

# Processes affecting molecular and stable isotope compositions of sediment gas in estuarine waters along the southern Baltic coast (Poland)

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Received: 30 March 2016 / Accepted: 4 November 2016 / Published online: 18 November 2016  
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**Abstract** This paper investigates the molecular and stable isotope compositions of sediment gases from seven coastal lakes along the southern Baltic coast in Poland. The aim is to extend the knowledge of the genesis and distribution of microbial gases in the zone of mixing of fresh and salt waters with special attention to the effect of salinity, climate-related seasonality, and vertical sediment mixing. We found differences in the compositions of gas between the studied lakes and within each lake. These differences are mainly controlled by lake water depth and the presence of macrophytes. Due to the dissolution of rising bubbles in highly oxygenated water, the concentrations of CH<sub>4</sub>

and CO<sub>2</sub> show up to 67% decline along the water column in favor of N<sub>2</sub> and O<sub>2</sub>. On the other hand, in vegetated parts of the lakes, the CH<sub>4</sub> is depleted in favor of CO<sub>2</sub>, and the residual CH<sub>4</sub> and CO<sub>2</sub> are enriched in <sup>13</sup>C. Despite the fact that the coastal lakes display highly oxidizing conditions in the water column and that the bottom sediments are mixed by wind waves the CH<sub>4</sub> reveals rather low oxidation. On the basis of the CH<sub>4</sub>/N<sub>2</sub> ratio we established that there are differences in the intensity of ebullition throughout the lakes. Higher intensities of ebullition were found in shallower parts of the lakes. Salinity has no effect on the stable C and H isotope composition of sediment gas. It seems, however, that salinity affects the molecular composition of hydrocarbons via preferential oxidation of CH<sub>4</sub> under higher salinity conditions.

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Responsible Editor: Leila J. Hamdan.

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**Keywords** Greenhouse gas · Coastal lake ·  
Biogeochemistry · Stable isotopes · Baltic

## Introduction

Substantial increases in tropospheric CH<sub>4</sub> and CO<sub>2</sub> over the past decades and the attendant climatic implications have prompted renewed studies on the productivity and emission of greenhouse gases from marine and terrestrial ecosystems.

Estuaries, where marine and fresh waters mix, are one of the largest sources of atmospheric CO<sub>2</sub>. The high production of CO<sub>2</sub> is a diagenetic consequence of the high delivery

and remineralization of organic and inorganic C from upstream rivers and from intense bacterial activity within estuaries (Bauer et al. 2013). Estuaries release from 0.27 to 0.60 Pg CO<sub>2</sub>-C y<sup>-1</sup> (Borges and Abril 2011), which is more than the emission from rivers and lakes (Borges et al. 2006; Cole et al. 2007) as well as wetlands (Bauer et al. 2013). In contrast, the contribution of estuaries to the global CH<sub>4</sub> budget is uncertain but assumed to be minor (Kirschke et al. 2013). Estimates of total estuarine CH<sub>4</sub> emissions vary but are in the range of 0.8–6.6 Tg CH<sub>4</sub> y<sup>-1</sup> (Borges and Abril 2011 and references therein). For comparison, wetlands and freshwater lakes and rivers emit 217 and 40 Tg CH<sub>4</sub> y<sup>-1</sup>, respectively (Kirschke et al. 2013). The low contribution of estuaries to global CH<sub>4</sub> production and emissions is caused by the effect of salinity on the activity on methanogenic archaeobacteria (MA). It is well established for saline environments, replete in dissolved sulphate, that the MA are outcompeted in the sulphates reduction zone (SRZ) by sulphate-reducing bacteria (SRB) for many methanogenic substrates (Whiticar 1999). In addition, anaerobic CH<sub>4</sub> oxidation by SRB in the SRZ effectively consumes CH<sub>4</sub> that fluxes into the SRZ from deeper layers or is formed locally from non-competitive substrates. Consequently, in saline waters, the zone of methanogenesis and CH<sub>4</sub> accumulation is displaced to deeper sediment layers beneath the SRZ. In these environments CH<sub>4</sub> is typically produced from more refractory substrates, including hydrogenotrophic methanogenesis (CO<sub>2</sub> reduction).

Due to their small global areal footprint, estuaries are thought to represent only a small fraction of the global atmospheric CH<sub>4</sub> emissions. However, individual estuaries can be highly methanogenic. For example, Bange (2006) and Harley et al. (2015) reported high CH<sub>4</sub> saturations in estuarine waters from 62 to 25,700,000% along the southwestern Baltic coast and from 100 to 13,100% along the north-western North Sea coast. The biogeochemical literature contains extensive discussion of the potential impact that estuaries will have in response to climate change and the sea level rise (Kjerfve et al. 1994; Scavia et al. 2002; Borges et al. 2006; Day et al. 2008). However, due to uncertainties with regard to the present day emissions of CH<sub>4</sub> and CO<sub>2</sub> from estuaries the prediction of future emissions of these gases is very complex (Borges and Abril 2011 and references therein). The uncertainties in the CH<sub>4</sub> and CO<sub>2</sub> fluxes mainly derive from divergent evaluations of the area covered by estuaries throughout the world, as well as from the complexity of the estuarine systems (Borges and Abril 2011).

Spatial and temporal variability in salinity and hydrodynamic conditions in estuaries make it challenging to select representative sites for CH<sub>4</sub> and CO<sub>2</sub> measurement. There is a need to make measurements at diverse field sites to recognize the controls and distribution of microbial gas production within estuaries. On the Polish, southern coast of the Baltic Sea, estuaries are typically coastal lakes. Cieśliński and Drwal (2005) pointed out that these lakes act as quasi-estuaries because there are no tides on this coast and the lakes are only episodically inundated by brackish waters inflowing from the sea during specific anemometric conditions. Woszczyk et al. (2011) suggested that these lakes are potentially a source for CH<sub>4</sub>. However neither saturation levels nor CH<sub>4</sub> fluxes out of the lakes have been determined so far.

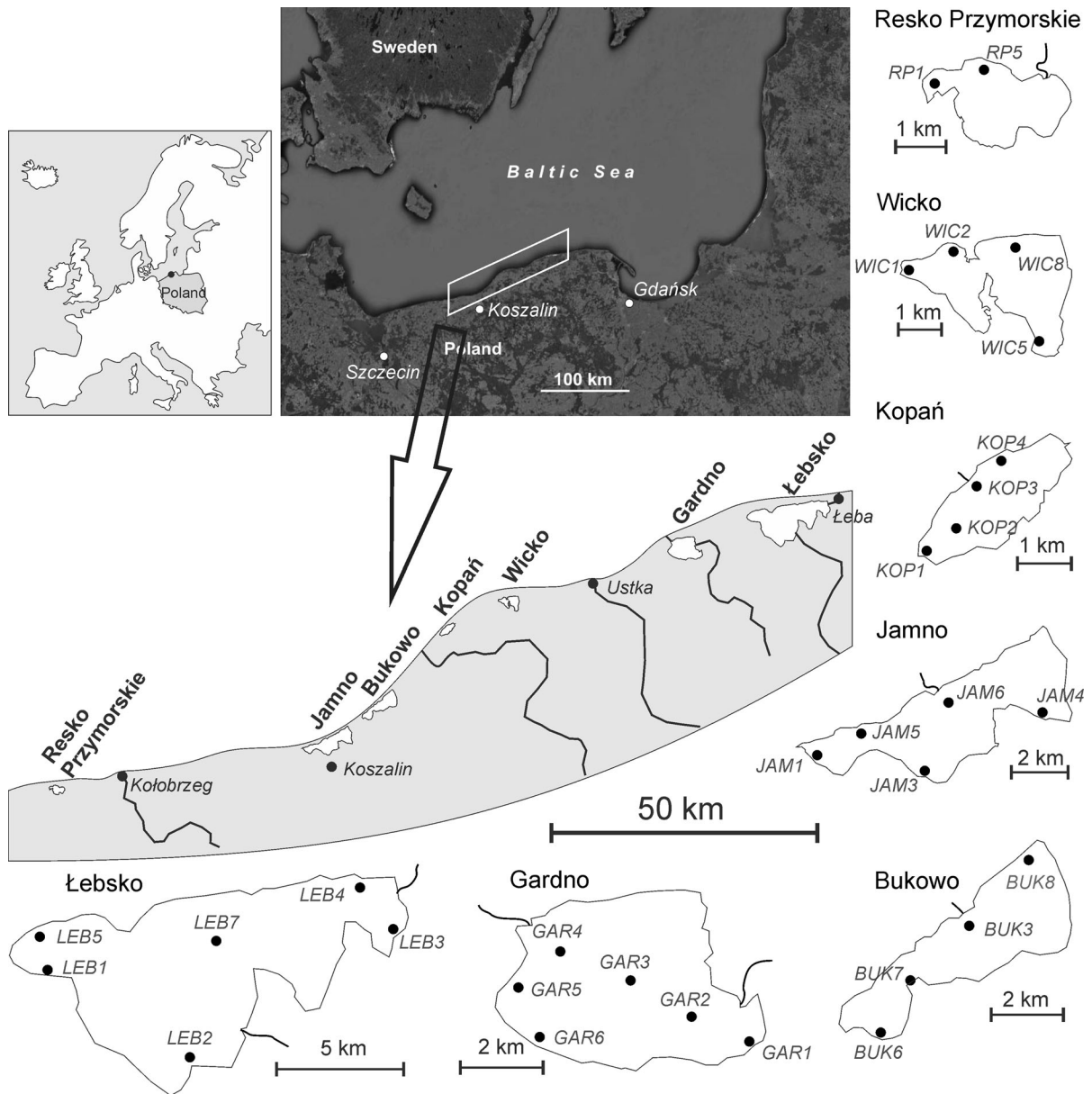
This paper provides the first comprehensive study on the sediment gases produced in coastal lakes. The aim of this study is to extend the knowledge of the genesis and distribution of microbial gases in coastal lakes, with special attention to (a) effects of salinity on gas compositions and spatial distribution; (b) climate-related seasonality in the compositions of sediment gases; (c) pathways of methanogenesis in the saline-freshwater mixing zone; and (d) CH<sub>4</sub> oxidation in these shallow water and dynamically mixed environments.

We investigated the bubbles of gas released from the lake sediments via ebullition, the most efficient pathway of gas emission from shallow (<50 m) and turbulent water bodies (Engle and Melack 2000; Kankaala et al. 2004; McGinnis et al. 2006; Del Sontro et al. 2010; Bastviken et al. 2011). Our approach was to combine the analysis of the molecular and stable isotope compositions of the gas collected in seven lakes along the southern Baltic area over a study period of several months. We provided evidence that the molecular and isotopic compositions of sediment gas show reasonable spatio-temporal variability and that they are prone to substantial transformation in the water column.

## Methods

### Study area

The lakes investigated are located along the 150 km-long section of the Poland Baltic Sea coast (Fig. 1). These coastal lakes were formed by isolation from the brackish Baltic Sea in the early-middle Atlantic period



**Fig. 1** Location of the seven lakes studied and distribution of sample sites in each lake

(Miotk-Szpiganowicz et al. 2008) and thus preserved some features of lagoons. The lakes are relatively large and shallow (mean water depth is less than 2 m) (Table 1) and are oriented parallel to the predominant wind directions (W–SW). These features result in high sensitivity of coastal lakes to wind-driven turbulence (Woszczyk et al. 2014). Consequently, the surface and bottom waters of the lakes were highly oxygenated throughout the sampling period. The dissolved  $O_2$

varied from 0.14 to 0.47  $\mu\text{mol L}^{-1}$ , and  $O_2$  saturation was between 51 and 165% (Table 1). The highest oxygenation occurred during winter, when the highest wind speeds (up to 24  $\text{m s}^{-1}$  in Ustka) were observed, and the minimum of dissolved  $O_2$  was obtained in summer. Due to the connection to the Baltic Sea, most of the lakes have brackish conditions, however, the salinity has appreciable spatial and temporal variability (Table 1). The salinity (expressed as total dissolved

**Table 1** Location and physical–chemical characteristics of the studied lakes

Lake	Location*		Area* (ha)	Mean depth (max depth)* (m)	TDS <sup>&amp;#</sup> (ppm)	Chlorophyll- <i>a</i> <sup>#</sup> ( $\mu\text{g L}^{-1}$ )	Secchi disc visibility <sup>#</sup> (cm)	O <sub>2</sub> dissolved	
	$\Phi$ (N)	$\lambda$ (E)						( $\mu\text{mol L}^{-1}$ )	(%)
Resko	54°08'32"	15°22'37"	686.6	1.3 (2.5)	1788–4243	17.2–175.3	28–58	0.21–0.38	61–118
Jamno	54°16'24"	16°09'02"	2239.6	1.4 (3.9)	178–319	52.6–192.5	23–38	0.14–0.44	51–138
Bukowo	54°20'35"	16°16'43"	1747.4	1.8 (2.8)	1333–2107	75.4–301.2	33–65	0.14–0.47	53–136
Wicko	54°32'22"	16°37'08"	1059.0	2.0 (6.1)	132–236	36.5–196.8	32–44	0.18–0.43	67–132
Kopań	54°29'04"	15°27'02"	789.7	1.9 (3.9)	301–2758	9.6–91.4	32–48	0.17–0.47	65–147
Gardno	54°39'14"	17°06'43"	2469.0	1.5 (2.6)	166–1140	67.6–194.5	22–41	0.25–0.47	82–141
Łebsko	54°42'22"	17°23'01"	7142.0	1.5 (6.3)	342–5542	44.9–130.7	29–110	0.18–0.43	61–165

$\Phi$  latitude

$\lambda$  longitude

\* Data from Jańczak (1997)

<sup>&</sup> TDS total dissolved solids (salinity)

<sup>#</sup> Measurements made between 05.2013 and 10.2014

solids (TDS)) ranged from 132 to 5542 ppm, but the majority of observations had TDS < 1000 ppm. The coastal lakes have high biological productivity, indicated by high chlorophyll-*a* and low Secchi disc visibility (Table 1) throughout the study period.

### Sampling

The lake sediment gas was sampled every 2–3 months between May 2013 and October 2014. In each lake, there were 2–6 sample stations (Fig. 1) located in different parts of the lakes displaying differences in salinity, water depth, macrophyte cover, and wind fetch (and thus wave action). The lowest salinity (TDS between 132 and 250 ppm) occurred throughout Lake Wicko and Lake Jamno, while Lake Resko and Lake Łebsko had the highest salinity (TDS > 1000 ppm). The water depth varied between c.a. 50 cm in Lake Kopań (site KOP1 and KOP4), Lake Wicko (WIC1), and Lake Jamno (JAM1) to >300 cm in Lake Łebsko (LEB5) and Lake Wicko (WIC8). Dense macrophyte cover was developed in western parts of Lake Wicko (WIC1), Lake Kopań (KOP1, KOP4), and Lake Bukowo (BUK6). WIC1, KOP1, KOP4 and BUK6 were located in wind-protected embayments and had low wind wave action. The highest wind wave action occurred in the sites located in the eastern (upwind) parts of the lakes studied (JAM8, BUK8, WIC8, GAR2, LEB5, and LEB4). The sediment gas was sampled from an anchored boat. The gas was released by gentle agitation of the sediments with a hammer

suspended from a string. Bubbles escaping from the sediment were trapped at the lake surface with a funnel and by displacement into 0.5 L dark glass bottles filled prior to sampling with lake water. After sampling, some water (~20–25 mL) was left in the neck of the sealed bottle to minimize gas escape. The surface 5 cm layer of lake sediments was sampled using a gravity sampler (Limnos). The physical–chemical properties of lake waters (temperature, TDS, pH, Red-ox potential, dissolved O<sub>2</sub>) were determined in situ with HI 9828 (Hannah Instruments) and HQD40 (Hach–Lange) probes. Measurements were made at the lake surfaces (5–10 cm below the water surface), near-bottom (5–10 cm above the lake bottom), and in sediment pore waters (uppermost 5–10 cm of sediments). The Redox potential measured in situ was corrected with the reference potential of the sensor to obtain the potential of a standard hydrogen electrode (Eh). Water depth was measured with a Humminbird 150 sonar. Wind action was determined only approximately in terms of wind fetch (F) and the depth of water mixed layer (D<sub>WML</sub>). The higher F and D<sub>WML</sub>, the deeper wave motion in lake water column. For calculating F and D<sub>WML</sub> we used formulae proposed by Douglas and Rippey (2000).

### Analytical procedures

The bulk composition of lake sediments was analyzed using lyophilized and powdered samples, as were the stable C isotope ratio measurements of TOC (total

organic carbon,  $\delta^{13}\text{C}_{\text{TOC}}$ ). The total carbon (TC), total nitrogen (TN), and total sulfur (TS) contents were determined by an elemental analyser (EA) (Elementar VarioMax CNS). TOC was also determined by an EA, except that prior to the measurement carbonates were removed by 1 M HCl. The total inorganic carbon (TIC) was calculated as  $\text{TIC} [\text{wt}\%] = \text{TC} - \text{TOC}$ . The TOC/N was calculated on a molar (at./at.) basis. The samples were analysed in duplicate. Quality control was performed using certified reference materials for peaty (BN225497), chalky (BN230229), and sandy soils (BN230227) (Elementar).

For  $\delta^{13}\text{C}_{\text{TOC}}$ , the carbonate fraction was removed beforehand with 10% HCl and rinsed with water until pH 7. Carbon isotope ratio analyses of TOC were performed with a Flash EA 2000 connected online to a ThermoFinnigan Delta V Plus mass spectrometer. All carbon isotope ratios are reported in the usual  $\delta$ -notation ( $\delta^{13}\text{C}_{\text{TOC}}$ ) relative to Vienna Pee Dee Belemnite (VPDB). The accuracy and reproducibility of the analyses were checked by replicate analyses of laboratory standards calibrated to international standards USGS 40 and 41. The  $\delta^{13}\text{C}_{\text{TOC}}$  reproducibility was  $\pm 0.2\%$ .

The molecular composition of hydrocarbons (HC) in the sediment gas bubbles was analysed with a Fisons Instrument GC 8160 gas chromatograph with a flame ionization detector (FID-GC). The volumetric concentrations (vol%) of  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ , and higher hydrocarbons ( $\text{HHC} \approx \sum \text{C}_{2+}$ ) were measured using a Carlo Erba Instruments GC 6300 gas chromatograph. Details of the procedure are given by Sechman et al. (2009). The precision of concentration measurements was equal:  $\text{HC} \pm 0.1$  ppm;  $\text{CO}_2$ :  $\pm 0.01$  vol%;  $\text{O}_2$ :  $\pm 0.02$  vol% for concentration  $< 5$  vol% and  $\pm 0.1$  vol% for concentration  $> 5$  vol%; and  $\text{N}_2$ :  $\pm 0.05$  vol% for concentration  $< 10$  vol% and  $\pm 0.1$  vol% for concentration  $> 10$  vol%. The  $C_{\text{HC}}$  (Bernard parameter) and  $\text{CO}_2$ – $\text{CH}_4$  index (CDMI), used to decipher the origin of sediment gases (Bernard et al. 1978; Kotarba and Nagao 2015), were calculated as follows:

$$C_{\text{HC}} = \frac{\text{CH}_4}{(\text{C}_2\text{H}_6 + \text{C}_3\text{H}_8)} \quad (1)$$

$$\text{CDMI}(\%) = \frac{\text{CO}_2}{(\text{CO}_2 + \text{CH}_4)} \times 100 \quad (2)$$

where  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ , and  $\text{CO}_2$  denominate volumetric percentages of the gases (Kotarba and Nagao 2015).

$\text{CH}_4$  and  $\text{CO}_2$  were isolated chromatographically for carbon and hydrogen isotope analyses.  $\text{CH}_4$  was combusted over hot CuO (850 °C) and converted to  $\text{CO}_2$ . Stable isotope analyses were performed using Finnigan Delta Plus and Micromass VG Optima isotope ratio mass spectrometers (IRMS). The stable C isotope data are expressed in the  $\delta$ -notation ( $\delta^{13}\text{C}$ , ‰) relative to VPDB, taking the reference NBS-22 (oil) to be  $-30.03\%$ . The stable H isotope data are reported in  $\delta$ -notation ( $\delta^2\text{H}$ , ‰) relative to the international standard, VSMOW (Vienna-standard mean ocean water = 0.0‰), and linearized to standard light arctic precipitation (SLAP) as recommended by Coplen (2011). Molecular  $\text{N}_2$  was separated chromatographically for stable N isotope analyses and was measured by on-line IRMS. The results of stable N isotope analyses were presented in  $\delta$ -notation ( $\delta^{15}\text{N}$ , ‰) relative to the air  $\text{N}_2$  standard. Analytical precision is estimated to be  $\pm 0.2\%$  for C,  $\pm 3\%$  for  $\text{H}_2$ , and  $\pm 0.4\%$  for  $\text{N}_2$ .

Statistical calculations were performed with Statistica 12 (StatSoft, Inc. 2014).

## Results

### Sediments

The sediments containing  $\text{CH}_4$  and  $\text{CO}_2$  bubbles had TOC contents from 7.5 to 21.1 wt%, and the TIC was between 0.4 and 4.9 wt%. The contents of TS were 1.0–2.6 wt%. The molar TOC/TN was between 7.9 and 10.0 (Table 2). The stable C isotope signatures in bulk organic carbon ( $\delta^{13}\text{C}_{\text{TOC}}$ ) varied from  $-29.1$  to  $-26.6\%$ , except for Lake Kopań which displayed less negative values of  $-24.7$  and  $-24.4\%$  (Table 2). There were appreciable differences in the sediment composition between the lakes and within each lake. The highest TOC values were obtained in Lake Wicko. Lake Gardno was distinguished by the highest TIC and the lowest TOC contents. Throughout the study period, the surface sediments were anoxic (dissolved  $\text{O}_2 = 0 \mu\text{mol L}^{-1}$ ) and displayed appreciable seasonal changes in Eh. During cold periods (Nov. 2013–Feb. 2014) the Eh was positive (+8 to +181 mV) at all but one study site, while during the warm season (Aug. 2014) Eh dropped to negative values ( $-32$  to  $-255$  mV).

**Table 2** Bulk chemical composition of surface sediments of the lakes studied

Lake	Study site	TN wt%	TOC	TIC	TS	TOC/N (at./ at.)	$\delta^{13}\text{C}_{\text{TOC}}$ ‰VPDB
Resko (LR)	RP 5	1.7	14.5	0.6	2.1	9.8	-29.0
	Jamno (LJ)	JAM 1	1.9	15.7	1.6	1.6	9.7
	JAM 5	1.5	12.5	0.9	1.3	10.0	-28.0
	JAM 6	1.0	7.5	0.7	1.2	8.9	-28.5
	Bukowo (LB)	BUK 3	1.2	9.8	0.6	1.9	9.3
	BUK 6	2.2	17.1	0.4	2.4	9.0	-28.2
	BUK 8	2.2	17.2	0.6	2.2	9.2	-29.0
	Kopań (LK)	KOP 1	2.3	18.8	2.6	1.4	9.5
	KOP 4	2.1	17.3	2.6	2.1	9.5	-24.7
	Wicko (LW)	WIC 1	2.9	21.1	1.7	1.8	8.5
	WIC 2	2.6	17.0	4.3	1.2	7.9	-28.1
	WIC 8	3.1	20.6	3.2	1.4	7.9	-29.1
	Gardno (LG)	GAR 2	1.2	8.7	4.2	1.0	8.3
	GAR 3	1.3	9.5	4.4	1.2	8.5	-26.7
	GAR 4	1.1	9.45	4.9	1.5	9.7	-27.0
Łebsko (LL)	LEB 4	1.6	17.3	2.6	1.4	9.5	-27.7
	LEB 5	1.7	13.6	1.1	1.5	9.6	-27.6
	LEB 7	1.2	14.7	1.7	2.6	9.9	-28.1

TN total organic N, TOC total organic C, TIC total inorganic C, TS total S

### Molecular composition of sediment gas

Up to 16 gas species were identified in the sediments, with  $\text{CH}_4$ ,  $\text{N}_2$ , and  $\text{CO}_2$  being by far the most abundant (see Table 3 in Appendix). The remaining fraction was comprised of  $\text{O}_2$  and HHC from saturated ( $\text{C}_2\text{H}_6$ ), unsaturated ( $\text{C}_2\text{H}_4$ ), and aromatic HC along with single-chain and branched chain compounds (see Table 4 Appendix). On average, the relative abundances were  $\text{CH}_4 \sim 72.0$  vol%,  $\text{N}_2 \sim 23.8$  vol%,  $\text{CO}_2 \sim 2.6$  vol%, and  $\text{O}_2 \sim 1.2$  vol%. The relative abundances of  $\text{CH}_4$  were strongly negatively correlated to  $\text{N}_2$  ( $r = -0.98$ ;  $n = 114$ ;  $p < 0.001$ ) and showed an overall positive relationship with  $\text{CO}_2$  ( $r = 0.54$ ;  $n = 114$ ;  $p < 0.001$ ).

Although the mean  $\text{CH}_4$  relative abundances for the lakes were similar (see Table 3 in Appendix), within each lake the  $\text{CH}_4$  displayed variations with water depth. In most lakes, except for Lake Łebsko and Lake Gardno, the concentrations of  $\text{CH}_4$  increased with decreasing water depth (Fig. 2a). The  $\text{CO}_2$  and CDMI showed differences between lakes. By far the highest values of both parameters occurred in Lake Kopań and the lowest occurred in Lake Gardno (see Table 3 in Appendix). Within lakes the changes in  $\text{CO}_2$  were negatively related to water depth (Fig. 2b), while

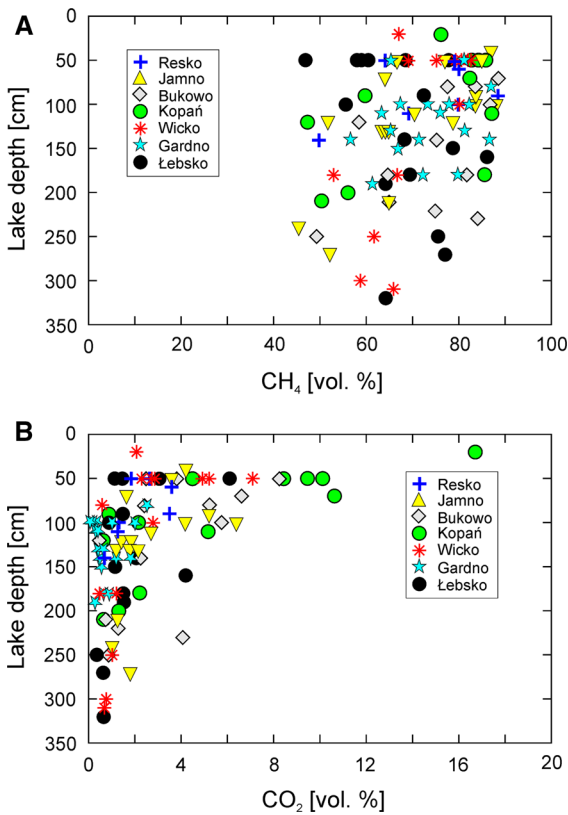
CDMI was different in vegetated and non-vegetated sites (Fig. 3a). In the former the CDMI was higher (i.e. there was more  $\text{CO}_2$  in relation to  $\text{CH}_4$ —4.72 on average) than in the latter (2.04 on average). The CDMI displayed a weak seasonal pattern, with a slight tendency to increase with increasing water temperatures (Fig. 3b).

The composition of HC (in terms of  $\text{C}_{\text{HC}}$  ratio) displayed some spatial and temporal variation. The highest values of  $\text{C}_{\text{HC}}$  occurred in Lake Wicko, and Lake Gardno, while the lowest values were obtained in Lake Resko and Jamno. The mean  $\text{C}_{\text{HC}}$  showed overall (statistically insignificant) negative relationship to salinity (Fig. 4a) and temperature (Fig. 4b) i.e. the high values of  $\text{C}_{\text{HC}}$  ( $>20,000$ ) occurred at low salinity ( $<2000$  ppm) and low temperature ( $<5$  °C).

### Stable isotope composition of sediment gas

#### $\text{N}_2$

The  $\delta^{15}\text{N}_2$  signatures showed minor changes from  $-2.1$  to  $+1.7$ ‰ (see Table 3 in Appendix). The  $\delta^{15}\text{N}_2$  showed differences between lakes. The highest values were measured in Lake Jamno, and Lake Gardno and the lowest in Lake Bukowo, and Lake Łebsko.



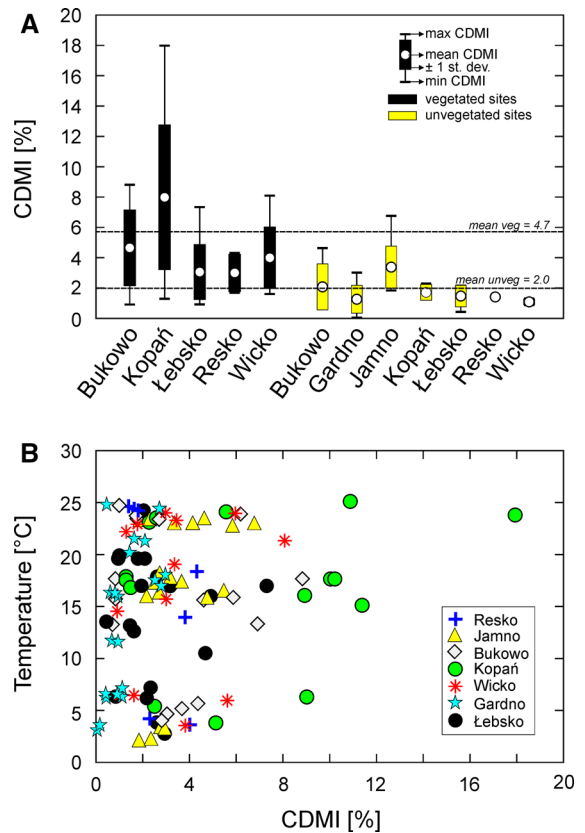
**Fig. 2** CH<sub>4</sub> (A) and CO<sub>2</sub> (B) concentrations versus lake water depth for the seven lakes studied. In most lakes, except for Lake Łebsko and Lake Gardno, there is an overall negative relationship between these parameters

**CO<sub>2</sub>**

The  $\delta^{13}\text{C}_{\text{CO}_2}$  varied over a very broad range from  $-51.5$  to  $+6.0\text{‰}$  (see Table 3 in Appendix), with a slight tendency towards higher values during colder seasons (Fig. 5). There was also a clear increasing trend in  $\delta^{13}\text{C}_{\text{CO}_2}$  values with decreasing water depth (except for Lake Łebsko) (Fig. 5) and increasing CO<sub>2</sub> concentrations (Fig. 6). The  $\delta^{13}\text{C}_{\text{CO}_2}$  values obtained in vegetated sites were higher than in non-vegetated sites (Fig. 7).

**CH<sub>4</sub>**

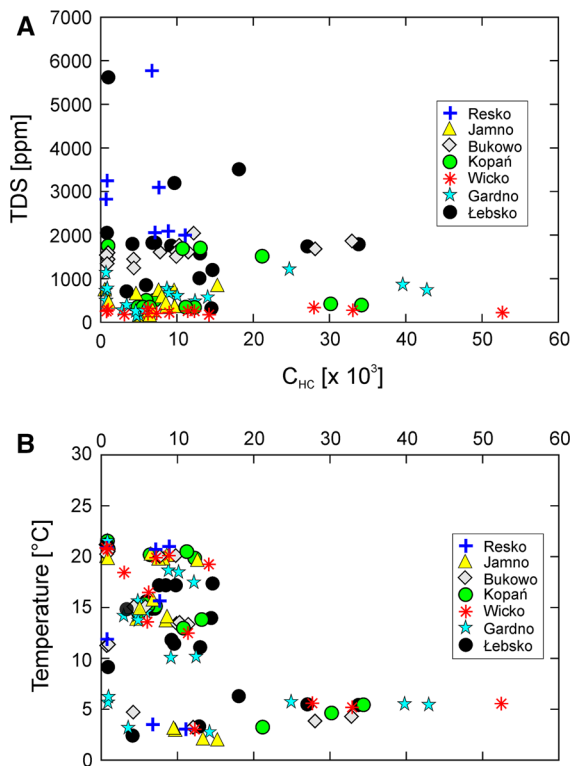
The  $\delta^{13}\text{C}_{\text{CH}_4}$  values ranged from  $-77.9$  to  $-55.1\text{‰}$  (see Table 3 in Appendix) and showed differences between lakes (Fig. 5). The highest mean  $\delta^{13}\text{C}_{\text{CH}_4}$  values were obtained in Lake Kopań, while the lowest were measured in Lake Bukowo, and Lake Resko. The



**Fig. 3** The CO<sub>2</sub>–CH<sub>4</sub> index (CDMI) differences between vegetated and unvegetated sites (A) and the relationship between the CDMI values and lake water temperature (B). The horizontal lines in A indicate average CDMI for vegetated and unvegetated sites (*mean veg* and *mean unveg*, respectively). Unvegetated sites in Lake Resko are represented by one measurement

mean  $\delta^{13}\text{C}_{\text{CH}_4}$  revealed overall seasonality. A decrease in  $\delta^{13}\text{C}$  in CH<sub>4</sub> occurred in warmer seasons ( $\delta^{13}\text{C}_{\text{CH}_4}$  for summer months was between  $-77.9$  and  $-55.4\text{‰}$ ), while during autumn and winter the CH<sub>4</sub> become isotopically heavier ( $\delta^{13}\text{C}_{\text{CH}_4}$  between  $-71.1$  and  $-57.4\text{‰}$ ).

The  $\delta^{13}\text{C}_{\text{CH}_4}$  showed changes within each lake. Except for Lake Łebsko and Lake Resko, spatial and temporal changes in  $\delta^{13}\text{C}_{\text{CH}_4}$  were strongly related to the concentrations of CH<sub>4</sub>. The more abundant the CH<sub>4</sub>, the higher the  $\delta^{13}\text{C}_{\text{CH}_4}$  signatures (the *r* values for this relationship are significant at  $p < 0.01$  and range from 0.71 to 0.88). In addition, in most of the lakes studied (except for Lake Gardno and Łebsko) the  $\delta^{13}\text{C}_{\text{CH}_4}$  revealed an overall negative relationship to water depth (Fig. 5), and the correlation coefficients for this relationship were between  $-0.52$  and  $-0.85$



**Fig. 4** Bernard index ( $C_{HC}$ ) versus lake water salinity (expressed as total dissolved solids, TDS) (A) and temperature (B). The  $C_{HC}$  was low throughout major parts of the TDS and temperature ranges except for TDS <2000 ppm and temperatures <5 °C. At low salinity and temperature the  $C_{HC}$  increased sharply

(at  $p < 0.04$ ). We obtained differences between the  $\delta^{13}C_{CH_4}$  signatures in vegetated and non-vegetated sites (Fig. 7):  $-63.6\text{‰}$  for vegetated sites and  $-67.2\text{‰}$  for unvegetated sites.

The  $\delta^2H_{CH_4}$  values varied between  $-378$  and  $-261\text{‰}$  (Fig. 8). There were no clear differences between the lakes.

## Discussion

Factors affecting the concentration of  $CH_4$ ,  $CO_2$ ,  $N_2$ , and  $O_2$  in sediment gas

The collected gas was enriched in  $N_2$  by up to 51%, and contained appreciable amounts of  $O_2$  (up to 5.5%). Furthermore, the  $\delta^{15}N_2$  signatures were too high for  $N_2$  produced via denitrification, a highly fractionating process resulting in  $\delta^{15}N_2$  between  $-40$  and  $-5\text{‰}$

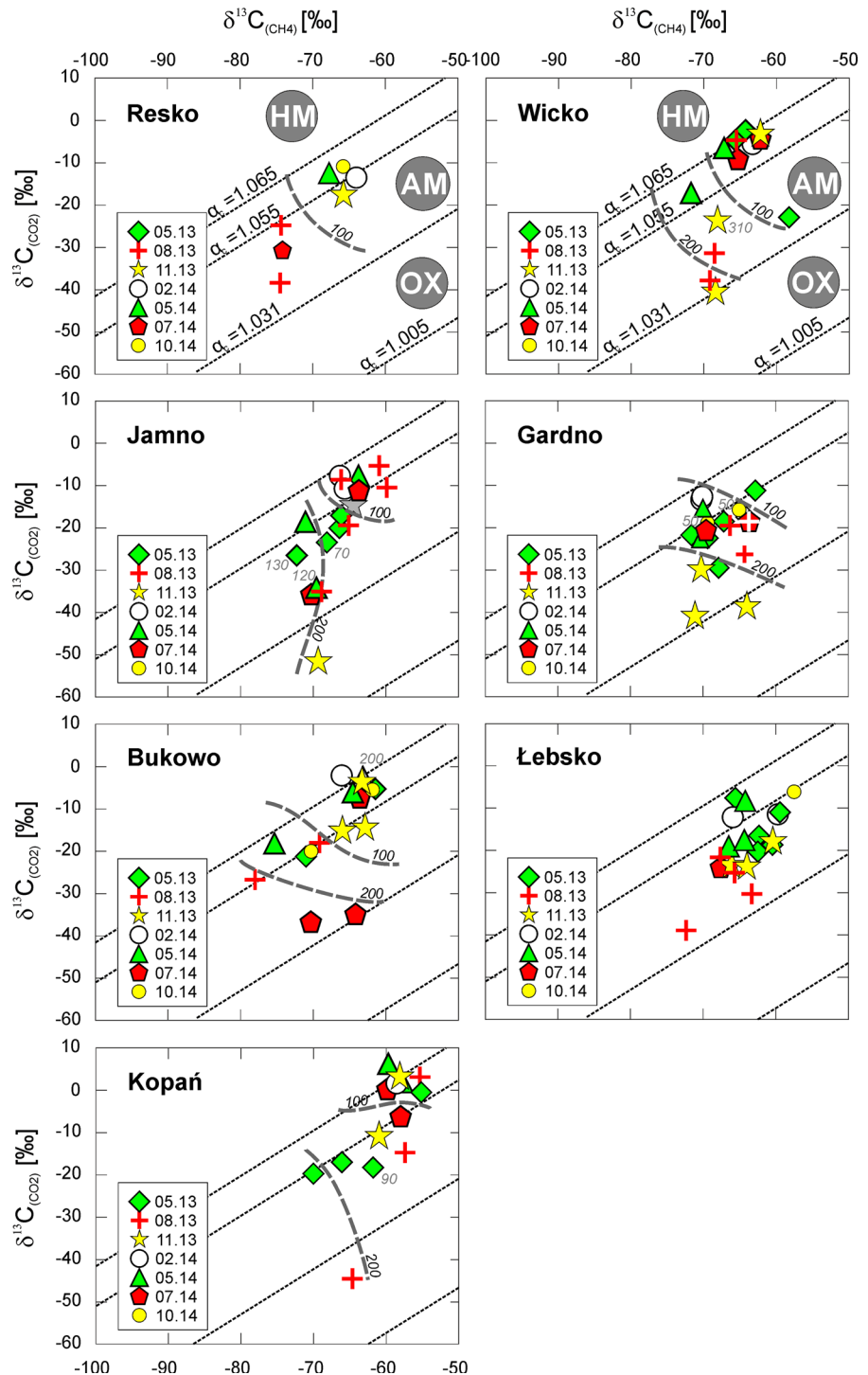
(Talbot 2001). Instead, the  $\delta^{15}N_2$  values obtained were close to the values in atmospheric  $N_2$  (in which  $\delta^{15}N_2$  is  $\sim 0\text{‰}$ ; Talbot 2001).  $N_2$  exchange between the atmosphere and water is accompanied by a very low fractionation (Talbot 2001), and consequently dissolved  $N_2$  preserves the  $\delta^{15}N_2$  values of atmospheric  $N_2$ . Hence, the  $\delta^{15}N_2$  values obtained argued for an atmospheric origin of the  $N_2$  occurring in the gas from the sediments of the lakes studied. Anoxia of pore waters indicated that the  $O_2$  present in the sediment gas was unlikely to be derived from processes occurring within the sediments (e.g. photosynthesis). It seems therefore that both  $N_2$  and  $O_2$  invaded the sediment gas via three possible routes.

First, the macrophytes act as conduits for gas exchange between the sediment and the atmosphere (Makhov and Bazhin 1999; Chanton et al. 2005; Laanbroek 2010). Plant ventilation was invoked to explain the sediment gas composition in the White Oak River estuary (Chanton et al. 1989). Chanton et al. (1989) demonstrated that  $N_2$  and  $CH_4$  were strongly negatively correlated and that sediment gas from densely vegetated sites was clearly  $N_2$ -enriched compared with “purely” microbial gas. Despite the fact, that in our study the sampling stations were located in both vegetated and non-vegetated parts of the coastal lakes, there were no differences in  $N_2$  concentrations between these sites. In addition, the  $\delta^{15}N_2$  signatures from vegetated and non-vegetated sites were similar. In the former,  $\delta^{15}N_2$  ranged between  $-1.3$  and  $0.7\text{‰}$  ( $-0.3\text{‰}$  on average), while in the latter it ranged from  $-2.1$  to  $1.7\text{‰}$  ( $-0.2\text{‰}$  on average). Moreover, vegetated and non-vegetated sites had the same  $O_2$  distribution. These features indicated that the  $N_2$  and  $O_2$  concentrations were likely little affected by plant ventilation.

Second,  $N_2$  and  $O_2$  can be supplied to the sediments in the form of large bubbles entrapped by solid particles settling in aerated water after a storm (Boudreau 2012) and/or via diffusion from overlying aerated water (Chanton et al. 1989; Walter et al. 2008). These bubbles act as nucleation sites (heterogenous nucleation) for larger bubbles containing microbial gas. The  $CH_4$  and  $CO_2$  from methanogenesis are delivered to these initial bubbles via diffusion in the pore waters; and when the critical size of a bubble is achieved, ebullition commences. There are some data indicating that the sediments of coastal lakes are deeply mixed due to wind-induced turbulence. Woszczyk et al. (2014) established that in Lake

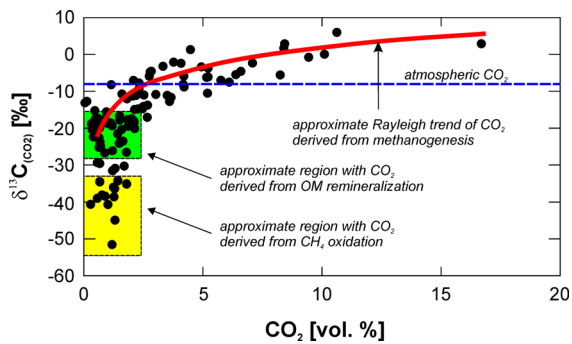


**Fig. 5** Stable C isotope composition of CH<sub>4</sub> and CO<sub>2</sub> in the lakes studied during different sampling campaigns and at different depth intervals. Lake water depth is indicated by grey dashed lines. The number attached to the lines denote the lake water depth in cm. In Lake Łebsko there was no relationship between the stable isotope composition of gases and water depth, and therefore the depth lines were not shown. The grey numbers next to data points show the collection depth of outliers. Note that there is an overall tendency for  $\delta^{13}\text{C}_{\text{CO}_2}$  and  $\delta^{13}\text{C}_{\text{CH}_4}$  to increase with decreasing water depth.  $\alpha_c$  denote apparent C isotope fractionation factors (according to Whiticar 1999). Stable C isotope composition indicate that the CH<sub>4</sub> is predominantly produced via acetoclastic methanogenesis (AM) with only minor contribution of hydrogenotrophic methanogenesis (HM). In a few sites the CH<sub>4</sub> is prone to oxidation (OX). The colors indicate seasons: white—winter, green—spring, red—summer, yellow—autumn

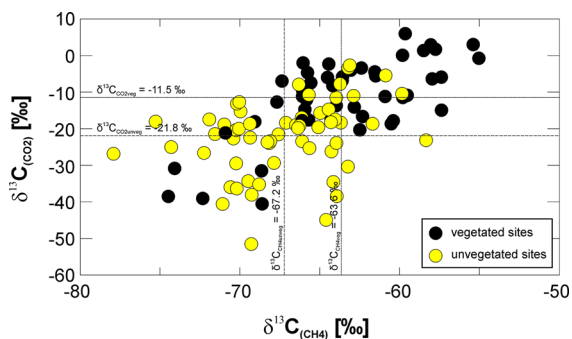


Sarbsko (located 3 km east of Lake Łebsko) the mixing was up to 50 cm depth. Unpublished data (<sup>210</sup>Pb, <sup>137</sup>Cs and <sup>7</sup>Be distributions) from Lake Gardno, Lake Bukowo and Lake Resko showed

mixing depth between 13 and 22 cm. These values supported the hypothesis on the potential effect of storm redeposition on air bubble entrapment in the sediments.

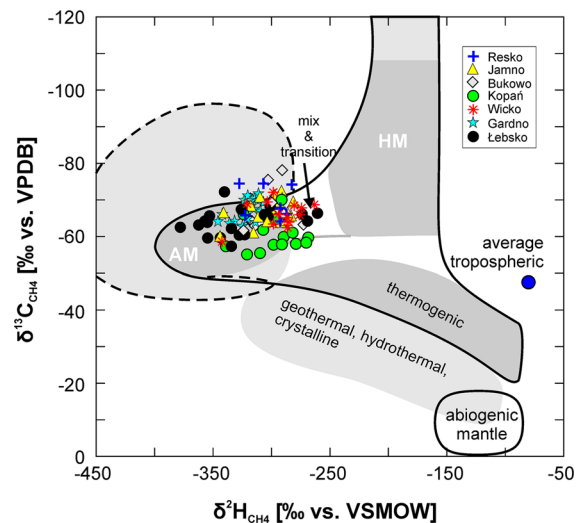


**Fig. 6** Stable C isotope signatures of  $\text{CO}_2$  ( $\delta^{13}\text{C}_{\text{CO}_2}$ ) versus concentration of  $\text{CO}_2$  in the sediment gas. There is a clear negative relationship between  $\delta^{13}\text{C}_{\text{CO}_2}$  and the  $\text{CO}_2$  concentration, explained by  $\text{CO}_2$  removal from rising bubbles owing to dissolution and gas exchange. The more strongly  $^{13}\text{C}$ -depleted  $\delta^{13}\text{C}_{\text{CO}_2}$  values can only be explained by methanotrophy. The  $^{13}\text{C}$ -enriched  $\delta^{13}\text{C}_{\text{CO}_2}$  values extending to  $+6\text{‰}$  were obtained in shallowest parts of the lakes and resulted from methanogenesis. The  $\delta^{13}\text{C}_{\text{CO}_2}$  values centered around  $-25\text{‰}$  can be derived from a variety of sources and processes, including the respiration of  $\text{CO}_2$  from organic matter



**Fig. 7** Stable C isotope signatures of  $\text{CO}_2$  ( $\delta^{13}\text{C}_{\text{CO}_2}$ ) and  $\text{CH}_4$  ( $\delta^{13}\text{C}_{\text{CH}_4}$ ) in vegetated and non-vegetated sites. The former display higher  $\delta^{13}\text{C}_{\text{CO}_2}$  and  $\delta^{13}\text{C}_{\text{CH}_4}$  signatures, which provides evidence for stable C isotope fractionation accompanying bioventilation. Mean  $\delta^{13}\text{C}_{\text{CO}_2}$  and  $\delta^{13}\text{C}_{\text{CH}_4}$  for vegetated ( $\delta^{13}\text{C}_{\text{CO}_2\text{veg}}$ ;  $\delta^{13}\text{C}_{\text{CH}_4\text{veg}}$ ) and unvegetated ( $\delta^{13}\text{C}_{\text{CO}_2\text{unveg}}$ ;  $\delta^{13}\text{C}_{\text{CH}_4\text{unveg}}$ ) sites are shown by horizontal and vertical dashed lines, respectively

Third, the  $\text{N}_2$  and  $\text{O}_2$  can invade ascending gas bubbles in a lake water column due to exchange between  $\text{CH}_4/\text{CO}_2$  and  $\text{N}_2/\text{O}_2$  dissolved in the column (Leifer and Patro 2002; McGinnis et al. 2006; Ostrovsky et al. 2008; Yamamoto et al. 2009; Del Sontro et al. 2010; McGinnis et al. 2011).  $\text{N}_2$  and  $\text{O}_2$  build up in lake waters due to dissolution of air bubbles forced by breaking wind waves, Langmuir currents, and rain drop impacts (Chiba and Baschek 2010; Liang et al.



**Fig. 8** Combination of  $\delta^{13}\text{C}_{\text{CH}_4}$  and  $\delta^2\text{H}_{\text{CH}_4}$  to delineate  $\text{CH}_4$  sources. The  $\delta^2\text{H}_{\text{CH}_4}$  and  $\delta^{13}\text{C}_{\text{CH}_4}$  indicative of acetoclastic methanogenesis (AM). Genetic fields after Whiticar (1999). AM acetoclastic methanogenesis, HM hydrogenotrophic methanogenesis

2011), and the concentration (supersaturation) of these gases is positively related to wind speed (Nakayama et al. 2002). At high wind speeds ( $>15 \text{ m s}^{-1}$ ) the air–water gas exchange is predominantly via bubbles (Chiba and Baschek 2010). Coastal lakes on the Polish Baltic coast reveal very high vulnerability to wind mixing. The Baltic coast is the windiest part of Poland (Lorenc 1996), and in 2013/2014 there were between 8 (meteorological station in Koszalin; Fig. 1) and 105–111 days (meteorological station in Łeba and Ustka, respectively; Fig. 1) with a strong wind (with speed  $v_w > 10 \text{ m s}^{-1}$ ). In addition, due to the parallel orientation of coastal lakes to the predominant and the strongest W–SW winds, the wind fetch (F) and the depth of water mixed layer ( $D_{\text{WML}}$ ) for the lakes were both high. The F varied between 0.9 km for RP5 and 5.9 km for LEB4, and the  $D_{\text{WML}}$  ranged from 0.5–2.8 m (at  $v_w = 1 \text{ m s}^{-1}$ ) to 2–6 m (at  $v_w = 10 \text{ m s}^{-1}$ ) which was higher than the water depth in most of the sampling stations. The obtained  $D_{\text{WML}}$  values indicated that the whole water column in the lakes was mixed by wind.

The air entrapped in water can be transported to appreciable depths in the lake water column, sometimes to more than 20 m below the water surface (Farmer et al. 1993). A rough estimation of the depth of bubble entrainment by wind waves in the distal (eastern) parts

of the lakes studied, according to the formula by Chiba and Baschek (2010), showed that during strong winds the bubbles could be drawn to c.a. 40 cm below the water surface. This value could be even higher when the Langmuir circulation was active (Langmuir circulation was observed in the lakes during field campaigns) because it is known to entrain air bubbles even deeper than wind waves (Liang et al. 2011). It is thus likely that in some parts of the coastal lakes there is a very deep air bubble penetration in the water.

The aeration of water during vigorous mixing leads to supersaturation with respect to  $N_2$  and  $O_2$ . According to Liang et al. (2011), the degree of supersaturation is inversely related to the solubility of the gases. Therefore  $N_2$  tends to be more supersaturated than  $O_2$  and the  $N_2/O_2$  ratio for equilibrium concentrations of both gases in water is c.a. 1.8–1.9 (at temperatures between 0 and 20 °C and 0‰ salinity) (Weiss 1970). However, the values obtained for  $N_2/O_2$  of 3–7000 are much higher than the equilibrium. Taking into account that some  $O_2$  is added to lake waters by the photosynthesis of phytoplankton (Ford et al. 2002; Walter et al. 2008), it appears that  $O_2$  is significantly underrepresented, particularly during summer. Indeed, the mean seasonal values of  $N_2/O_2$  displayed a positive correlation to lake water temperature ( $r = 0.70$ ,  $n = 7$ ,  $p < 0.08$ ), and during the summer there were the lowest concentrations of dissolved  $O_2$  in the lake waters. A plausible reason for  $O_2$  depletion might be the enhanced oxidation of organic matter (Schubert et al. 2010; Woszczyk et al. 2011).

It seems that gas exchange between bubbles and surrounding water strongly affected the molecular composition of the sediment gas from the coastal lakes. This influence explains the strong negative correlation between  $CH_4$  and  $N_2$  ( $r = -0.98$ ,  $n = 114$ ,  $p < 0.001$ ), as well as the overall negative relationship between the  $CH_4$  or  $CO_2$  and water depth observed in most of the lakes studied (Fig. 2). The greater the water depth, the longer the exposure of bubbles to highly aerated water and the higher the loss of the original gas composition.

The relationship between lake water depth and  $CO_2$  concentrations is stronger than the relationship between depth and  $CH_4$  concentrations (Fig. 2), which can be explained using the model by McGinnis et al. (2011). These authors claimed that  $CO_2$  “lifetime” in rising bubbles is very short compared with  $CH_4$  due to rapid dissolution of the former. Solubility of  $CO_2$  in

water is c.a. 24 times higher than  $CH_4$  (Yamamoto et al. 1976), and consequently the concentration of  $CO_2$  in the bubbles decreases more rapidly than  $CH_4$  over the same distance in the water column.

However, the amount of  $CH_4$  exchanged seems surprisingly high in such shallow water bodies. Assuming an initial 0% contents of  $N_2$  and  $O_2$  and a predominance of  $CH_4$  and  $CO_2$  in the sediment gas, the fraction of lost  $CH_4/CO_2$  varies between 10 and 67% (26% on average). Despite 30% bubble  $CH_4$  dissolution being reported from Lake Wohlen (Switzerland), a shallow (10 m on average) reservoir lake (DeSontro et al. 2010), up to 67%  $CH_4$  loss in coastal lakes seems high in relation to the depth of the sampling stations (maximum 3 m). On the basis of the model proposed by McGinnis et al. (2006), losses of  $CH_4$  are strongly dependent on the initial bubble size and the release depth. In our study we were unable to measure bubble diameters. However, for typical bubbles, 6–10 mm in diameter (McGinnis et al. 2006; Ostrovsky et al. 2008; Yamamoto et al. 2009), a trajectory 10–30 m long is required to cause such a depletion in  $CH_4$ . On the other hand, for bubbles 20 mm in diameter, reported as being representative of gassy sediments (Haeckel et al. 2007), a dissolution of 10–67%  $CH_4$  would occur at water depths between ca. 20 and 150 m.

There are different possible explanations for the high loss of  $CH_4$  from the bubbles collected in shallow coastal lakes. It seems that the dissolution of bubbles is enhanced by the low concentrations of dissolved  $CH_4$  ( $CH_{4diss}$ ) in lake water (Yamamoto et al. 2009). In the lakes studied, the concentrations of  $CH_{4diss}$  vary from 0.024 to 3.770  $\mu\text{mol L}^{-1}$  (0.495  $\mu\text{mol L}^{-1}$  on average) (unpubl. data) which is rather low compared with anoxic bottom waters of productive lakes where the  $CH_{4diss}$  can be as high as several hundred  $\mu\text{mol L}^{-1}$  (Liu et al. 1996; Juutinen et al. 2008; Schubert et al. 2010). Moreover, the high  $CH_4$  loss may be triggered by the supersaturation with respect to  $N_2$  and  $O_2$  in intensely wind-agitated surface waters (Nakayama et al. 2002). In the seven coastal lakes studied, the saturation of  $O_2$  can be as high as 165% (Table 1). The concentrations of  $CH_4$  in sediment gas can be modified by the rate of ebullition, which is water depth-dependent. Engle and Melack (2000), Liikanen et al. (2003), Kankaala et al. (2004), and Boudreau (2012) suggested enhancement of  $CH_4$  ebullition under low hydrostatic pressure (i.e. in shallow waters). In turn, the intensity of bubble release is known to control the

CH<sub>4</sub>/N<sub>2</sub> ratio. Chanton et al. (1989) and Walter et al. (2008) showed that intense ebullition removes N<sub>2</sub> from pore waters and results in higher CH<sub>4</sub>/N<sub>2</sub> ratios in sediment gas. In some of the coastal lakes studied, there is an overall negative relationship between CH<sub>4</sub>/N<sub>2</sub> and water depth (LW  $r = -0.62$ ,  $n = 13$ ,  $p < 0.03$ ; LK  $r = -0.62$ ,  $n = 14$ ,  $p < 0.02$ ; LJ  $r = -0.45$ ,  $n = 17$ ,  $p < 0.07$  and LB  $r = -0.59$ ,  $n = 15$ ,  $p < 0.03$ ), arguing for a more intense ebullition in the shallowest parts of these lakes. Chanton et al. (1989) and Walter et al. (2008) used the CH<sub>4</sub>/N<sub>2</sub> ratio to document spatial and temporal changes in ebullition rate. Ebullition usually intensifies during summer (Makhov and Bazin 1999; Liikanen et al. 2003; Sapulveda-Jauregui et al. 2015). However, in the seven coastal lakes studied, the CH<sub>4</sub>/N<sub>2</sub> displayed irregular temporal changes. We believe that the seasonality was obscured by the forcing of gas ebullition by wind action which is known to enhance bubble release (Leventhal and Guntenspergen 2004; Bussmann 2005). On the other hand, the distribution of CH<sub>4</sub> seems to be related to the distribution of macrophytes. This is corroborated by differences in CDMI between vegetated and non-vegetated sites (Fig. 3a). The highest CDMI (the more CO<sub>2</sub> in relation to CH<sub>4</sub>) in Lake Kopań are explained by the fact that a large part of the lake bed (sites KOP1 and KOP4) is covered by macrophyte meadows, with *Potamogeton* as the predominant species. Aquatic (mainly emergent) plants are known to channel considerable amounts of CH<sub>4</sub> from the sediments (Chanton 2005; Borges and Abril 2011). CO<sub>2</sub> is removed in much lower rates (Olsson et al. 2015). Consequently, bioventilation leads to the increase in the CDMI in the sediment gas. Emergent plants (i.e. *Phragmites*, *Typha* etc.) transfer CH<sub>4</sub> directly from the rhizosphere to the atmosphere, while submersed plants (i.e. *Potamogeton*) transmit CH<sub>4</sub> to the water column, where it is oxidized (Laanbroek 2010). It was shown that in pore waters, in densely vegetated sites, the concentrations of dissolved CH<sub>4</sub> were c.a. 50% lower than those in non-vegetated areas. The lower CH<sub>4</sub> concentrations reduce the CH<sub>4</sub> bubble formation and gas ebullition (Chanton 2005).

The transformation of the molecular composition of sediment gas in the water column of the coastal lakes studied conflicts with the findings of Del Sontro et al. (2010) and Katsman et al. (2013). These authors claimed that ascending gas bubbles rise quickly through the sediment and water columns, essentially

by-passing the zones of anaerobic and aerobic microbial oxidation and, as a consequence, only a small fraction of gas fluxing into the boundary layer is lost.

#### Higher hydrocarbons (HHC) in sediment gas

C<sub>HHC</sub> values in the gas samples from Polish coastal lakes are typical for microbial gases produced via methanogenesis (Bernard et al. 1978). Trace amounts of HHC were previously reported from microbial systems in lakes (Oremland and Des Marais 1983; Woszczyk et al. 2011), estuaries (Oremland 1981), and the ocean (Hinrichs et al. 2006). However, to the best of our knowledge, there are few data showing the production of HHC in lake sediments, and the mechanisms of gas formation remain unclear. Hinrichs et al. (2006) showed that CH<sub>4</sub> and HHC can be co-produced during bacterial degradation of OM and established that the production of HHC is favored under low salinity (low sulfate) conditions. Therefore, the increase in salinity would result in an increase in C<sub>HHC</sub>, which conflicts with our observations (Fig. 4a). On the other hand, Whiticar and Faber (1986) found that changes in C<sub>HHC</sub> values might be caused by selective removal of CH<sub>4</sub> during anaerobic oxidation of hydrocarbons. CH<sub>4</sub> shows lower resistance to this process than HHC (Whiticar and Faber 1986). In contrast, during aerobic oxidation HHC are preferentially decomposed compared with CH<sub>4</sub> (Kinnaman et al. 2007). Thus the overall negative relation between the average C<sub>HHC</sub> values and the lake water salinity in our lakes (Fig. 4a) may indicate that saltwater intrusions enhance anaerobic oxidation of CH<sub>4</sub> in the sediments. This process is triggered by archaea in concert with SRB (Schouten et al. 2001). The latter were found to be one of the most predominant microbial communities in coastal lakes (Skórczewski and Mudryk 2005). The oxidation of CH<sub>4</sub> becomes possible when the concentrations of dissolved sulfate are  $>1 \text{ mmol SO}_4^{2-} \text{ L}^{-1}$  (Segers 1998). During the study period, the dissolved SO<sub>4</sub><sup>2-</sup> in the lakes varied between 0.17 and 3.9 mmol L<sup>-1</sup> (unpubl. data), which made the CH<sub>4</sub> oxidation thermodynamically possible.

In accord with previous reports (Utsumi et al. 1998; Whiticar 1999; Karim et al. 2011; Harley et al. 2015), the oxidation of CH<sub>4</sub> is enhanced by higher water temperatures. This conclusion is supported by the decrease in C<sub>HHC</sub> in warmer seasons (Fig. 4b) and a concomitant increase in CDMI (Fig. 3b). However, the

increase in CDMI is not accompanied by a decline in  $\delta^{13}\text{C}_{\text{CO}_2}$ , which would be expected during  $\text{CH}_4$  oxidation (Jędrysek 1999). It appears, therefore, that anaerobic oxidation plays only a minor role in the  $\text{CH}_4$  cycling in coastal lakes albeit its effect on the  $C_{\text{HC}}$  may be strong. The concentrations of  $\text{CH}_4$  are 4–5 orders of magnitude higher than the HHCs and even a small decline in  $\text{CH}_4$  due to oxidation drives the  $C_{\text{HC}}$  towards higher values.

### Mechanisms of methanogenesis in coastal lakes

The two primary methanogenic pathways suspected in the lakes are acetoclastic methanogenesis (AM) and hydrogenotrophic methanogenesis (HM). Whiticar and Faber (1986) and others argued that in marine sediments HM predominates. This is due to the utilization of potential methanogenic precursor organic substrates by SRB in the sulfate reduction zone, before they reached the diagenetic depth for methanogenesis. To complicate the issue, aerobic and anaerobic  $\text{CH}_4$  oxidation consume some of the  $\text{CH}_4$ , while the remainder can flux out of the lakes into the troposphere.

The  $\text{CH}_4$  production and consumption pathway can be recognized on the basis of the apparent C isotope fractionation factor between  $\text{CO}_2$  and  $\text{CH}_4$  (Whiticar 1999):

$$\alpha_C = (\delta^{13}\text{C}_{\text{CO}_2} + 10^3) / (\delta^{13}\text{C}_{\text{CH}_4} + 10^3) \quad (3)$$

as well as by using the  $\delta^2\text{H}_{\text{CH}_4}$  signatures. The  $\delta^{13}\text{C}_{\text{CO}_2}$  versus  $\delta^{13}\text{C}_{\text{CH}_4}$  relationships assume so-called co-existing pairs, i.e., that  $\text{CO}_2$  and  $\text{CH}_4$  are mechanistically linked. When this condition is fulfilled,  $\alpha_C > 1.065$  is characteristic for HR, while  $\alpha_C < 1.055$  indicates the predominance of AM (Conrad 2005; Hershey et al. 2014). On the other hand, in the C/H isotope systematics of  $\text{CH}_4$ , the demarcation lines between AM and HM are made at  $\delta^{13}\text{C}_{\text{CH}_4} \sim -60\text{‰}$  and  $\delta^2\text{H}_{\text{CH}_4} \sim -250\text{‰}$  (Whiticar 1999). The lower values denote AM, while HM has  $\delta^{13}\text{C}_{\text{CH}_4} > -60\text{‰}$  and  $\delta^2\text{H}_{\text{CH}_4} > -250\text{‰}$ . For  $\text{CH}_4$  oxidation, in turn, the C isotope fractionation factor is usually  $1.005 < \alpha_C < 1.031$  (Whiticar and Faber 1986).

In the previous section we showed that the molecular composition of gas in rising bubbles can change significantly in a lake water column. It seems, however, that the gases preserve their original stable C isotope signatures because the isotope effects associated with dissolving  $\text{CH}_4$  and  $\text{CO}_2$  in water are

small (0.3–0.6 and 1‰, respectively) (Bergamaschi 1997; Sansone et al. 1999; McGinnis et al. 2011).

Most of the gas samples from coastal lakes reveal the stable C and H isotopic signatures indicative of AM (Figs. 5, 8). However, several samples show  $\alpha_C > 1.055$ , arguing for minor contribution from HM; and a few samples display  $\alpha_C < 1.031$ , characteristic for  $\text{CH}_4$  oxidation. In the case of a few samples from Lake Bukowo, Lake Wicko and Lake Kopań, both  $\delta^{13}\text{C}_{\text{CO}_2} - \delta^{13}\text{C}_{\text{CH}_4}$  and  $\delta^{13}\text{C}_{\text{CH}_4} - \delta^2\text{H}_{\text{CH}_4}$  signatures consistently indicate some HM contribution. The dominance of AM in the lakes is consistent with low sulphate, freshwater conditions. The shift towards HM for some samples may indicate the exhaustion of the labile AM substrates and a shift in methanogenic pathway. Hornibrook et al. (2000) claimed that recalcitrance of sedimentary organic matter (SOM) acts as one of key factors controlling the mechanism of  $\text{CH}_4$  production. The more labile the organic matter delivered to the methanogenic zone, the higher the preference for AM.

The  $\delta^{13}\text{C}_{\text{CO}_2}$  and  $\delta^{13}\text{C}_{\text{CH}_4}$  show weak seasonality, with a tendency to enhanced HM during colder periods and enhanced AM during warmer periods (Fig. 5). This agrees with previous reports (Hornibrook et al. 2000; Avery et al. 2003; Chanton et al. 2005) and may be related to formation and abundance of precursor substrates for AM. However, the temporal patterns of  $\delta^{13}\text{C}_{\text{CO}_2}$  and  $\delta^{13}\text{C}_{\text{CH}_4}$  are different in each lake; consequently, there is no compelling evidence of a significant climatic (temperature) control on methanogenesis.

Based solely on  $\delta^{13}\text{C}_{\text{CO}_2}$  vs  $\delta^{13}\text{C}_{\text{CH}_4}$ , the methanogenic pathway in the lakes would appear to be influenced by water depth (Fig. 5). The  $\delta^{13}\text{C}_{\text{CO}_2}$ , and to a lesser extent the  $\delta^{13}\text{C}_{\text{CH}_4}$ , become  $^{12}\text{C}$ -enriched with increasing water depth. There is also a shift in  $\alpha_C$  to lower values with depth. This would suggest enhanced AM over HM at depth. This conclusion contrasts with observations by Jędrysek (1999) and Alstad and Whiticar (2011) who argued that HM should dominate in deeper waters. The transition from AM to HM with depth is hypothesized to be due to a depletion by utilization of labile AM precursor substrates in the deeper waters, and by higher availability of dissolved  $\text{CO}_2$  in deeper waters. We believe that such reasoning is not valid for the seven lakes studied, because in our data there is neither clear evidence for substantial differences in dissolved  $\text{CO}_2$  within lakes nor differences in the decomposition of SOM throughout the lakes (the TOC/N and  $\delta^{13}\text{C}_{\text{TOC}}$  show only minor variability

within each lake) (Table 2). In addition, because the  $\delta^2\text{H}_{\text{CH}_4}$  values are not related to water depth, the overall isotope evidence does not support a shift from HM to AM with depth. Therefore, we suggest that the stable isotope composition of microbial gases is altered by secondary processes.

### Methane oxidation

The observed shifts in  $\alpha_{\text{C}}$  in the lakes are determined more by changes in  $\delta^{13}\text{C}_{\text{CO}_2}$  than in  $\delta^{13}\text{C}_{\text{CH}_4}$ , and with increasing water depth the  $\delta^{13}\text{C}_{\text{CO}_2}$  values decline to  $<-35\%$  (the minimum  $\delta^{13}\text{C}_{\text{CO}_2}$  is  $-51\%$ ) (Fig. 5). Such low  $\delta^{13}\text{C}_{\text{CO}_2}$  values can only be explained by methanotrophy, i.e., the oxidation of  $^{13}\text{C}$ -depleted microbial  $\text{CH}_4$ . Other remineralization reactions, such as organic matter respiration, could not result in the observed highly negative  $\delta^{13}\text{C}_{\text{CO}_2}$  because these processes produce  $\text{CO}_2$  in which  $\delta^{13}\text{C}$  signatures are close to  $\delta^{13}\text{C}_{\text{TOC}}$  (i.e. between  $-24$  and  $-29\%$ ; Table 2). The oxidation of  $\text{CH}_4$  occurred during summer and autumn (Fig. 5). We hypothesize that enhanced oxidation in deeper water is related to the intense wind-induced lake water mixing which is known to drive methanogenesis to greater depths within the sediments (Blair 1998). The oxidation of  $\text{CH}_4$  can be performed within the pore waters and in the water column. In the former case the oxidation is under reducing conditions and enhanced  $\text{SO}_4$  concentration. Earlier in this paper we postulated that the oxidation of  $\text{CH}_4$  at the expense of  $\text{SO}_4$  could be responsible for the lowered  $\text{C}_{\text{HC}}$  values in the gas collected during saltwater inflows to coastal lakes. However, the lack of correlation between  $\delta^{13}\text{C}_{\text{CH}_4}$  and lake water salinity shows that this process has a negligible isotope effect.

Methanotrophic bacteria existing in lake water column consume methane during its diffusion and/or bubble transport via the oxidized water (Schubert et al. 2010). However, in the case of ascending bubbles the oxidation is minor due to the very short contact of bubble  $\text{CH}_4$  with  $\text{O}_2$  in the water column (Liikanen et al. 2003; Chanton 2005). Interestingly  $^{12}\text{C}$ -enriched  $\delta^{13}\text{C}_{\text{CO}_2}$  values correspond to low concentrations of  $\text{CO}_2$  (Fig. 6) which seems inconsistent with methanotrophy because the enhanced oxidation of  $\text{CH}_4$  and OM is expected to deliver more  $\text{CO}_2$  than  $\text{CH}_4$  (Hornibrook et al. 2000) and thus leads to higher CDMI. Interpreting the low  $\text{CO}_2$  and  $^{12}\text{C}$ -enriched  $\delta^{13}\text{C}_{\text{CO}_2}$  values in terms of methanotrophy would

imply that all the excess  $\text{CO}_2$  was removed from the gas phase. In light of the model proposed by McGinnis et al. (2011), the plausible explanation for the  $\text{CO}_2$  removal is rapid dissolution of  $\text{CO}_2$  from ascending bubbles in the water column.

The effect of  $\text{CH}_4$  oxidation fades out in gas samples from the shallow water sections of the lakes where less negative or even highly positive  $\delta^{13}\text{C}_{\text{CO}_2}$  values of 0 to  $+6\%$  were obtained. These signatures are attributed to methanogenesis. Methanogenic origin of shallow water  $\text{CO}_2$  is corroborated by the mass balance calculation relating stable C isotope composition of  $\text{CO}_2$  and  $\text{CH}_4$  to the  $\delta^{13}\text{C}_{\text{OM}}$  of the precursor organic material. From the equation proposed by Corbett et al. (2013):

$$\delta^{13}\text{C}_{\text{OM}} = 0.5 \cdot \delta^{13}\text{C}_{\text{CO}_2} + 0.5 \cdot \delta^{13}\text{C}_{\text{CH}_4} \quad (4)$$

we derived  $\delta^{13}\text{C}_{\text{OM}}$  values ranging from  $-26.2$  to  $-29.9\%$ , which are close to the measured  $\delta^{13}\text{C}_{\text{TOC}}$  of  $-24.4$  to  $-29.1\%$  (Table 2) thus indicating that  $\delta^{13}\text{C}_{\text{CO}_2}$  fits well the expected stable C isotope composition of  $\text{CO}_2$  produced from the organic matter in the lakes' sediments.

Shallow water sites are less affected by oxidation, presumably due to location in wind-protected embayments and/or dissipation of water energy by macrophytes.

### The effect of ebullition on $\delta^{13}\text{C}_{\text{CH}_4}$ and $\delta^{13}\text{C}_{\text{CO}_2}$

The stable isotope composition of the gas can be influenced by the rate of ebullition. Ebullition itself causes rather low C fractionation, with a tendency for the dissolved forms of  $\text{CH}_4$  and  $\text{CO}_2$  ( $\text{CH}_{4\text{diss}}$  and  $\text{CO}_{2\text{diss}}$ , respectively) to be slightly enriched in  $^{12}\text{C}$  (Hornibrook et al. 2000). However, when methanogenically derived  $\text{CH}_4$  and  $\text{CO}_2$  are constantly removed from the sediments by intense ebullition  $\delta^{13}\text{C}$  in remaining gases becomes progressively heavier in accordance with the Rayleigh relationship (Whiticar 1999). Moreover, since the solubility of  $\text{CO}_2$  and  $\alpha_{\text{C}}$  for this reaction are higher than for  $\text{CH}_4$ , the increase in  $\delta^{13}\text{C}_{\text{CO}_2}$  is expected to be higher than in  $\delta^{13}\text{C}_{\text{CH}_4}$ . We believe that this process contributes to the variability in the stable C isotope composition of gases throughout the coastal lakes, because there are differences in the rate of ebullition as shown by the  $\text{CH}_4/\text{N}_2$  ratio. The shallower parts of the lakes display more intense ebullition as well as higher  $\delta^{13}\text{C}_{\text{CH}_4}$  and  $\delta^{13}\text{C}_{\text{CO}_2}$  compared with the deeper parts. On the other hand, the lower rate of ebullition in deeper parts of the lakes may be

responsible for the prolonged contact of CH<sub>4</sub> with oxygenated water and thus lead to more intense oxidation of CH<sub>4</sub>.

The effect of bioventilation on  $\delta^{13}\text{C}_{\text{CH}_4}$  and  $\delta^{13}\text{C}_{\text{CO}_2}$

It was shown earlier that the composition of gas may be modified due to ventilation by macrophytes (Fig. 3a). It has been recognized that the removal of CH<sub>4</sub> by macrophytes is an isotope fractionating process discriminating against <sup>13</sup>C and leaving residual CH<sub>4</sub> with higher  $\delta^{13}\text{C}_{\text{CH}_4}$  signatures (Chanton 2005). Whether or not there is an analogous effect for methanogenically derived CO<sub>2</sub> in the rhizosphere is uncertain, as is the magnitude of the isotope fractionation. On the other hand, the macrophytes are known to shift  $\delta^{13}\text{C}_{\text{CH}_4}$  towards higher values by the enhanced deposition of metabolizable OM in the proximity of vegetation (Blair 1998). The influence of macrophytes on the stable C isotope composition of CO<sub>2</sub> and CH<sub>4</sub> can be seen in Fig. 7, where there is a noticeable difference between vegetated and non-vegetated sites. The former have 3.6‰ higher  $\delta^{13}\text{C}_{\text{CH}_4}$  and 10.5‰ higher  $\delta^{13}\text{C}_{\text{CO}_2}$  values than the latter.

## Conclusions

This paper provides a comprehensive study of microbial gas production in the ecosystem of Polish coastal lakes located on the non-tidal Baltic coast. The molecular and stable isotope compositions of the gases show differences between the seven lakes studied and within each lake, due to variations in the biogeochemical processes. These are modulated by the overall complexity of coastal lakes, including the high biological activity, spatial and temporal salinity changes, the very high water column turbulence and vertical mixing of sediments. The increasing lake depth results in a depletion in CH<sub>4</sub> and CO<sub>2</sub> in the bubbles in favor of N<sub>2</sub> and O<sub>2</sub>. A large part of microbially produced CH<sub>4</sub> and CO<sub>2</sub> in the sediments is removed in the lake water column by the dissolution of rising bubbles and gas exchange with the ambient water. The aquatic macrophytes also affect the compositions of microbial gas. From our data it emerged that in vegetated parts of the lakes, the CH<sub>4</sub> is depleted in favor of CO<sub>2</sub> and that the

residual CH<sub>4</sub> and CO<sub>2</sub> are enriched in <sup>13</sup>C. The removal of CH<sub>4</sub> from the bubbles via dissolution and bioventilation acts as a primary source of the dissolved CH<sub>4</sub> pool in the water column of coastal lakes. Despite the fact that the coastal lakes display highly oxidizing conditions in the water column and that the bottom sediments are prone to intense mixing by wind waves, the CH<sub>4</sub> reveals rather low oxidation, except for the CH<sub>4</sub> produced in the deepest parts of the lakes. The oxidation of CH<sub>4</sub> in deeper waters seems to be related to lower rates of ebullition and thus longer exposure to oxygenated waters, as well as to the penetration of O<sub>2</sub> to the pore waters during vertical mixing of sediments.

In the seven lakes studied there is no clear relationship between salinity and the stable C and H isotope composition of sediment gas. It seems, however, that salinity may influence the molecular composition of hydrocarbons via preferential oxidation of CH<sub>4</sub>.

Given the remarkable dissolution of gas bubbles in the water column, the effect of salinity on CH<sub>4</sub> oxidation and the C isotope effects accompanying bioventilation both require further investigations to decipher the mechanisms driving these processes.

On the other hand, the data obtained in the current study will assist in the assessment of the emissions of CH<sub>4</sub> and CO<sub>2</sub> from coastal lakes. Our observations have provided the basis for establishing the representative monitoring sites in which reliable estimations of ebullitive and diffusive emission of gases from the lakes can be performed.

**Acknowledgements** The study was funded by the National Science Center (Poland) (Grant No. 2012/05/B/ST10/00295). The assistance of Tomasz Kurczaba, Paweł Młodkowski, and Paweł Kaczmarek during the field campaigns is greatly appreciated. The molecular and stable isotope compositions of sediment gas were determined by Tomasz Kowalski and Adam Kowalski (AGH UST Kraków, Poland).

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## Appendix

See Tables 3 and 4.

**Table 3** Molecular and stable isotope compositions of sediment gas from Polish coastal lakes

Date of collection	Sample name	CH <sub>4</sub> vol%	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	N <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	C <sub>HC</sub>	CDMI	$\delta^{13}\text{C}_{\text{CH}_4}$ VPDB (‰)	$\delta^{13}\text{C}_{\text{CO}_2}$	$\delta^2\text{H}_{\text{CH}_4}$	$\delta^{15}\text{N}_{\text{N}_2}$ Air (‰)	$\alpha_{\text{C}}$
<b>Lake Bukowo</b>														
05.2013	BUK-6*	58.70	0.00038	0.00097	37.4	3.23	0.52	43.481	0.9	-70.9	-21.1	-293	-0.1	1.054
	BUK-7*	85.44	0.00087	0.00059	6.02	0.39	8.26	58.521	8.8	-61.5	-5.5	-323	-0.1	1.060
08.2013	BUK-3	48.30	0.0003	0.00015	50.4	0.49	0.87	107.333	1.8	-77.9	-26.7	-291	0.2	1.055
	BUK-6*	74.95	0.00075	0.00022	22.8	0.09	2.11	77.268	2.7	-69.1	-18.1	-299	n.a.	1.055
11.2013	BUK-6*	79.80	0.00017	0.00012	17.4	0.23	2.51	275.172	3.0	-66.0	-14.7	-304	-0.5	1.055
	BUK 3*	87.10	0.0006	0.00011	10.1	0.30	2.5	122.676	2.8	-62.8	-14.1	-314	-0.8	1.052
02.2014	BUK-8	88.76	0.00013	0.00014	6.94	0.76	3.33	328.741	3.6	-63.3	-3.2	-309	-0.5	1.064
	BUK-6*	82.58	0.00177	0.00017	12.1	1.54	3.78	42.567	4.4	-66.0	-2.0	-289	n.a.	1.069
05.2014	BUK-3	84.14	0.00068	0.00006	10.3	1.50	4.09	113.703	4.6	-63.1	-2.4	-273	-2.1	1.065
	BUK-6*	83.61	0.0007	0.00012	10.8	0.42	5.23	101.963	5.9	-64.5	-6.1	-318	-0.6	1.062
07.2014	BUK-8	64.72	0.00047	0.00018	33.3	1.42	0.57	99.569	0.9	-75.3	-18.1	-303	-0.3	1.062
	BUK-3	64.70	0.00914	0.00018	29.1	5.5	0.68	6942	1.0	-64.2	-34.5	-317	-0.3	1.032
10.2014	BUK-6*	87.01	0.00954	0.00022	6.96	0.27	5.75	8915	6.2	-63.6	-6.9	-309	-0.7	1.060
	BUK-8	74.62	0.00963	0.00043	23.8	0.27	1.30	7417	1.7	-70.3	-36.3	-318	-0.3	1.036
02.2014	BUK-6*	88.65	0.00934	0.00028	4.5	0.24	6.60	9215	6.9	-61.6	-4.6	-307	0.1	1.061
	BUK-8	81.83	0.00945	0.00036	15.6	1.95	0.62	8341	0.8	-70.2	-20.1	-297	-0.1	1.054
<b>Lake Gardno</b>														
05.2013	GAR-1	65.50	0.00063	0.00075	32.4	0.17	2.05	47.464	3.0	-64.1	-17.4	-345	1.3	1.050
	GAR-2	56.75	0.00057	0.00061	41.4	1.10	0.55	48.093	1.0	-71.6	-21.5	-311	0.0	1.054
08.2013	GAR-3	67.04	0.00057	0.00087	31.1	1.29	0.57	46.556	0.8	-67.9	-29.3	-315	-0.2	1.041
	GAR-4	63.53	0.0006	0.0016	33.8	2.40	0.37	28.877	0.6	-69.4	-22.4	-307	-0.4	1.050
11.2013	GAR-5	87.13	0.00094	0.00057	10.3	0	2.53	57.702	2.8	-62.9	-11.0	-325	-0.1	1.055
	GAR-6	81.36	0.00084	0.00076	16.6	0	2.12	50.850	2.5	-67.2	-18.4	-309	0.4	1.052
02.2014	GAR-2	80.31	0.00061	0.00007	16.7	1.90	1.21	118.103	1.5	-64.3	-26.1	-345	n.a.	1.041
	GAR-3	84.71	0.00074	0.00012	10.2	3.27	1.87	98.500	2.2	-63.7	-18.4	-335	n.a.	1.048
02.2014	GAR-4	71.75	0.00067	0.00015	26.4	0.76	1.20	87.500	1.6	-66.3	-19.4	-342	n.a.	1.050
	GAR-2	64.76	0.00009	0.00006	32.6	2.07	0.39	431.733	0.6	-71.1	-40.6	-319	0.0	1.033
02.2014	GAR-3	80.65	0.00009	0.00011	16.9	1.45	0.90	403.250	1.1	-63.9	-38.4	-313	-0.4	1.027
	GAR-4	73.32	0.00013	0.00016	23.0	2.91	0.77	252.828	1.0	-70.2	-29.5	-314	-0.7	1.044
02.2014	GAR-2	67.54	0.00189	0.00004	29.6	2.73	0.13	34.995	0.2	-70.1	-12.7	-312	n.a.	1.062
	GAR-4	67.49	0.00041	0.00006	27.6	4.87	0.05	143.596	0.1	-70.2	-13.1	-309	n.a.	1.061



Table 3 continued

Date of collection	Sample name	CH <sub>4</sub> vol%	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	N <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	C <sub>HC</sub>	CDMI	δ <sup>13</sup> C <sub>CH<sub>4</sub></sub> VPDB (‰)	δ <sup>13</sup> C <sub>CO<sub>2</sub></sub>	δ <sup>2</sup> H <sub>CH<sub>4</sub></sub>	δ <sup>15</sup> N <sub>N<sub>2</sub></sub> Air (‰)	α <sub>C</sub>
05.2014	GAR-2	65.67	0.0004	0.0001	32.0	1.84	0.47	131,340	0.7	-70.0	-15.2	-323	-0.2	1.059
	GAR-4	65.44	0.0005	0.0002	32.1	1.78	0.64	93,486	1.0	-70.4	-22.6	-291	-0.5	1.051
	GAR-2	73.38	0.0092	0.0001	21.6	2.92	2.06	7890	2.7	-64.3	-18.2	-331	-0.2	1.049
	GAR-4	76.08	0.0093	0.0005	22.2	1.30	0.37	7763	0.5	-70.3	-20.5	-318	-0.5	1.054
10.2014	GAR-2	82.35	0.0092	0.0001	15.5	1.16	0.95	8855	1.1	-65.0	-15.6	-321	-0.1	1.053
	GAR-4	78.11	0.0095	0.0003	19.9	1.60	0.34	7970	0.4	-69.4	-18.6	-315	-0.2	1.055
Lake Jamno														
05.2013	JAM-1	65.06	0.00061	0.00066	32.7	0	2.14	51,228	3.2	-66.4	-20.1	-341	0.6	1.050
	JAM-2	64.20	0.00081	0.00045	34.1	0	1.66	50,952	2.5	-68.1	-23.5	-317	0.3	1.048
	JAM-4	70.28	0.0006	0.00066	24.0	2.88	2.68	55,778	3.7	-66.2	-17.0	-289	-0.6	1.053
	JAM-5	64.07	0.00076	0.00017	32.8	1.19	1.80	68,892	2.7	-72.3	-26.5	-292	1.7	1.049
	JAM-1	86.92	0.00118	0.00014	8.89	0	4.22	65,848	4.6	-66.1	-8.8	-299	n.a.	1.061
08.2013	JAM-2	83.75	0.00062	0.00005	11.0	0.13	5.19	125,000	5.8	-59.9	-10.5	-344	n.a.	1.053
	JAM-4	78.79	0.00074	0.00017	18.9	0.16	1.86	86,582	2.3	-65.1	-19.5	-312	n.a.	1.049
	JAM-5	88.09	0.00095	0.00015	5.61	0.08	6.39	80,082	6.8	-60.9	-5.4	-316	n.a.	1.059
	JAM-6	53.28	0.0006	0.00009	44.7	0.15	1.80	77,217	3.3	-68.8	-35.1	-293	-0.1	1.036
	JAM-1	81.29	0.00077	0.00007	15.8	0.38	2.29	96,774	2.7	-64.5	-14.8	-287	-0.6	1.053
	JAM-5	65.62	0.0003	0.00012	32.2	1.02	1.20	156,238	1.8	-69.3	-51.5	-282	0.6	1.019
02.2014	JAM-1	66.73	0.00044	0.00006	27.8	3.87	1.61	133,460	2.4	-65.7	-10.7	-284	n.a.	1.059
	JAM-5	76.94	0.00067	0.00012	19.7	1.03	2.33	97,392	2.9	-66.3	-7.8	-287	n.a.	1.063
	JAM-1	51.80	0.00049	0.00011	46.6	0.22	1.44	86,333	2.7	-69.5	-34.2	-297	n.a.	1.038
	JAM-5	83.70	0.00084	0.00014	11.9	0.22	4.18	85,408	4.8	-63.7	-8.0	-292	-0.8	1.060
	JAM-6	45.50	0.0009	0.00008	53.0	0.45	1.01	46429	2.2	-71.0	-18.7	-296	0.0	1.056
07.2014	JAM-1	84.98	0.00965	0.00017	11.3	0.03	3.68	8654	4.2	-64.0	-11.6	-303	-0.5	1.056
	JAM-6	64.82	0.00934	0.00019	33.1	0.80	1.25	6802	1.9	-70.6	-35.9	-310	-0.1	1.037
Lake Kopan														
05.2013	KOP-1*	47.38	0.00053	0.00044	50.9	1.00	0.62	48,845	1.3	-66.1	-17.4	-324	0.0	1.052
	KOP-2	50.76	0.00032	0.00056	47.0	1.58	0.67	57,682	1.3	-70.0	-20.0	-291	0.3	1.054
	KOP-3	59.79	0.00072	0.00051	38.2	0.85	0.9	48,610	1.5	-61.7	-18.5	-306	-0.4	1.046
	KOP-4*	84.78	0.00079	0.0004	5.4	0.21	9.45	71,244	10.0	-55.1	-0.8	-320	0.1	1.057

Table 3 continued

Date of collection	Sample name	CH <sub>4</sub> vol%	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	N <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	C <sub>HC</sub>	CDMI	$\delta^{13}\text{C}_{\text{CH}_4}$ VPDB (‰)	$\delta^{13}\text{C}_{\text{CO}_2}$	$\delta^2\text{H}_{\text{CH}_4}$	$\delta^{15}\text{N}_{\text{N}_2}$ Air (‰)	$\alpha_{\text{C}}$
08.2013	KOP-1*	80.38	0.00118	0.00006	17.2	0.21	2.16	64.823	2.6	-57.4	-14.9	-339	n.a.	1.045
	KOP-2	56.17	0.00037	0.00008	42.2	0.44	1.31	124.822	2.3	-64.6	-44.9	-296	n.a.	1.021
	KOP-4*	74.20	0.0006	0.00008	8.01	1.44	16.29	109.118	18.0	-55.4	3.0	-309	n.a.	1.062
	KOP-1*	86.68	0.00018	0.00007	4.51	0.41	8.42	346.720	8.9	-58.0	3.0	-291	-0.4	1.065
11.2013	KOP-4*	87.69	0.00017	0.00011	8.98	0.79	2.27	313.179	2.5	-60.9	-11.1	-281	-0.6	1.053
	KOP-4*	82.85	0.00033	0.00006	11.1	1.61	4.48	212.436	5.1	-58.5	1.4	-270	n.a.	1.064
	KOP-1*	82.51	0.00072	0.00005	6.00	0.88	10.61	107.156	11.4	-59.7	6.0	-269	0.3	1.070
	KOP-4*	85.72	0.00058	0.00008	5.11	0.76	8.41	129.879	8.9	-57.8	1.8	-298	-0.6	1.063
07.2014	KOP-1*	82.62	0.00921	0.00016	7.02	0.23	10.11	8818	10.9	-59.8	0.1	-290	0.3	1.064
	KOP-4*	87.23	0.00933	0.00021	7.50	0.10	5.16	9144	5.6	-58.0	-6.3	-279	-1.1	1.055
Lake Łebsko														
05.2013	LEB-1*	58.96	0.00016	0.00025	36.4	1.50	3.03	143.805	4.9	-59.5	-10.8	-355	-1.3	1.052
	LEB-2*	77.68	0.0011	0.0012	15.8	0.23	6.11	33.774	7.3	-65.6	-7.5	-304	0.5	1.062
	LEB-3*	59.71	0.00064	0.00037	38.3	0.34	1.6	59.119	2.6	-62.5	-20.3	-378	0.7	1.045
	LEB-4*	46.88	0.0003	0.00037	50.8	1.04	1.52	69.970	3.1	-62.3	-16.6	-335	-0.2	1.049
08.2013	LEB-3	81.19	0.00075	0.00008	16.7	0.18	1.69	97.819	2.0	-63.2	-30.3	-363	n.a.	1.035
	LEB-4*	62.87	0.00042	0.00039	36.2	0.26	0.58	77.617	0.9	-72.3	-39.0	-341	0.2	1.036
	LEB-5	64.02	0.00031	0.00013	33.0	2.52	0.64	145.500	1.0	-65.7	-25.2	-353	n.a.	1.043
	LEB-7	77.99	0.00069	0.00024	20.0	0.28	1.48	83.860	1.9	-67.6	-21.5	-326	n.a.	1.049
	LEB-4*	64.97	0.00031	0.00004	32.5	0.82	1.55	185.629	2.3	-60.4	-17.8	-328	-1.1	1.045
02.2014	LEB-5	78.31	0.00015	0.00013	17.4	3.70	0.64	279.679	0.8	-66.1	-23.4	-274	-0.6	1.046
	LEB-7	69.91	0.00018	0.00003	28.0	0.32	1.54	332.905	2.2	-64.0	-23.7	-355	-0.6	1.043
	LEB-4*	68.09	0.00158	0.00008	28.9	0.90	2.06	41.018	2.9	-59.8	-11.3	-344	n.a.	1.052
	LEB-5*	68.41	0.00045	0.00009	28.2	1.55	1.82	126.685	2.6	-65.9	-12.0	-307	n.a.	1.058
	LEB-4*	78.68	0.00062	0.0002	16.5	3.70	1.16	95.951	1.5	-64.2	-8.2	-270	-0.8	1.060
	LEB-5*	55.49	0.00038	0.00005	42.8	0.81	0.9	129.047	1.6	-64.3	-17.5	-357	0.0	1.050
	LEB-7	75.46	0.00063	0.00019	20.7	3.52	0.33	92.024	0.4	-66.5	-19.0	-261	-1.1	1.051
07.2014	LEB-7	72.33	0.0094	0.00032	26.1	0.06	1.49	7441	2.0	-68.2	-24.1	-302	-0.5	1.047
	LEB-4*	86.08	0.00932	0.00017	8.78	0.93	4.2	9071	4.7	-57.4	-5.9	-335	-0.2	1.055
Lake Resko Przymorskie														
08.2013	RP-1	48.93	0.00036	0.000187	50.3	0.17	0.71	89.452	1.4	-74.3	-24.9	-327	-0.2	1.053
	RP-5*	69.65	0.00064	0.00033	28.7	0.18	1.27	71.804	1.8	-74.5	-38.5	-307	n.a.	1.039

Table 3 continued

Date of collection	Sample name	CH <sub>4</sub> vol%	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	N <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	C <sub>HC</sub>	CDMI	$\delta^{13}\text{C}_{\text{CH}_4}$ VPDB (‰)	$\delta^{13}\text{C}_{\text{CO}_2}$	$\delta^2\text{H}_{\text{CH}_4}$	$\delta^{15}\text{N}_{\text{N}_2}$ Air (‰)	$\alpha_{\text{C}}$
11.2013	RP-5*	79.19	0.00078	0.00039	18.4	0.28	1.86	67.684	2.3	-65.7	-17.6	-322	-0.3	1.052
02.2014	RP-5*	64.17	0.00044	0.00013	28.9	4.25	2.68	112.579	4.0	-64.0	-13.7	-292	n.a.	1.054
05.2014	RP-5*	80.07	0.00075	0.0003	14.7	1.66	3.61	76.257	4.3	-67.7	-12.7	-292	-0.6	1.059
07.2014	RP-5*	80.01	0.00969	0.00067	18.59	0.05	1.34	7723	1.6	-74.1	-30.9	-282	-0.9	1.047
10.2014	RP-5*	88.58	0.00951	0.00045	7.9	0.01	3.51	8894	3.8	-66.1	-11.1	-287	-0.1	1.059
LAKE WICKO														
05.2013	WIC-1*	80.57	0.00073	0.0019	11.7	0.45	7.09	30.635	8.1	-64.4	-2.2	-286	0.2	1.066
	WIC-2*	80.16	0.00088	0.0004	16.2	0.75	2.79	62.625	3.4	-65.8	-4.7	-275	-0.4	1.065
	WIC-5	24.48	0.00014	0	66.86	8.2	0.61	174.857	2.4	-58.4	-23.1	-341	-0.5	1.038
08.2013	WIC-1*	79.41	0.0008	0.00009	17.2	0.27	2.83	89.225	3.4	-65.7	-4.5	-294	n.a.	1.066
	WIC-2*	67.85	0.00084	0.00008	30.5	0.23	1.21	73.750	1.8	-68.6	-31.6	-319	0.2	1.040
	WIC-8	60.68	0.00035	0.00006	37.8	0.70	0.77	148.000	1.3	-69.3	-38.0	-303	n.a.	1.034
11.2013	WIC-1*	82.86	0.00021	0.00004	11.7	0.36	4.93	331.440	5.6	-62.4	-3.3	-286	-0.9	1.063
	WIC-2*	62.65	0.00019	0.00003	35.2	0.96	1.04	284.773	1.6	-68.6	-40.6	-263	-0.4	1.030
	WIC-8	65.89	0.00009	0.00004	30.6	2.79	0.69	506.846	1.0	-68.2	-23.8	-280	-0.7	1.048
02.2014	WIC-1*	69.24	0.00053	0.00003	25.3	2.68	2.76	123.643	3.8	-63.6	-5.9	-285	n.a.	1.062
05.2014	WIC-1*	67.08	0.00105	0.00004	30.4	0.41	2.09	61.541	3.0	-67.4	-7.0	-274	-0.8	1.065
	WIC-8	53.05	0.00043	0.00004	44.2	2.24	0.49	112.872	0.9	-71.9	-17.4	-298	-0.3	1.059
07.2014	WIC-1*	75.25	0.00926	0.0001	22.2	0.26	2.32	8040	3.0	-66.2	-9.3	-294	-0.5	1.061
	WIC-2*	82.14	0.00919	0.00011	12.3	0.30	5.22	8832	6.0	-63.1	-3.7	-297	-0.2	1.063

n.a. Not analysed

\* Vegetated sites  $\alpha_{\text{CO}_2\text{-CH}_4}$  - apparent C isotope fractionation factor

$$\alpha_{\text{CO}_2\text{ CH}_4} = \frac{\delta^{13}\text{C}(\text{CO}_2) + 1000}{\delta^{13}\text{C}(\text{CH}_4) + 1000}$$

**Table 4** Molecular composition of higher hydrocarbons in the sediment gas from Polish coastal lakes

Date of collection	Sample name	$i\text{-C}_4$ $10^{-4}$ vol%	$n\text{-C}_4$	$\text{C}_2\text{H}_2$	<i>Trans</i> -2-buten	<i>Cis</i> -2-buten	<i>i</i> - $\text{C}_5$	$n\text{-C}_5$	$n\text{-C}_6$	$\text{C}_2\text{H}_4$	$\text{C}_3\text{H}_6$	$\text{C}_4\text{H}_8$
<b>Lake Bukowo</b>												
05.2013	BUK-6	4.85	6.89	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	BUK-7	0	5.81	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
08.2013	BUK-3	0.39	2.21	n.d.	0.11	0.28	0.32	0.32	n.d.	n.d.	0.04	n.d.
	BUK-6	0.97	4.42	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
11.2013	BUK-6	0.35	2.94	n.d.	n.d.	n.d.	n.d.	0.55	n.d.	n.d.	n.d.	n.d.
	BUK-3	0.24	2.52	2.42	n.d.	n.d.	0.29	0.12	n.d.	1.23	0.01	n.d.
	BUK-8	0.38	3.78	n.d.	n.d.	n.d.	0.44	n.d.	0.02	n.d.	n.d.	n.d.
02.2014	BUK-6	0.54	3.51	6.18	n.d.	n.d.	n.d.	n.d.	n.d.	5.25	n.d.	n.d.
05.2014	BUK-3	0.78	0.3	n.d.	n.d.	n.d.	n.d.	0.71	n.d.	n.d.	n.d.	n.d.
	BUK-6	0	1.69	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	BUK-8	0.41	1.41	n.d.	n.d.	n.d.	0.29	0.5	n.d.	n.d.	n.d.	n.d.
07.2014	BUK-3	0.38	2.1	n.d.	n.d.	n.d.	0.2	0.16	n.d.	0.13	n.d.	n.d.
	BUK-6	0.54	2.57	n.d.	n.d.	n.d.	n.d.	0.43	n.d.	n.d.	n.d.	n.d.
	BUK-8	0.58	2.89	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.78	n.d.	n.d.
10.2014	BUK-6	0.89	2.66	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	BUK-8	0.33	2.57	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.0	n.d.	n.d.
<b>Lake Gardno</b>												
05.2013	GAR-1	13.13	5.51	n.d.	n.d.	n.d.	0.76	0	n.d.	n.d.	n.d.	n.d.
	GAR-2	7.95	4.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.37	n.d.	n.d.
	GAR-3	8.36	6.22	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	GAR-4	10.79	10.73	n.d.	n.d.	n.d.	0.48	n.d.	n.d.	n.d.	n.d.	n.d.
	GAR-5	6.81	4.51	n.d.	n.d.	n.d.	n.d.	0.21	n.d.	n.d.	n.d.	n.d.
	GAR-6	12.16	4.78	n.d.	n.d.	n.d.	0.68	0	n.d.	n.d.	n.d.	n.d.
08.2013	GAR-2	1.13	2.14	n.d.	n.d.	n.d.	0.72	n.d.	n.d.	n.d.	n.d.	n.d.
	GAR-3	1.26	2.52	n.d.	n.d.	n.d.	0.68	n.d.	n.d.	n.d.	n.d.	n.d.
	GAR-4	1.48	4.4	n.d.	n.d.	n.d.	1.08	0.65	n.d.	n.d.	n.d.	n.d.
11.2013	GAR-2	0.91	1.02	n.d.	n.d.	n.d.	0.55	n.d.	0.01	n.d.	n.d.	n.d.
	GAR-3	1.13	2.42	n.d.	n.d.	n.d.	0.37	0.12	0.03	n.d.	n.d.	n.d.
	GAR-4	1.2	3.73	n.d.	n.d.	n.d.	0.56	n.d.	n.d.	n.d.	n.d.	n.d.
02.2014	GAR-2	0.95	1.14	n.d.	n.d.	n.d.	n.d.	0.56	n.d.	n.d.	n.d.	n.d.
	GAR-4	0.97	2.5	n.d.	n.d.	n.d.	n.d.	0.39	n.d.	n.d.	n.d.	n.d.

Table 4 continued

Date of collection	Sample name	$i\text{-C}_4$ $10^{-4}$ vol%	$n\text{-C}_4$	$\text{C}_2\text{H}_2$	<i>Trans</i> -2-buten	<i>Cis</i> -2-buten	<i>i</i> - $\text{C}_5$	<i>n</i> - $\text{C}_5$	<i>n</i> - $\text{C}_6$	$\text{C}_2\text{H}_4$	$\text{C}_3\text{H}_6$	$\text{C}_4\text{H}_8$	
05.2014	GAR-2	1.3	0.89	n.d.	n.d.	n.d.	n.d.	0.84	n.d.	n.d.	n.d.	n.d.	
	GAR-4	1.56	1.89	n.d.	n.d.	n.d.	0.56	n.d.	n.d.	n.d.	n.d.	n.d.	
	07.2014	GAR-2	1.69	0.97	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		GAR-4	2.58	4.38	n.d.	n.d.	n.d.	n.d.	0.68	n.d.	0.08	n.d.	n.d.
		GAR-2	1.78	0.94	n.d.	n.d.	n.d.	n.d.	0.32	n.d.	n.d.	n.d.	n.d.
		GAR-4	1.99	2.76	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Lake Jamno	05.2013	JAM-1	2.72	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
		JAM-2	2.59	4.84	n.d.	n.d.	n.d.	n.d.	n.d.	0.44	n.d.	n.d.	n.d.
		JAM-4	4.92	4.67	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		JAM-5	3.99	8.88	n.d.	n.d.	n.d.	n.d.	6.8	n.d.	n.d.	n.d.	n.d.
		JAM-1	2.72	2.73	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		JAM-2	2.59	4.84	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.44	n.d.	n.d.
	11.2013	JAM-4	4.92	4.67	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		JAM-5	3.99	8.88	n.d.	n.d.	n.d.	n.d.	6.8	n.d.	n.d.	n.d.	n.d.
		JAM-6	0.44	1.84	1.51	n.d.	n.d.	0.37	0.56	n.d.	n.d.	n.d.	n.d.
		JAM-1	0.26	1.42	2.99	n.d.	n.d.	n.d.	n.d.	n.d.	2.01	n.d.	n.d.
		JAM-5	0.4	1.39	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		JAM-1	0.27	1.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
05.2014	JAM-5	0.71	2.07	n.d.	n.d.	n.d.	n.d.	0.34	n.d.	3.08	n.d.	n.d.	
	JAM-1	0	0.75	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
	JAM-5	0.97	1.07	0.77	n.d.	n.d.	n.d.	n.d.	n.d.	1.0	n.d.	n.d.	
	JAM-6	0.54	0.53	2.83	n.d.	n.d.	n.d.	0.55	n.d.	3.62	n.d.	n.d.	
	JAM-1	0.93	1.14	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.76	n.d.	n.d.	
	JAM-8	0.88	1.58	n.d.	n.d.	n.d.	n.d.	0.29	n.d.	n.d.	n.d.	n.d.	
Lake Kopan	05.2013	KOP-1	0	2.62	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
		KOP-2	5.22	3.69	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
		KOP-3	3.14	3.93	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
	08.2013	KOP-4	3.09	0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
		KOP-1	n.d.	1.1	0.79	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	

Table 4 continued

Date of collection	Sample name	$i\text{-C}_4$ $10^{-4}$ vol%	$n\text{-C}_4$	$\text{C}_2\text{H}_2$	<i>Trans</i> -2-buten	<i>Cis</i> -2-buten	<i>i</i> - $\text{C}_5$	$n\text{-C}_5$	$n\text{-C}_6$	$\text{C}_2\text{H}_4$	$\text{C}_3\text{H}_6$	$\text{C}_4\text{H}_8$
11.2013	KOP-2	0.82	1.45	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	KOP-4	0.68	1.75	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	KOP-1	0.81	1.46	n.d.	n.d.	n.d.	0.83	n.d.	n.d.	n.d.	n.d.	n.d.
	KOP-4	1.08	2.08	n.d.	n.d.	n.d.	0.66	n.d.	n.d.	n.d.	n.d.	n.d.
	KOP-4	0.44	1.19	n.d.	n.d.	n.d.	n.d.	0.25	n.d.	n.d.	n.d.	n.d.
07.2014	KOP-1	0.6	0.4	0.26	n.d.	n.d.	n.d.	n.d.	n.d.	0.55	n.d.	n.d.
	KOP-4	0.69	0.74	n.d.	n.d.	n.d.	0.45	0.18	n.d.	n.d.	n.d.	n.d.
	KOP-1	0.67	1.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.14	n.d.	n.d.
	KOP-4	1.44	1.71	n.d.	n.d.	n.d.	n.d.	0.52	n.d.	0.12	n.d.	n.d.
Lake Lebsko	LEB-1	n.d.	2.17	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0	n.d.	n.d.
	LEB-2	7.59	6.27	n.d.	n.d.	n.d.	n.d.	0.95	n.d.	1.1	n.d.	n.d.
	LEB-3	1.98	2.72	n.d.	n.d.	n.d.	n.d.	4.3	n.d.	2.88	n.d.	n.d.
	LEB-4	0	2.55	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	LEB-3	0.42	3.1	0.3	n.d.	0.53	0.5	0.64	n.d.	n.d.	n.d.	n.d.
	LEB-4	n.d.	4.63	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	LEB-5	0.74	6.42	n.d.	n.d.	0.29	0.7	0.51	n.d.	n.d.	n.d.	n.d.
	LEB-7	0.95	5.33	n.d.	n.d.	n.d.	0.67	n.d.	n.d.	n.d.	n.d.	n.d.
	LEB-4	0.2	0.87	n.d.	n.d.	n.d.	0.16	0.2	n.d.	n.d.	0.08	n.d.
	LEB-5	0.92	0.53	n.d.	n.d.	n.d.	0.4	n.d.	n.d.	n.d.	n.d.	n.d.
02.2014	LEB-7	0	0.84	n.d.	n.d.	n.d.	n.d.	0.16	n.d.	n.d.	n.d.	n.d.
	LEB-4	0	1.87	5.75	n.d.	n.d.	n.d.	n.d.	n.d.	8.06	n.d.	n.d.
	LEB-7	0.56	1.73	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	LEB-4	0	1.87	5.75	n.d.	n.d.	n.d.	n.d.	n.d.	8.06	n.d.	n.d.
	LEB-7	0.56	1.73	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
07.2014	LEB-7	1.46	0.33	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	LEB-7	1.39	2.22	n.d.	n.d.	n.d.	n.d.	0.27	n.d.	0.69	n.d.	n.d.
	LEB-4	0.27	0.41	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.01	n.d.	n.d.
Lake Wicko	WIC-1	38.51	31.54	n.d.	n.d.	n.d.	9.04	5.61	n.d.	n.d.	n.d.	3.22
	WIC-2	3.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	WIC-5	0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table 4 continued

Date of collection	Sample name	$i\text{-C}_4$ $10^{-4}$ vol%	$n\text{-C}_4$	$\text{C}_2\text{H}_2$	<i>Trans</i> -2-buten	<i>Cis</i> -2-buten	<i>i</i> - $\text{C}_5$	<i>n</i> - $\text{C}_5$	<i>n</i> - $\text{C}_6$	$\text{C}_2\text{H}_4$	$\text{C}_3\text{H}_6$	$\text{C}_4\text{H}_8$
08.2013	WIC-1	1.92	3.3	n.d.	n.d.	n.d.	6.01	4.77	1.78	n.d.	n.d.	n.d.
	WIC-2	1.26	1.4	1.7	n.d.	n.d.	1.15	n.d.	n.d.	n.d.	n.d.	n.d.
11.2013	WIC-8	0.86	1.09	n.d.	n.d.	n.d.	0.81	0.31	n.d.	n.d.	n.d.	n.d.
	WIC-1	0	1.99	1.45	n.d.	n.d.	2.83	2.18	0.81	n.d.	n.d.	n.d.
	WIC-2	0.38	0.13	0.33	n.d.	n.d.	0.17	n.d.	n.d.	n.d.	n.d.	n.d.
	WIC-8	0.54	0.59	n.d.	n.d.	n.d.	0.38	n.d.	n.d.	n.d.	n.d.	n.d.
02.2014	WIC-1	0.14	0.17	n.d.	n.d.	n.d.	n.d.	0.06	n.d.	n.d.	n.d.	n.d.
05.2014	WIC-1	0.39	0.06	3.67	n.d.	n.d.	n.d.	n.d.	n.d.	4.88	n.d.	n.d.
	WIC-8	0.81	0.19	n.d.	n.d.	n.d.	0.81	0.29	n.d.	n.d.	n.d.	n.d.
07.2014	WIC-1	1.05	0.43	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	WIC-2	1.56	0.4	n.d.	n.d.	n.d.	n.d.	0.49	n.d.	n.d.	n.d.	n.d.
Lake Resko Przymorskie												
08.2013	RP-1	0.14	2.13	n.d.	n.d.	0.1	0.1	0.1	n.d.	n.d.	0.09	n.d.
	RP-5	n.d.	3.2	n.d.	n.d.	n.d.	0.21	0.33	n.d.	n.d.	n.d.	n.d.
11.2013	RP-5	0.61	4.03	n.d.	n.d.	n.d.	1.25	1.11	0.22	n.d.	n.d.	n.d.
	RP-5	0.05	2.06	n.d.	n.d.	n.d.	n.d.	0.11	n.d.	n.d.	n.d.	n.d.
02.2014	RP-5	0	2.28	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
05.2014	RP-5	0.15	3.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
07.2014	RP-5	0.3	3.27	n.d.	n.d.	n.d.	n.d.	0.29	n.d.	n.d.	n.d.	n.d.
10.2014	RP-5	0.3	3.27	n.d.	n.d.	n.d.	n.d.	0.29	n.d.	n.d.	n.d.	n.d.

*n.d.* Not detected

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