Methane and Carbon Dioxide Fluxes at the Sediment-Water Interface in Reservoirs

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Abstract

Methane (CH_4) and carbon dioxide (CO_2) fluxes at the sediment-water interface were studied during autumn in three reservoirs in Poland. The theoretical diffusive fluxes of dissolved pore-water carbon gases to the overlying water ranged from 0.16 mg·m^{-2}d^{-1} to 3.84 mg·m^{-2}d^{-1} and from 20.68 mg·m^{-2}d^{-1} to 99.88 mg·m^{-2}d^{-1} for methane and carbon dioxide, respectively. The comparison between the diffusive fluxes of methane at the sediment-water interface and its fluxes at the water-atmosphere interface showed that an ebullition is probably the major pathway for CH_4 transport from the sediment to the atmosphere. The fluxes of CO_2 at the sediment-water interface were considerably lower than its fluxes at the water-atmosphere interface. This indicates that most CO_2 is generated in the water column, whereas only a small portion originates from sediments.

Keywords: methane, carbon dioxide, greenhouse gases, sediment, reservoir

Introduction

Increasing atmospheric concentrations of the radiatively active gases during the past few decades [1] have stimulated research on their emission from terrestrial and aquatic environments [2-10]. The results of these studies show that stratified lakes and reservoirs represent a favorable environment for the production of the two major carbon-containing greenhouse gases (methane and carbon dioxide). St. Louis et al. [11] estimated that greenhouse gas emissions from reservoirs may be equivalent to as much as 7% of the total global warming potential of other anthropogenic carbon emissions. Greenhouse gases can be produced in both the water column and sediments of water bodies.

Sediments are reservoirs of autochthonous and allochthonous material and are therefore important sites of organic matter mineralization. Degradation in sediment produces the two major carbon-containing greenhouse gases, i.e. methane (CH_4) and carbon dioxide (CO_2). These can be emitted to the atmosphere via three pathways: molecular diffusion from deeper sediments to the sediment-water interface, coupled with diffusion or advection through the interface into the overlying water [12]; transport through plant roots [13]; and bubble ebullition [14]. Ebullition probably only constitutes a major pathway for CH_4 transport from bottom sediments to the atmosphere in shallow waters. In deeper environments diffusion would be the major transport pathway for sediments.

CO_2 production takes place in both the aerobic water column during respiration and organic matter decomposition, as well as in anaerobic sediments. In contrast to CH_4, CO_2 is a minor component of gas bubbles [15], leading to an expectation that ebullition will not be a major pathway for this gas.

In our knowledge there is much information about emissions of CH_4 and CO_2 from reservoir surfaces, but little on diffusive flux from sediments to overlying water. The lack of data probably follows from difficulties experienced with extraction and measurement for sediment pore-water gases.

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Table 1. Morphometric properties of the studied reservoirs.

Reservoir/ Parameter	Volume (mln m³)	Area (km²)	Mean depth (m)	Maximum depth (m)	Mean residence time (days)
Solina	504	22	22	60	215
Rzeszów	1.1	1.18	0.5	6	2
Wilcza Wola	4.4	1.6	2.6	30	36

The goal of the work described in this paper was thus the study of sediment carbon gas concentrations, and the determination of diffusive fluxes of CH_4 and CO_2 at the sediment-water interface, in three reservoirs in SE Poland.

Methodology

Study Site

The study sites, comprising two small reservoirs (Wilcza Wola and Rzeszów) and one large hydroelectric reservoir (Solina), are located in southeastern Poland (Fig. 1). Characteristics of these reservoirs are as presented in Table 1.

The Solina Reservoir, Poland's largest man-made lake, is situated on the San River in the Bieszczady Mountains. It accounts for some 15% of overall water storage in Poland. Filled in 1968, it was initially used to generate power, but later also became a source of water supply and a recreation centre. Apart from its natural tributaries, the Solina Reservoir is supplied by the double rotation turbines of a power plant situated in the low-lying Myczkowce stilling basin. Economic activity in the reservoir's watershed is limited. The main part of the basin is occupied by forests, and only to a lesser extent by meadows and pastures. The drainage basin is sparsely populated. Farmed agricultural land and settlements are mainly located at the mouths of the tributary valleys.

Constructed in 1973, the Rzeszów Reservoir is located on the River Wisłok in SE Poland. After 20 years of exploitation, its water volume has decreased considerably, with fast growth of aquatic plants ensuring encroachment on to previously open surface water. Despite an attempt at reconstruction in 1996, the reservoir has mostly silted up [16]. Furthermore, both of its tributaries, the Rivers Wisłok and Strug, are highly polluted with nutrients, the drainage basin of here being mainly agricultural, with a few industrial centers.
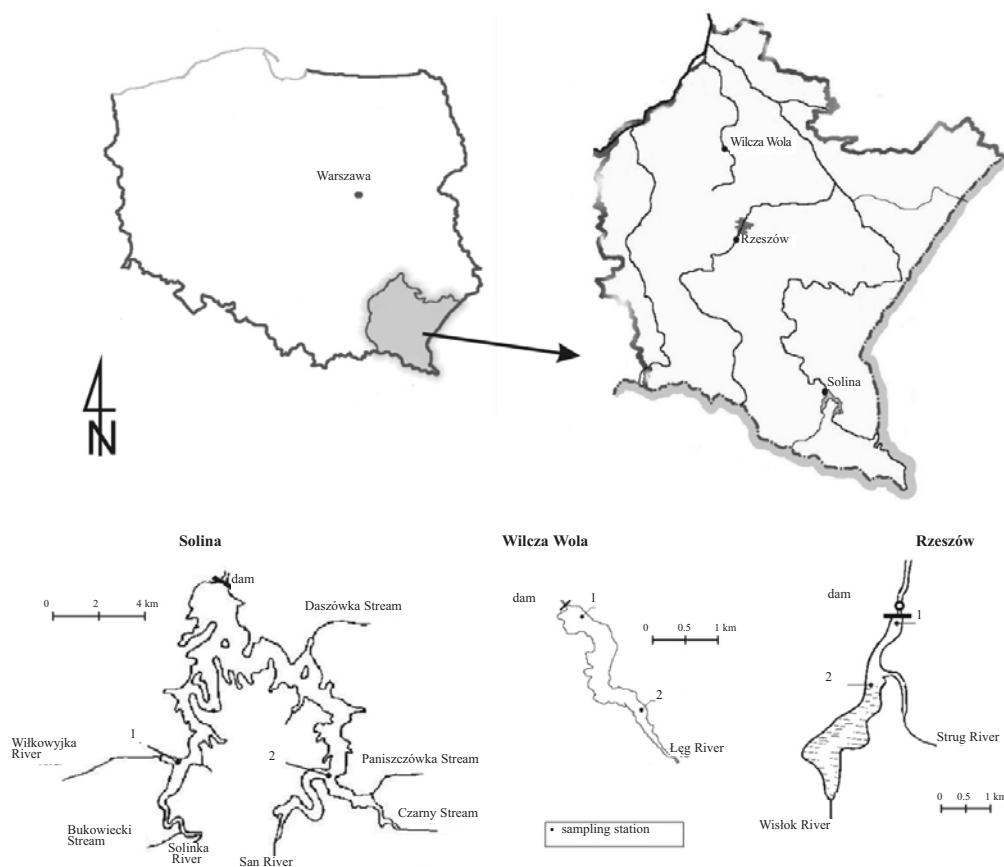

Fig. 1. Locations of the reservoirs in which gas fluxes have been studied. The sites are: the Solina Reservoir, Rzeszów Reservoir and Wilcza Wola Reservoir.

Table 2. Gas concentrations and sediment characteristics of the reservoirs studied.

Sampling time	Station	Methane [mg dm^{-3}]	Total carbon dioxide [mg dm^{-3}]	LOI [%]	Organic carbon [%]	Porosity
Solina Reservoir						
27.10.2009	1	n.d.	33.43	16.12	5.22	0.98
	2	n.d.	33.49	15.58	4.15	0.96
Rzeszów Reservoir						
20.10.2009	1	0.116	49.21	9.84	2.67	0.92
	2	0.619	51.98	10.77	2.81	0.95
Wilcza Wola Reservoir						
26.10.2009	1	n.d.	25.60	1.85	0.87	0.90
	2	0.597	30.94	2.47	0.98	0.83

LOI – loss on ignition
n.d – not detected

The Wilcza Wola Reservoir is situated on the River Łeg. It was filled in 1988, having been mainly constructed for recreational purposes. Forestry prevails in the vicinity of this reservoir.

The locations of the sampling stations for all the reservoirs studied are shown in Fig. 1.

Sampling and Analysis

Sediment samples were taken from the studied reservoirs once, in October 2009 (Table 2), cores being taken from the littoral using a gravity sediment corer (KC Kajak of Denmark). The overlying water temperature was 8ºC (at station 1) and 7ºC (at station 2) in the Rzeszów Reservoir, as well as 12ºC for all stations in the Solina and Wilcza Wola Reservoirs. Sampled cores together with overlying water were immediately transported to the laboratory. Although sediment cores are normally processed for sediment gases in helium-filled glove bags, because sediment nitrogen could not be measured, the 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 glass gastight vials using a modified pore-water squeezer [17]. The overlying water was also collected into glass gastight vials using a polypropylene syringe connected to a hose.

Immediately after collection, the samples of water in vials were acidified using 6N HCl (final concentration ~50 mM) to quantitatively convert all carbonate anions into CO_2 [18]. The gas concentrations in the overlying and pore water were analyzed using a headspace equilibration technique. Gases were extracted from the water in glass gastight vials, by replacing a known volume of water with helium. Water was equilibrated in the vials with added helium by means of 5 minutes of vigorous shaking. The gas phase was immediately analyzed for the concentrations of CH_4 and CO_2.

Both CH_4 and CO_2 concentrations were measured 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. The methanizer is packed with a nickel catalyst powder and heated to 380ºC. 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 a flow rate of 30 cc/min. Gas concentrations were expressed in mg L^{-1} of gas in the water.

For porosity measurements, the water content per volume of sediment was determined by drying a known volume of the wet sediment to a constant weight at 105ºC.

Sediment subsamples were dried and further measured for loss on ignition (LOI) at 550ºC for 4 h. Another subsample was analyzed for organic carbon using a CN analyzer (CN Flash EA 1112, ThermoQuest). Total organic carbon was measured after the removal of inorganic carbon with 1M HCl [19].

Flux Calculation

The diffuse fluxes of pore-water gases from sediments were calculated using Fick's first law of diffusion:

$$J = -\phi D_s\ (dc/dz),\ [\text{mg·m}^{-2}\ \text{d}^{-1}]$$

...where: J is the diffusive flux, ϕ porosity, D_s the sediment diffusion coefficient for each individual gas, and dc/dz – the concentration change for each gas with depth.

D_s was calculated in two ways. According to Berner [20] $D_s = D_0\ \theta^{-2}$, where: D_0 is the molecular diffusion coefficient in pure water (D_0), and θ^2 the tortuosity of sediments. Sediment tortuosity was estimated using the empirical relationship developed by Sweerts et al. [21] for freshwater environments: $\theta^2 = -0.73\phi + 2.17$. According to Lerman [22], $D_s = D_0\ \phi^2$, where: D_0 is the molecular diffusion coefficient in pure water, and (D_0), ϕ sediment porosity.

D_0 diffusion coefficients for CH_4 in water were calculated using linear interpolation between values 0.95×10^{-5} cm^2 sec^{-1} (5ºC) and 1.5×10^{-5} cm^2 sec^{-1} (20ºC) [22]. D_0 values for CO_2 in water were calculated after Hobler [23].

The concentration gradient was determined between the value in the water just above the sediment-water interface, and the first pore-water gas measurement (c. 1 cm depth interval).

An arithmetic average of two calculations was used for the diffusion values shown in Fig. 2.

Results and Discussion

The results of the research are as presented in Table 2 and Fig. 2. The methane concentration in the upper (1 cm) layer of sediment was low, ranging from 0 to 0.619 mg dm^{-3}. There was no methane at either sampling station in the Solina Reservoir and at station 1 in the Wilcza Wola Reservoir. The highest methane concentration of 0.619 mg dm^{-3} was recorded at station 2 in the Rzeszów Reservoir, while a very similar value was obtained at station 2 in the Wilcza Wola Reservoir. Carbon dioxide concentration in the sediments ranged between 25.60 and 51.98 mg dm^{-3}, the highest values being observed in Rzeszów Reservoir bottom sediments, and the lowest ones in the sediments of the Wilcza Wola Reservoir. The bottom sediments of all reservoirs are characterized by a rather low organic matter content (expressed as loss on ignition, Table 2), ranging between 1.85 and 16.12. The greatest amount of organic matter was observed in the bottom sediments of the Solina Reservoir, and the lowest in the Wilcza Wola Reservoir's bottom sediments.

The methane diffusive flux from sediments to overlying water (Fig. 2) was low, in the range 0 to 3.84 mg·m^{-2} d^{-1}. There was no methane flux from sediments to overlying water in the Solina Reservoir. The highest methane diffusive flux was reported from station 2 in the Wilcza Wola Reservoir. And the same parameter at Rzeszów Reservoir's station 1 was much lower than at station 2.

The carbon dioxide diffusive fluxes from bottom sediments to overlying water were in the range 20.68-99.88 mg·m^{-2} d^{-1} (Fig. 2), while the lowest values were obtained for the Rzeszów Reservoir and the highest for the Wilcza Wola Reservoir (station 2).

Comparison of the results of this study with those obtained by other researchers (Table 3) sustains the conclusion that the methane and carbon dioxide diffusive fluxes from bottom sediments to overlying water noted for the Rzeszów and Wilcza Wola Reservoirs are in line with values obtained for eutrophic reservoirs in the temperate zone.

The comparison of fluxes of the examined carbon greenhouse gases at the sediment-overlying water interface and at the interface between the water surface and the atmosphere (publication in preparation) reveals significantly greater CH_4 and CO_2 emission at the latter than the former.

In the case of methane, ebullition (loss of gas bubbles) may be the main pathway for emission from sediments to the atmosphere. Although the selected reservoirs had low or even zero concentrations of methane in the upper layer of sediments, those deeper down could achieve considerable values that favor gas-bubble production [24]. Supporting the idea that ebullition is the main pathway for methane transport from the sediment to the atmosphere was the visibility of gas bubbles during sampling. Physical disturbance of sediment structure may therefore cause gas-bubble loss from reservoir sediments [27]. Other researchers drew similar conclusions about the main transport pathway for methane from bottom sediments to the atmosphere, maintaining that this was the production and loss of gas bubbles [24, 28]. However, such a mechanism only occurs in shallow reservoirs or lakes. In deeper areas, diffusive flux would seem to be the main pathway for methane transport from sediment to the atmosphere [12].

Carbon dioxide in not a main component of gas bubbles [15], so it is supposed that emission of this gas to the atmosphere does not occur via gas-bubble loss from bottom sediments. Some researchers suppose that CO_2 amounts emitted to the atmosphere constitute less than 1% of emitted carbon sediment gases [3, 29]. A significantly greater CO_2 flux at the water-atmosphere interface than at the sediment-overlying water interface shows that most CO_2 is generated in the water column. According to Abe et al. [2], only 20% of carbon dioxide emitted to the atmosphere comes from bottom sediments, the remainder coming from water.
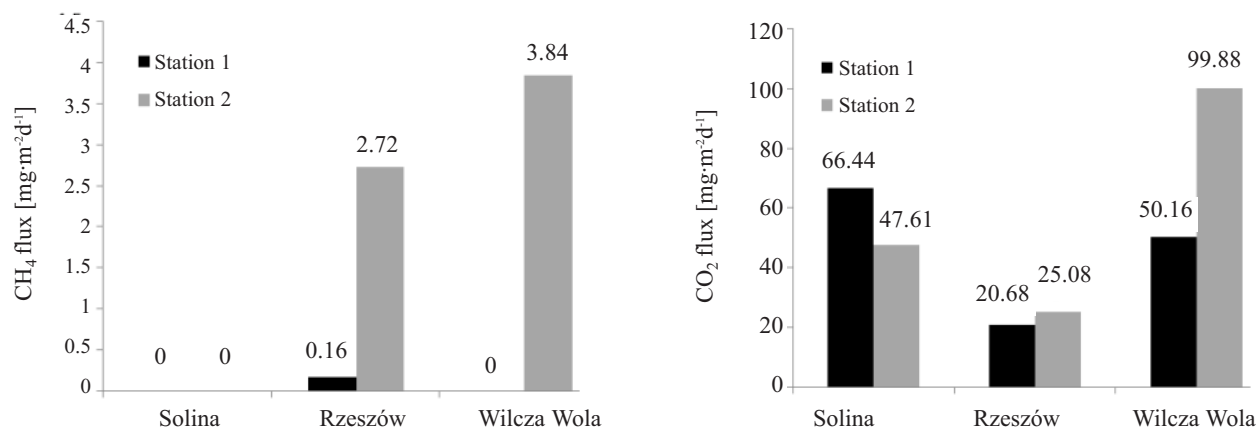

Fig. 2. Theoretical diffusive fluxes of CH_4 and CO_2 at the sediment-water interfaces of the reservoirs studied.

Table 3. Theoretical diffusion of gases at the sediment-water interface in certain lakes and reservoirs.

Lake/Reservoir	Methane flux [mg·m⁻² d⁻¹]	Carbon dioxide [mg·m⁻² d⁻¹]	Reference
Solina (Poland)	n.d.	67.61-66.44	This study
Rzeszów (Poland)	0.16-2.27	20.68-25.08	This study
Wilcza Wola (Poland)	0-3.84	50.16-99.88	This study
Tuusulanjärvi (Finland)	72		[24]
Postilampi (Finland)	105		[24]
Soiviojärvi (Finland)	8.6		[24]
Takajärvi (Finland)	4.8		[24]
Luminkajärvi (Finland)	27		[24]
Ranuajärvi (Finland)	76		[24]
Lokka (Finland)	0.44		[24]
Porttipahta (Finland)	25		[24]
Orta (Italy)	2.08-117.92		[4]
Taupo (New Zealand)	3.2-20.8		[26]
Sempach (Switzerland)	22.4-49.6		[25]
Baldeg (Switzerland)		96.8-136	[25]
Stechlin (Germany)	0.8-3.2	101.2-149.6	[14]

n.d – not detected

Acknowledgments

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