volume of the chamber. Positive values indicated emissions of gas from a reservoir, while negative ones indicated consumption.

2.3. Sediment Analysis

Organic matter (OM) content was determined as loss on ignition of the sediment dried for 4 h at 550 °C. Sediment pH was determined potentiometrically (MultiLine P4, WTW, Germany), in a suspension with 1 N KCl.

The contents of total organic carbon (TOC) and total nitrogen (TN) were determined using a CN elemental analyzer (Flash EA 1112, ThermoQuest). A standard of the known composition of C and N (acetanilide) was used in quality control. Prior to the TOC determination, dried and comminuted samples of the sediment were maintained for 72 h in a desiccator with vapor of concentrated HCl to remove carbonates. Before analysis, the sediment sample was again dried at 60 °C to constant weight [33].

2.4. Statistical Calculations

Results were analyzed statistically by reference to minimum and maximum values, arithmetic means and standard deviations (SD). Calculations used Excel for Office 365. The non-parametric Kruskal–Wallis test (for lack of homogeneity to the variance in groups) was used to assess differences between the mean values for several groups. The probability of error associated with confirmation of a hypothesis as to the existence of differences between mean values was set at 5% ($p < 0.05$). The Statistica 12 PL program was used in calculations.

3. Results

3.1. Sediment Characteristics

Maximum, minimum and mean values of parameters characterizing of the sediments are presented in Table 1, and detailed data in Figures S1–S3 (Supplementary Materials).

The studied reservoirs were characterized by relatively low OM contents in their sediments—a feature rather typical for Poland. OM contents ranged from 0.16% to 19.32% (Table 1), with differences present between stations as well as reservoirs. Mean contents of OM in sediments at the individual stations of Rzeszów Reservoir were in the 5.66–9.71% range. Corresponding values for Maziarnia and Nielisz Reservoirs were 0.82–14.57% and 0.95–5.96%. The lowest OM content characterized sandy sediments at stations M5 and N5.

TOC in the studied sediments represented some 30% of OM, with content in the 0.08–9.76% range (Table 1). In all cases, trends for TOC similar to those for OM could be observed.

Values for the TN content ranged from 0.01% to 0.67% (Table 1). As with OM and TOC, highest and lowest values for this indicator characterized Maziarnia Reservoir (respectively at station M6, as well as M2, M5 and N5).

pH values for sediment varied from 5.08 to 9.43 (Table 1). An acid reaction was most often recorded for Maziarnia Reservoir, while the Nielisz site had the most alkaline sediments.

Table 1. Values for selected parameters characterizing sediments; min.–max. (mean ± SD).

Reservoir	**Rzeszów**					
Station	**R1**	**R2**	**R3**	**R4**	**R5**	
OM (%)	6.15–8.44 (7.42 ± 1.16)	4.44–16.56 (9.71 ± 2.92)	4.23–8.57 (6.44 ± 1.29)	3.38–6.86 (5.66 ± 1.29)	6.63–10.57 (8.53 ± 1.29)	
TOC (%)	1.79–3.02 (2.40 ± 0.62)	1.62–6.54 (3.06 ± 1.50)	1.45–2.79 (2.25 ± 0.21)	1.69–2.27 (1.95 ± 0.21)	1.61–3.34 (2.24 ± 0.60)	
TN (%)	0.13–0.22 (0.19 ± 0.05)	0.12–0.50 (0.25 ± 0.11)	0.08–0.22 (0.17 ± 0.02)	0.12–0.18 (0.15 ± 0.02)	0.14–0.31 (0.21 ± 0.06)	
pH	7.33–7.58	7.07–8.35	7.54–8.58	7.65–8.60	7.04–7.40	
Reservoir	**Maziarnia**					
Station	**M1**	**M2**	**M3**	**M4**	**M5**	**M6**
OM (%)	5.17–7.80 (6.78 ± 1.17)	0.55–7.09 (2.55 ± 2.34)	2.38–5.80 (4.02 ± 1.21)	2.47–19.32 (12.96 ± 5.64)	0.16–1.85 (0.82 ± 0.61)	13.78–17.17 (14.57 ± 1.04)
TOC (%)	1.72–4.28 (2.80 ± 0.96)	0.16–3.06 (0.99 ± 1.06)	0.77–2.40 (1.37 ± 0.62)	0.98–5.90 (4.06 ± 1.93)	0.08–0.87 (0.22 ± 0.27)	4.11–9.76 (5.94 ± 1.53)
TN (%)	0.14–0.38 (0.24 ± 0.08)	0.01–0.20 (0.07 ± 0.07)	0.05–0.18 (0.10 ± 0.05)	0.06–0.59 (0.36 ± 0.18)	0.01–0.22 (0.04 ± 0.07)	0.32–0.67 (0.48 ± 0.10)
pH	5.70–6.92	5.30–6.95	5.71–7.28	5.08–6.80	7.36–7.80	5.33–6.59
Reservoir	**Nielisz**					
Station	**N1**	**N2**	**N3**	**N4**	**N5**	
OM (%)	1.25–9.64 (5.96 ± 3.19)	1.88–13.02 (5.10 ± 2.99)	0.68–5.35 (2.39 ± 1.73)	0.75–8.04 (2.55 ± 2.90)	0.39–1.52 (0.95 ± 0.48)	
TOC (%)	0.56–4.55 (2.63 ± 1.63)	0.84–4.77 (2.08 ± 1.11)	0.24–2.76 (1.10 ± 0.98)	0.21–2.54 (0.82 ± 0.80)	0.16–0.58 (0.34 ± 0.18)	
TN (%)	0.05–0.44 (0.23 ± 0.16)	0.06–0.23 (0.14 ± 0.06)	0.02–0.21 (0.08 ± 0.07)	0.02–0.22 (0.08 ± 0.08)	0.01–0.03 (0.03 ± 0.01)	
pH	7.70–8.99	7.20–8.88	8.44–9.24	7.40–7.99	8.40–9.43	

3.2. CH_4 and CO_2 Fluxes at the Water–Air Interface

Characteristic flux rates for CH_4 and CO_2 at the water–air interface are as presented in Table 2, with temporal changes shown in Figures 3–5.

Rates of CH_4 flux from the surface of Rzeszów Reservoir varied across a wide range from 0 (R2 and R5) to 1817.00 (R1) $mmol{\cdot}m^{-2}{\cdot}d^{-1}$ (Table 2, Figure 3). Statistical analysis showed significant differences between the stations: H(4, N = 48) =19.5563, p = 0.0006. The highest median values for fluxes characterized stations located in the Reservoir's upper part (R1 and R2), with the median for station R1 about nine times as high as that applying in the case of R2. The lowest median of CH_4 flux—of 2.55 $mmol{\cdot}m^{-2}{\cdot}d^{-1}$—was noted for station R3.

In turn, values for the flux of CO_2 at the water–air interface varied from 6.06 (R2) to 621.69 (R1) $mmol{\cdot}m^{-2}{\cdot}d^{-1}$ (Table 2, Figure 3). As with CH_4, it was R1 that reported the highest median value (155.25 $mmol{\cdot}m^{-2}{\cdot}d^{-1}$), in contrast to R3 with the lowest (22.28 $mmol{\cdot}m^{-2}{\cdot}d^{-1}$). In other cases, median values reported for the CO_2 flux oscillated around 40 $mmol{\cdot}m^{-2}{\cdot}d^{-1}$. Such major differences in fluxes between the stations were confirmed as significant by statistical analysis, with H (4, N = 48) = 10.3476, p = 0.0350. At no point during the research period was it possible to note CO_2 absorption from the atmosphere.

Table 2. Minimum, maximum and mean values for fluxes of CH_4 and CO_2 at the water–air interface; *n*—number of measurements.

Reservoir	**Rzeszów**									
Station	**R1**		**R2**		**R3**		**R4**		**R5**	
Gas	**CH_4**	**CO_2**	**CH_4**	**CO_2**	**CH_4**	**CO_2**	**CH_4**	**CO_2**	**CH_4**	**CO_2**
					(mmol·m^{-2}·d^{-1})					
Min.	137.21	71.80	0.00	6.06	0.14	6.52	0.88	20.41	0.00	11.49
Max.	1817.00	621.69	1181.90	183.78	26.68	41.20	88.61	81.89	235.60	162.51
Median	413.89	155.25	45.98	43.66	2.55	22.28	17.14	40.97	2.68	38.82
n	3	3	21	21	6	6	6	6	12	12

Reservoir	**Maziarnia**											
Station	**M1**		**M2**		**M3**		**M4**		**M5**		**M6**	
Gas	**CH_4**	**CO_2**	**CH_4**	**CO_2**	**CH_4**	**CO_2**	**CH_4**	**CO_2**	**CH_4**	**CO_2**	**CH_4**	**CO_2**
					(mmol·m^{-2}·d^{-1})							
Min.	1.11	3.74	1.15	−10.96	0.32	5.73	27.70	29.05	0.00	−4.70	0.02	−6.77
Max.	347.62	33.60	293.42	36.24	14.59	128.84	758.18	138.33	2.23	96.70	7.64	43.96
Median	61.68	21.68	8.55	22.47	1.18	14.10	392.06	74.06	0.00	25.00	0.41	9.18
n	6	6	6	6	6	6	8	8	8	8	5	5

Reservoir	**Nielisz**									
Station	**N1**		**N2**		**N3**		**N4**		**N5**	
Gas	**CH_4**	**CO_2**	**CH_4**	**CO_2**	**CH_4**	**CO_2**	**CH_4**	**CO_2**	**CH_4**	**CO_2**
					(mmol·m^{-2}·d^{-1})					
Min.	10.14	22.12	17.46	4.96	4.97	−4.63	0.00	3.58	0.55	5.20
Max.	2513.48	429.27	426.50	495.35	61.73	27.52	46.75	52.48	17.43	27.73
Median	89.75	74.7793	72.35	46.32	12.93	20.20	12.45	9.79	3.59	17.00
n	5	5	13	13	6	6	8	8	4	4

In Maziarnia Reservoir, recorded fluxes of CH_4 at the water–air interface ranged from 0 (M5) to 758.18 (M4) mmol·m^{-2}·d^{-1} (Table 2, Figure 4). The fluxes varied significantly between the stations: H (5, $N = 39$) = 25.7885, $p = 0.0001$. The median of the CH_4 fluxes at the M4 station was much higher than at other stations (for example, 6 times higher than at the M1 station and 46 times higher than at the M2 station).

Fluxes of CO_2 ranged from −10.96 (M2) to 138.33 mmol·m^{-2}·d^{-1} (M4; Table 2, Figure 4). Negative values pointing to the absorption of this gas from the atmosphere were recorded three times—in July 2011 at station M5, in July 2018 at M6, and in September 2018 at M2. In June 2011, station M5 could be described as neither emitting nor absorbing CO_2. In other cases, only emissions of gases from water were to be observed. As in the case of CH_4, statistically significant differences in flux rates between the stations could be noted: H (5, $N = 39$) = 13.2522, $p = 0.0211$.

The CH_4 fluxes recorded at the water–air interface in Nielisz Reservoir ranged from 0 (N4) to 2513.48 (N1) mmol·m^{-2}·d^{-1} (Table 2, Figure 5). The fluxes differed significantly between measuring stations: H (4, $N = 36$) = 19.1495, $p = 0.0007$, and were found to be progressively lower along the reservoir.

CO_2 fluxes in the analyzed period ranged from −4.63 mmol·m^{-2}·d^{-1} at N3 to 495.35 mmol·m^{-2}·d^{-1} at N2 (Table 2, Figure 5). The differences between CO_2 flux rates between individual stations achieved statistical significance: H (4, $N = 36$) = 14.8133, $p = 0.0051$, being higher in the upper part of the Reservoir. Values at stations N3 and N5 proved very similar, however.

For comparison, 1 mmol CH_4 and CO_2 corresponds to approximately 25,000 ppm under normal conditions.

Comparing the reservoirs in terms of their CH_4 fluxes revealed no statistically significant differences between them: H (2, $N = 123$) = 5.8920, $p = 0.0526$. However, statistically significant differences did apply in the case of CO_2: H (2, $N = 123$) = 7.1818, $p = 0.0276$, with the highest and lowest fluxes recorded for Rzeszów and Maziarnia Reservoirs, respectively.

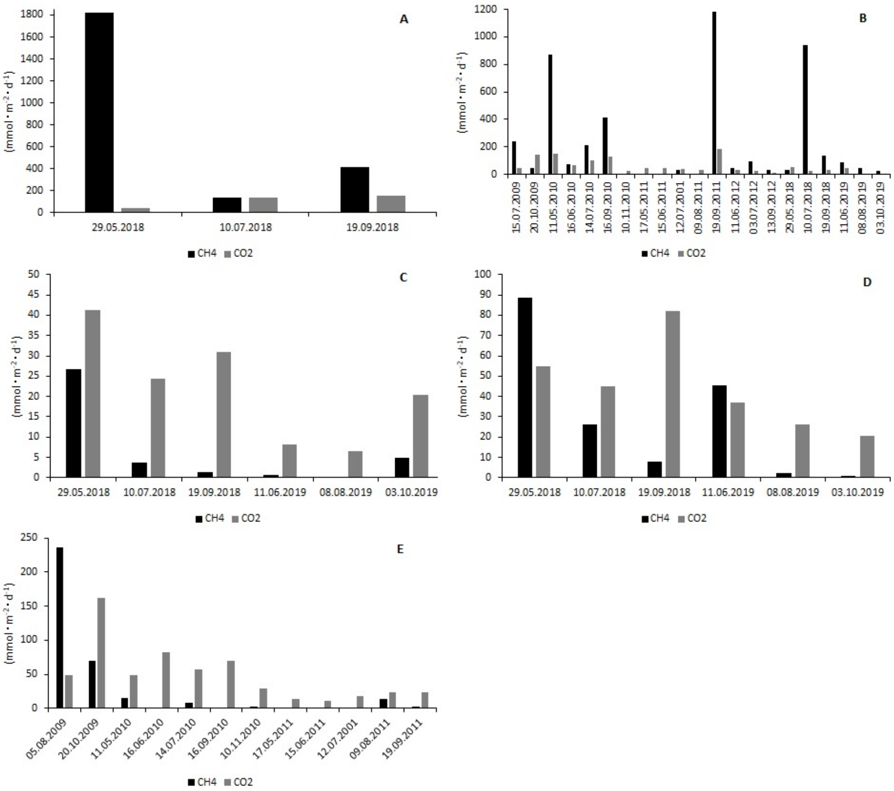


Figure 3. Time series of CH_4 and CO_2 fluxes at the water–air interface in Rzeszów Reservoir (panel A—station R1, panel B—R2, panel C—R3, panel D—R4 and panel E—R5).

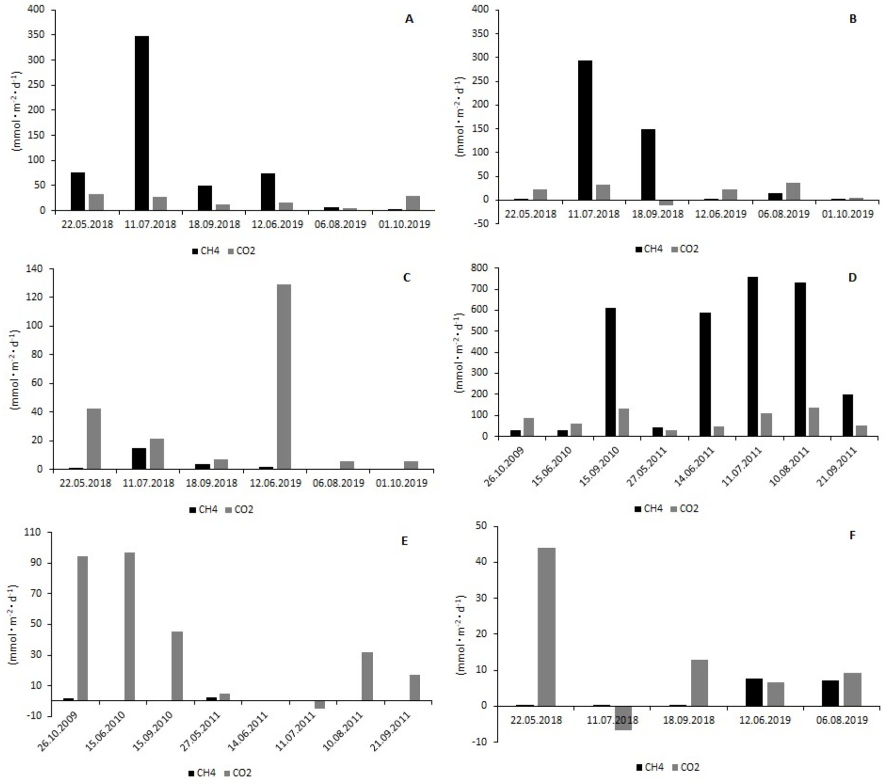


Figure 4. Time series of CH_4 and CO_2 fluxes at the water–air interface in Maziarnia Reservoir (panel A—station M1, panel B—M2, panel C—M3, panel D—M4, panel E—M5 and panel F—M6).

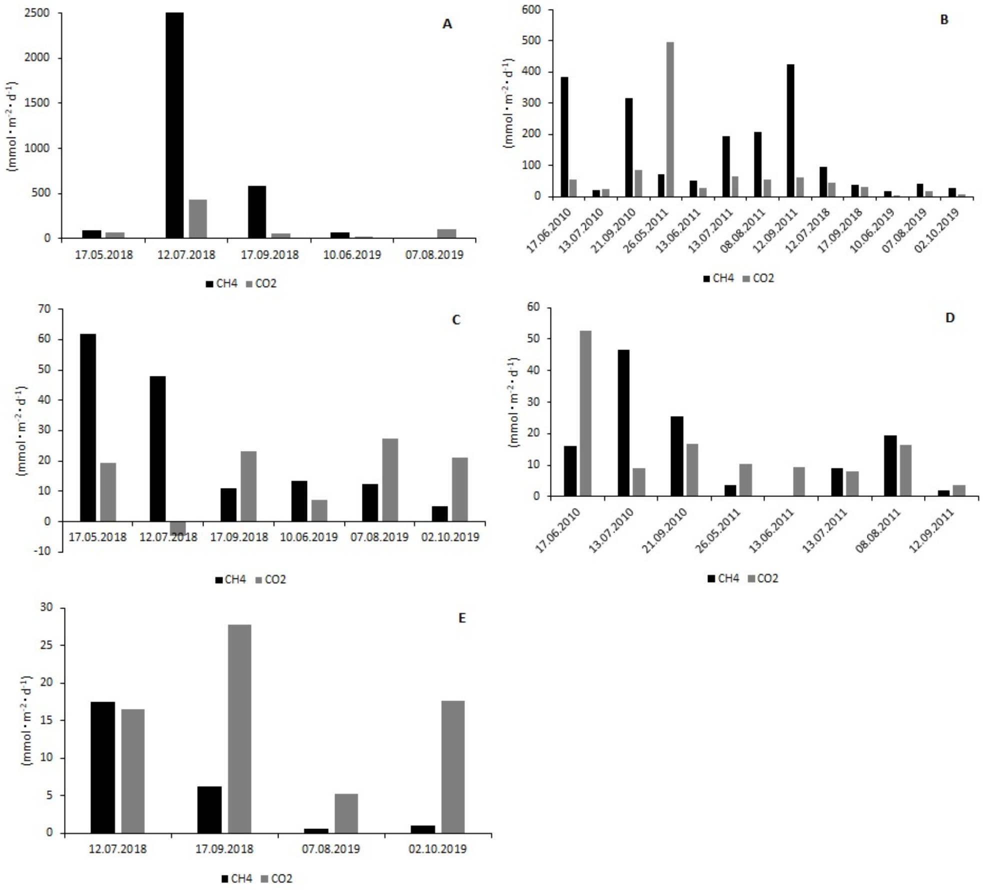


Figure 5. Time series of CH_4 and CO_2 fluxes at the water–air interface in Nielisz Reservoir (panel A—station N1, panel B—N2, panel C—N3, panel D—N4 and panel E—N5).

4. Discussion

While the literature does offer plentiful information on emissions of GHGs from various reservoirs, reports relate to large tropical (especially Brazilian) reservoirs, as opposed to those elsewhere, given that about 85% of Brazil's energy comes from large hydropower plants [34]. Temperate-zone data on CH_4 and CO_2 fluxes are much less numerous, as Tables 3 and 4 make clear. Equally obvious is the fact that emissions of the two gases from reservoir surfaces differ greatly from one climate zone to another. It is also typical for CO_2 fluxes at the water–air interface to be greater are usually higher than the fluxes of CH_4, though reservoirs sometimes take CO_2 from the atmosphere. Tanks in boreal (as opposed to temperate or tropical) locations are only emitters of far smaller amounts of GHGs. However, notwithstanding the major differences in levels of GHG emissions between climate zones, significant differences between reservoirs in the same zone are also to be noted, as are differences in fluxes in the course of a single season, or even a single month [32,35,36]. This phenomenon indicates that, not only temperature, but also other factors regulate losses of GHGs to the atmosphere.

St. Louis et al. [27] found values for CH_4 diffusion fluxes to the atmosphere from the surfaces of temperate reservoirs that ranged from 0.63 to 5 $mmol \cdot m^{-2} \cdot d^{-1}$ (mean 1.25 $mmol \cdot m^{-2} \cdot d^{-1}$), while corresponding figures for the tropical zone were 1.25–93.75 $mmol \cdot m^{-2} \cdot d^{-1}$ (mean 18.75 $mmol \cdot m^{-2} \cdot d^{-1}$). Against that background, CH_4 fluxes measured for the reservoirs under study here (range 0–2513.48 $mmol \cdot m^{-2} \cdot d^{-1}$) were mostly significantly larger.

In the case of CO_2, St. Louis et al. [27] reported mean temperate-zone fluxes to the atmosphere of 31.82 $mmol \cdot m^{-2} \cdot d^{-1}$ (range 17.05–70.45 $mmol \cdot m^{-2} \cdot d^{-1}$), as compared with a tropical-zone mean of 79.55 (range 10.23–231.82 $mmol \cdot m^{-2} \cdot d^{-1}$). This leaves most of the measured fluxes reported here for Polish reservoirs (ranging from −10.96 to 621.69 $mmol \cdot m^{-2} \cdot d^{-1}$) as within the cited range.

Of the many factors that may influence sizes of CH_4 and CO_2 fluxes from reservoirs, temperature is the one mentioned most frequently. This gains confirmation as data from Tables 3 and 4 were analyzed, given that reservoirs located in the warmer tropics emit far more GHGs than do reservoirs in boreal regions.

Higher temperatures can raise the level of activity of microorganisms decomposing organic matter under anaerobic conditions, contributing to increased CH_4 production in this way [37]. The optimal temperature for methanogenesis is approximately 25–30 °C [38,39], while a raising of temperature by 10 °C is shown to produce a fourfold acceleration in CH_4 production [2]. Positive, linear or exponential correlations between temperature and CH_4 emissions have gained regular description in a range of publications [40–45].

Temperature changes can also influence CO_2 fluxes, given effects on the solubility of the gas in water [46], on primary production process and the rate of decomposition of organic carbon [47]. The literature reports positive effects of temperature on CO_2 emissions to the atmosphere [43,48,49], but also negative ones [6,43,50].

However, analysis of the research results presented here reveals no relationship between temperature and values noted for CH_4 and CO_2 fluxes to the atmosphere, even as undoubtedly significant differences relating to the season of the year could be observed. The literature likewise reports cases of no significant correlations being found as the impact of season on GHG emissions to the atmosphere is studied [14,35,51].

A positive relationship between CH_4 and CO_2 fluxes and the content of organic matter or total organic carbon in sediment has also been described very often [48,51,52]. Both gases are end products of organic-matter decomposition, so a greater content of OM in sediment is likely to stimulate their production. For the reservoirs under study here, higher values for CH_4 and CO_2 fluxes were also observed at stations where sediments were characterized by higher OM content (and thus TOC). The lack of relationships between these variables can be explained by the focus on the impact of OM deposited in sediment on fluxes of the gases at the water–air interface, given that proportionality between CH_4 and CO_2 released to the atmosphere can change greatly under the influence of microbiological processes, ensuring a lack of correspondence with amounts of gases sediments produce. Oxidation processes consume a large amount of CH_4 (either in sediments or the water column), while CO_2 is transported to the atmosphere with a loss due to consumption in photosynthesis [53].

However, it is not only the quantity, but also the quality, of organic matter that affects the production of CH_4 and CO_2. More-readily decomposable matter of an autochthonous origin proves to be a better substrate for methanogenesis than a matter of terrigenous origin [5,54], because the algae that form a component of autochthonous organic matter decompose ten times faster than lignocellulose [55]. A high level of primary production raises the amount of substrate available for degradation [7], ensuring that eutrophic systems generally present high levels of emission of GHGs, especially CH_4 [18,27]. The objects under analysis in the work detailed here are small, relatively shallow and eutrophic reservoirs, with past analysis regarding the impact of their trophic state on GHG emissions confirming a positive relationship that achieves statistical significance [56]. It can thus be supposed that the trophic state of the studied reservoirs is the main reason for emissions of CH_4 that are very high (even exceeding the values characteristic for tropical tanks), along with the presence of high primary production as typically a negative source of CO_2 [43], and hence a contributor to disproportionately more-limited fluxes of CO_2.

Table 3. Review of CH_4 and CO_2 fluxes from boreal and temperate reservoir/lakes; mean values are given in brackets.

Reservoir/Lake	CH_4	CO_2	Source
	($mmol \cdot m^{-2} \cdot d^{-1}$)	($mmol \cdot m^{-2} \cdot d^{-1}$)	
Boreal Zone			
Grand Rapids (Canada)	−0.004–1.73 (0.036)	−8.00–165.00 (14.00)	[57]
Jenpeg (Canada)	−0.004–0.68 (0.069)	−21.00–48.00 (7.00)	[57]
Kettle (Canada)	−0.012–0.06 (0.000)	−16.00–128.00 (12.00)	[57]
McArthur (Canada)	−0.002–0.45 (0.002)	−24.00–81.00 (8.00)	[57]
EM-1 (Canada)	0.00–0.51 (0.048)	0.00–447.00 (55.00)	[57]
RDP (Canada)	0–0.40 (0.031)	−5.00–213.00 (15.00)	[57]
LG-2 (Canada)	0–0.16 (0.009)	1.00–148.00 (15.00)	[57]
Lokka (Finland)	0.33–7.40 (1.44)	11.00–73.00 (34.50)	[3]
Porttipahta (Finland)	0.16–0.30 (0.22)	20.00–52.00 (35.00)	[3]
Temperate Zone			
Wohlen (Switzerland)	(53.44)		[44]
Gruyere (Switzerland)	(0.009)	(22.25)	[58]
Lungern (Switzerland)	(0.008)	(5.50)	[58]
Sihl (Switzerland)	(0.013)	(25.00)	[58]
Luzzone (Switzerland)	(0.008)	(32.14)	[58]
Solina (Poland)		−20.78–14.73	[59]
F. D. Roosevelt (USA)	0.10–0.51 (0.20)	−19.36–5.70 (−10.5)	[35]
Dworshak (USA)	0.04–0.93 (0.21)	−51.77–−16.36 (−27.16)	[35]
Wallula (USA)	0.22–1.06 (0.56)	−37.02–24.09 (−7.93)	[35]
Shasta (USA)	−0.09–1.83 (0.59)	7.98–48.86 (28.34)	[35]
Oroville (USA)	0.07–0.66 (0.26)	6.05–55.23 (23.32)	[35]
Eagle Creek (USA)	(0.66)	(45.68)	[60]
5 lakes (Netherlands)	2.10–27.15 (5.85)	−3.27–67.58 (33.60)	[51]
Three Gorges (China)	0–0.99 (0.24)		[45]
Three Gorges (China)	(0.08)	(56.96)	[48]
Three Gorges (China)		(89.07)	[61]
Shuibuya (China)	(0.08)	(85.00)	[62]
Temperate reservoirs	0.63–5.00 (1.25)	17.05–70.45 (31.82)	[27]

The impact of the pH of water and sediment on values for CH_4 and CO_2 fluxes was also analyzed. Maziarnia and Rzeszów Reservoirs displayed weak negative trends between CH_4 fluxes and sediment pH. Zinder [63] regarded the pH range optimal for methanogenesis as 5–6, with higher CH_4 fluxes at the water–air interface being observed where such acidity was characteristic. Earlier studies also showed how sediment pH could influence, not only the magnitude of CH_4 production, but also the mechanism underpinning it. Lower pH values promote hydrogenotrophic methanogenesis [54]. A negative relationship between CO_2 fluxes and the pH of water is also described often [35,42,48,49,51,64,65], given that an alkaline reaction of water can favor the formation of carbonates; in turn reducing water's saturation with dissolved CO_2, such that absorption of this gas from the atmosphere is observed, rather than release [64]. Analysis of the impact of water pH on CO_2 fluxes to the atmosphere in the studied reservoirs reveals no relationship, even though fluxes were higher where values for the pH of water were lower.

Another factor affecting GHG emissions from reservoirs is the latter's age [18]. It is believed that the flooding of land is followed by massive emissions of gases [66] that nevertheless decrease over time, to then remain relatively constant through the life of the reservoir. However, our reservoirs showed no relationship between age and CH_4 or CO_2 emissions to the atmosphere, with equally high fluxes of these GHGs recorded for both the oldest reservoir (Rzeszów), and the youngest (Nielisz). It should be noted that these two reservoirs were assigned to the same trophic state, with the waters of the youngest in fact manifesting the highest trophic level [32]. This therefore rules out an impact of reservoir age on GHG emissions.

Table 4. Review of CH_4 and CO_2 fluxes from subtropical/tropical reservoir; mean values are given in brackets.

Reservoir	CH_4	CO_2	Source
	($mmol \cdot m^{-2} \cdot d^{-1}$)	($mmol \cdot m^{-2} \cdot d^{-1}$)	
Subtropical zone			
Gold Creek (Australia)	0.41–306.25		[67]
Tropical zone			
Balbina (Brazil)	(0.31)	(36.36)	[53]
Balbina (Brazil)		28.59–710.75 (314.66)	[68]
Miranda (Brazil)	1.25–296.72 (16.40)	0.36–1390.51 (113.18)	[69]
Tres Marias (Brazil)	0.06–90.38 (23.89)	−282.64–0.94 (-3.23)	[69]
Barra Bonita (Brazil)	0.19–3.13 (1.20)	36.68–759.64 (146.23)	[69]
Segredo (Brazil)	0.00–5.81 (0.62)	0.00–1064.98 (108.84)	[69]
Xingó (Brazil)	0.21–9.81 (1.87)	0.66–2027.34 (223.57)	[69]
Samuel (Brazil)	0.31–152.63 (11.48)	52.57–371.56 (183.80)	[69]
Tucurui (Brazil)	0.00–6.81 (12.84)	29.86–3243.73 (237.11)	[69]
Itaipu (Brazil)	0.09–3.13 (0.81)	−60.14–181.38 (27.39)	[69]
Serra da Messa (Brazil)	−0.24–63.21 (7.56)	−14.34–134.14 (29.91)	[69]
Funil (Brazil)	0.04–13.50 (0.99)		[34]
Santo Antonio (Brazil)	0.33–72.10 (9.30)		[34]
Petit Saut (French Guyana)	0.31–237.50 (71.25)	13.18–238.59 (101.36)	[70]
Nam Ngum (Laos)	0.10–0.60	−21.20–−2.70	[71]
Nam Leuk (Laos)	0.80–11.90	−10.60–38.20	[71]
Tropical reservoir	1.25–93.75 (18.75)	10.23–231.82 (79.55)	[27]

5. Summary

A key overall finding was that CH_4 fluxes to the atmosphere reported on here for the reservoirs studied were very differed and often unusually high—to the extent that they exceeded the values quoted for large tropical reservoirs. CO_2 fluxes were markedly lower, however, such that they only exceeded values described for temperate-zone reservoirs in some cases. This suggests that values present in the literature may be leading to underestimates of GHG emissions from reservoirs globally, given (as noted in the Introduction) that current analytical methods multiply up average flux rates for a given gas as obtained through local or regional measurements, by a global surface taken to be covered appropriately by water. This work has shown that differences in the values of fluxes can be very large, even within a single ecosystem. Many long-term research on more reservoirs would thus seem to be needed if their true role in global warming is to be determined accurately.

An attempt should also be made to explain precisely what factors are conducive to an increase in GHGs to the atmosphere (and to what extents). The production and emission of the gases under study prove to be very complex processes, making it impossible to identify any one most crucial factor—in line with actual dependence on many variables operating simultaneously. An additional difficulty is the very large spatial-temporal differences of the measured fluxes, especially in the case of CH_4. The literature in fact continues to supply much contradictory information on this subject.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4433/11/3/286/s1, Figure S1: Organic matter (OM), total organic carbon (TOC), total nitrogen (TN) contents and pH in studied sediments in Rzeszów Reservoir. Figure S2: Organic matter (OM), total organic carbon (TOC), total nitrogen (TN) contents and pH in studied sediments in Maziarnia Reservoir. Figure S3: Organic matter (OM), total organic carbon (TOC), total nitrogen (TN) contents and pH in studied sediments in Nielisz Reservoir.

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