Greenhouse gas emissions from Baltic coastal lakes

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HIGHLIGHTS
• Diffusive emissions of GHGs from coastal lakes on a non-tidal coast were estimated.
• Coastal lakes act as net sources of CH₄, CO₂ and N₂O to the atmosphere.
• GHG concentrations in coastal lakes waters controlled by temperature, salinity, water depth and wind fetch.
• Diffusive emissions of GHGs from coastal lakes display dependence on catchment area/lake area and lake surface area.

GRAPHICAL ABSTRACT

Abstract
Coastal lakes (CL) act as limnetic-β-oligohaline systems located on non-tidal coastlines in fresh and salt water mixing zone. Owing to considerable terrestrial nutrient input and a high autochthonous productivity CLs release greenhouse gases (GHG) to the ambient atmosphere, however, neither emission from the system was assessed nor controls on the emission were recognized so far. In this study we attempted to quantify diffusive emissions of CH₄, CO₂ and N₂O from CLs based on data collected from seven lakes located on a south coast of the Baltic Sea in Poland. Lake water samples were collected with quarterly resolution along salinity, water depth and wind fetch gradients. From our data it emerged that the concentrations of GHGs were determined by temperature. CH₄ showed dependence on salinity, lake water depth and wind fetch. N₂O was controlled by dissolved O₂ and NO₃⁻ and CO₂ was largely related to wind fetch. It also appeared that concentrations of N₂O and CO₂ were influenced by terrestrial nutrient input. The mean fluxes of CH₄, CO₂ and N₂O for the whole system were 21.7 mg·m⁻²·d⁻¹, 12.7 g·m⁻²·d⁻¹ and 0.74 mg·m⁻²·d⁻¹, respectively which was equivalent to 7.9 g CH₄·m⁻²·y⁻¹, 4.6 kg CO₂·m⁻²·y⁻¹ and 269 mg N₂O·m⁻²·y⁻¹. CH₄ and N₂O were released throughout the year and CO₂ was predominantly emitted during winter. We showed that diffusive emissions of the GHGs showed relationships to the surface area of the lakes as well as the ratio of catchment area to lake area (CA/LA). The study would benefit from further extension with higher resolution analyses of the lakes over longer timescales and quantification of ebullitive GHG emission (CH₄ in particular).

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1. Introduction

Ongoing global environmental changes are triggered by the accumulation of atmospheric greenhouse gases (GHGs) such as CO₂, CH₄ and N₂O in the troposphere which lead to climate warming. In turn,
atmospheric heat is conveyed to water ecosystems, ocean in particular, which fuels microbial activity therein and further strengthens CO₂, CH₄ and N₂O emissions to the ambient air thus creating a positive feedback between climate and GHG production (Avery et al., 2003; Scheffer et al., 2006; Frank et al., 2010; Xiao et al., 2019). The GHG emissions from different aquatic systems and their long-term trends have well been recognized (Seitzinger et al., 2000; Prather et al., 2001; Borges et al., 2005; Tranvik et al., 2009; Borges and Abril, 2012; Kirschke et al., 2013; Holgerson and Raymond, 2016; Xiao et al., 2020b), however, there is still a debate as to the effectiveness of different ecosystems in producing GHGs, and their contributions to the global budget of GHGs.

Natural production of GHGs relies on the availability of degradable organic matter as well as its oxidizing agents (Capone and Kiene, 1988). With this respect along salinity gradient rates and mechanisms of GHGs production change considerably. Marine sediments have low albeit labile organic matter, which is mainly decomposed via sulphate reduction (Whitehill, 1999; Jørgensen and Parkes, 2010). The overall effect is that CO₂ rather than CH₄ production is favoured. On the contrary, organic matter in freshwater lakes displays rather low reactivity but, due to low sulphate concentrations, it is preferentially degraded by fermentation resulting in the build-up of methane. N₂O production is in general much lower than CO₂ and CH₄ but owing to higher N₂O availability in freshwaters it shows a landward increase although many irregularities exist in this general trend (Seitzinger et al., 2000; Law, 2009).

Estuaries are among the most bioproductive ecosystems (Cloern et al., 2014) and are supplied by considerable terrestrial input. These two factors contribute to a high accumulation of organic C in estuaries (of moderate reactivity; Capone and Kiene, 1988). On the other hand, however, location of estuaries in between salt- and freshwater endmembers creates spatial and temporal hydrochemical variability therein thus resulting in a complexity of GHG forming processes and raising differences between and within particular estuaries (Borges and Abril, 2012; Woszczyk et al., 2016). Generalizations on a global scale clearly show that estuaries act as effective GHG emitters, CO₂ in particular, as they release 0.27–0.60 Pg CO₂·C·y⁻¹, which is ca. 30% of the global emission from water systems (Borges and Abril, 2012) and 2–6 times more than the emission from rivers and inland lakes (Borges et al., 2006). The contribution of estuaries to the global budget of CH₄ and N₂O is minor albeit non negligible given that the areal share of estuaries is rather low. The estuarine CH₄ and N₂O fluxes are estimated to 0.8–6.6 Tg CH₄·y⁻¹ (Borges and Abril, 2012) and 0.7 Tg N₂O·y⁻¹ (Seitzinger et al., 2000), which is equivalent to 0.5–4% and 1.8% of global emissions from natural sources, respectively.

Estuaries can be classified into different types distinguished based on their physical and chemical features (Dürr et al., 2011). On non-tidal coastlines lagoon-type estuaries predominate and on the coast of south Baltic these lagoons are referred to as coastal lakes, intermittently closed and open lakes, and lagoons (ICOLLS; Astel et al., 2016) or quasi-estuaries (Cieśliński and Drwal, 2005). The latter term is proposed because, unlike typical estuaries, the lakes are only episodically penetrated by brackish waters from the Baltic Sea and consequently they act as limnetic–fl-oligohaline systems (Astel et al., 2016; Obolewski et al., 2018b) with very weak salinity gradients (Cieśliński and Drwal, 2005). While biogeochemistry of estuaries with permanent connection to the sea received much attention (Borges and Abril, 2012 and references therein) far less research effort has been devoted to ICOLLS. The ICOLLS are indeed quite rare (ca. 3% of all estuaries) and are concentrated in mid-latitudes (McSweeney et al., 2017). However, these ecotone systems display a high vulnerability to human pressure and environmental change (Bechtel et al., 2007; Schallenberg et al., 2010; Obolewski et al., 2018a). Currently, in face of the observed sea level rise coastal areas worldwide are exposed to enhanced saltwater ingressions and salinization of surface waters (Nichols and Cazenave, 2010). We hypothesize that ICOLLS, generally freshwater systems influenced by incidental saltwater inflows, can act as a test case of possible biogeochemical processes in coastal zone affected by long-term environmental perturbations.

The present paper provides a comprehensive data set on GHG production of coastal lakes. The aim of this research was to broaden the knowledge of the genesis and distribution of CO₂, CH₄ and N₂O in the lakes, with special attention to i) fluxes of GHGs to the atmosphere and ii) controls over GHG distribution in time and space. To achieve this we investigated seven coastal lakes along the south Baltic area. GHGs concentrations were determined in each lake during different seasons and analyzed in relation to lake water depth, salinity, temperature and wind fetch. Our results provide new insights into the GHGs emission from estuaries and its conditions.

2. Study area

The studied coastal lakes are distributed along 150 km-long section of the Baltic coast in Poland (Fig. 1). These lakes are relatively large and very shallow (mean water depth is below 2 m) (Table 1), which, in combination with the orientation parallel to the predominant wind directions, results in their high sensitivity to wind-driven mixing of water and sediments, and consequently causes high water turbulence (Woszczyk et al., 2014, 2016, 2017). Owing to their connection to the Baltic, most of the lakes have permanently or episodically brackish water conditions; however, the salinity displays spatial and temporal variability (Table 1). Average salinity of coastal lakes (expressed as chloride concentrations) is 703 ± 924 mg Cl⁻·L⁻¹, however, median salinity is as low as 131 mg Cl⁻·L⁻¹ (Astel et al., 2016). The coastal lakes are largely flow-through lakes and horizontal water exchange is the predominating component of the water balance (Cieśliński et al., 2016; Chlost, 2019). The water exchange index for coastal lakes varies between 0.8 and 9.7 (Cieśliński et al., 2016; Table 1) indicating that lake water is replaced completely by potamic water within 0.1–1.25 year. The potamic contribution to the total budget of the lakes is estimated to c.a. 45–75% while the contribution from Baltic water inflows is 18.5–48.3% (Cieśliński et al., 2016; Table 1). As shown by the high chlorophyll-a and a gross primary production (Table 1) the coastal lakes are highly productive.

3. Methods

3.1. Water sampling and in situ measurements

Owing to considerable variability of coastal lakes with regard to chemical and physical conditions (Astel et al., 2016; Woszczyk et al., 2016) it is difficult to select one lake that would be representative of the whole ecosystem. Hence, we decided to collect samples from 7 lakes (Lake Łębsko, Lake Gardno, Lake Wicko, Lake Kopań, Lake Bukowo, Lake Jamno and Lake Ręko Przymorskie; Fig. 1).

The water column of each lake was sampled in 2015 with quarterly resolution (February, May, July and October) in 1–3 sites (Fig. 1) from the surface (SW) and the near-bottom layer (BW: c.a. 5 cm above the lake bottom). The SW samples were collected directly at the air-water interface by hand and the BW was sampled using a Ruttner sampler (KC Denmark A/S). Locations of the sites were chosen so that they covered as wide salinity and lake depth ranges as possible as well as different hydrodynamic conditions (open-water vs wind-protected sites). Water depth in the sites was between c.a. 50 and 280 cm. Detailed information on sampling sites are provided in Supplementary materials (Table S2). The samples for major ion composition were stored unpreserved in 500 mL HDPE containers and the water for dissolved gases was alkalinized with KOH and kept in amber glass 100 mL serum bottles stoppered with butyl septa and crimped with Al seals. KOH was chosen as a stabilizing agent because of its well-known effectiveness in stopping bacterial activity and the ease of neutralization.

Lake water temperature, pH, electrolytic conductivity (EC) as well as dissolved O₂ were determined in situ with a YSI Professional Plus probe,
calibrated and checked with certified reference material (Harbour water, NWHAML-20.2) beforehand. Ion composition of water was analyzed within a few days after collection. CH4 and N2O were analyzed within a 2–4 weeks after collection and until the measurements were performed the samples were stored in darkness in a cool room. Based on Lange et al. (2008) 2–4 week-long storage does not affect CH4 and N2O concentrations in rubber butyl-stoppered samples greatly.

3.2. Analytical methods

Total organic carbon (TOC) was analyzed using the non-purgeable organic carbon (NPOC) method via 680 °C catalytic combustion using a TOC-L analyzer (Shimadzu) with non-dispersive infrared (NDIR) detector. Inorganic carbon was removed by acidification and inert gas flushing. Ionic composition of water was analyzed in the samples filtered through 0.45 μm membrane disc filters. NO3− was measured with ion-exchange chromatography (ICS2000 Dionex equipped with IonPac AS18 column) and HCO3− was determined via titration with HCl with regard to phenolphthalein (to pH = 8.3) and methyl orange (to pH = 4.5). Analytical quality was ascertained with CRMs (CRANBERRY-05 and NWHAML-20.2, BATTLE-02, HURON-20 and TROIS-94). On the basis of CRMs recovery of the pH results was 94–97% and for TOC, NO3− and HCO3− varied between 93 and 104%. For the purpose of CH4 and N2O analysis a 20% N2-filled headspace volume was created.

Table 1

<table>
<thead>
<tr>
<th>Lake</th>
<th>Area [km²]</th>
<th>Mean depth [max depth] [m]</th>
<th>Cl− [mg·L−1]</th>
<th>Chlorophyll-a [μg·L−1]</th>
<th>GPPd [gC·m−2·y−1]</th>
<th>Water exchange index (ά)</th>
<th>Catchment area/lake area (CA/LA)</th>
<th>Baltic Sea waters in lake water balancef [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bukowo</td>
<td>17.47</td>
<td>1.8 (2.8)</td>
<td>531–1188</td>
<td>75.4–301.2</td>
<td>–</td>
<td>0.9</td>
<td>5.9</td>
<td>48.3</td>
</tr>
<tr>
<td>Gardno</td>
<td>24.69</td>
<td>1.5 (2.6)</td>
<td>14–1512</td>
<td>67.6–194.5</td>
<td>431</td>
<td>8.6</td>
<td>39.0</td>
<td>28.6</td>
</tr>
<tr>
<td>Jarno</td>
<td>22.40</td>
<td>1.4 (3.9)</td>
<td>15–698</td>
<td>52.6–192.5</td>
<td>–</td>
<td>–</td>
<td>22.5</td>
<td>–</td>
</tr>
<tr>
<td>Kopań</td>
<td>7.90</td>
<td>1.9 (3.9)</td>
<td>85–112</td>
<td>9.6–91.4</td>
<td>–</td>
<td>0.8</td>
<td>4.8</td>
<td>18.5</td>
</tr>
<tr>
<td>Lebsko</td>
<td>71.42</td>
<td>1.5 (6.3)</td>
<td>409–1970</td>
<td>44.9–130.7</td>
<td>347</td>
<td>3.6</td>
<td>22.3</td>
<td>24.7</td>
</tr>
<tr>
<td>Resko</td>
<td>6.87</td>
<td>1.3 (2.5)</td>
<td>1560–2700</td>
<td>17.2–175.3</td>
<td>–</td>
<td>9.7</td>
<td>45.9</td>
<td>47.2</td>
</tr>
<tr>
<td>Wicko</td>
<td>10.59</td>
<td>2.0 (6.1)</td>
<td>38–67</td>
<td>36.5–196.8</td>
<td>–</td>
<td>10.2</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

a From Jańczak (1997).
c From Woszczyzk et al. (2016).
d Gross primary production; from Wielgat-Rychert and Rychert (2008).
e ά = volume of outflow / volume of the lake.
f From Cieśliński et al. (2016).
Then the samples were equilibrated overnight at room temperature and analyzed with a gas chromatograph (GC; Agilent). For the analysis of CH₄ a Carboxen 1010 Plot 30 m × 0.53 mm × 30 μm column (Supelco) and a flame ionization detector (FID) was used and for N₂O a GS-Carbonplot 30 m × 0.32 mm × 3 μm (Agilent Technologies) column and an electron capture detector (ECD) was applied. Concentrations of CH₄ and N₂O in headspace gas were obtained via peak integration and using the functions for gas pressure, headspace volume, ambient temperature, salinity and Bunsen solubility coefficients summarized by Wiesenburg and Guinasso Jr. (1979) and Weiss and Price (1980). To control the quality of the measurements gas standards (CH₄ in N₂ 100.0 ± 1.5 ppm mol and N₂O in N₂ 100.0 ± 1.5 ppm mol; PanGas) were used. Limit of quantification of our GC measurement was 1 ppm for CH₄ and 0.2 ppm for N₂O.

Because of alkalization of the samples after collection (see Section 3.1) the CO₂ could not be reliably measured using GC. Instead, CO₂ concentrations ([CO₂aq]; bar) in lake water were determined computationally on the basis of pH and activity of HCO₃⁻ (Borges et al., 2004; Cole and Prairie, 2009; Balmer and Downing, 2011; Henley et al., 2012; Raymond et al., 2013; Hastie et al., 2017). The mathematical expression for this calculation is as follows:

\[
[\text{CO}_2]_{\text{aq}} = \frac{10^{-\text{pH}} \cdot [\text{HCO}_3^-]}{K_1}
\]  

(1)

In Eq. (1) \(K_1\) indicates equilibrium constant in \(H_2CO_3 \rightarrow \text{H}^+ + \text{HCO}_3^-\) system and is obtained from the formula reported by Kelts and Hsu (1978).

Stable C isotopic composition of CH₄ was determined by oxidizing methane to CO₂ by means of a Trace gas (GV Instruments) connected to a mass spectrometer (GV Instruments) and expressed in δ notation vs V-PDB.

3.3. GHG flux calculations

The fluxes (\(F\); mg·m⁻²·d⁻¹) were calculated from the Fick’s first law of diffusion

\[
F = 240 \cdot k \cdot (C_w - C_{eq})
\]

(2)

where \(k\) is the gas transfer velocity (cm·h⁻¹), \(C_w\) is measured concentration of the gas in lake surface water (mg·L⁻¹), \(C_{eq}\) is equilibrium concentration of gas in water (mg·L⁻¹) and 240 is unit conversion factor (from cm·h⁻¹ and mg·L⁻¹ to m·d⁻¹ and mg·m⁻³, respectively). Positive values of \(F\) indicate release of gases from lake waters to the atmosphere while negative values show the opposite (i.e. absorption of the gas by lake waters).

Gas transfer velocity \(k\) was calculated with the following formulae by Crusius and Wanninkhof (2003):

\[
k = k_{600} \left( \frac{Sc}{600} \right)^{-1/2}
\]

(3)

and

\[
k_{600} = 4.33 \cdot U_{10}^{-13.3}
\]

(4)

In the above equations \(Sc\) denotes Schmidt number of a gas at the temperature and salinity of sample collection, \(k_{600}\) is gas transfer velocity adjusted to \(Sc = 600\) and \(U_{10}\) is wind speed at 10 m above water surface (m·s⁻¹). Sc values were taken from Ramsing and Gundersen (1994). As \(U_{10}\) we used averaged monthly wind speeds values for two stations (Łeba and Kołobrzeg) obtained at the Institute of Meteorology and Water Management (IMGW-PIB), Warsaw, Poland. \(C_w\) were calculated on the basis of mean atmospheric concentrations of CO₂, CH₄ and N₂O over Europe in 2015 and relevant Henry constants (\(K_H\)). The data used for the calculations are summarized in Table S1.

Wind fetch (\(F_W\); m) of the predominant WSW winds was derived from the equation employed by Gons et al. (1986):

\[
F_W = \frac{\sum x_i^2 \cdot \cos \alpha_i}{13.5}
\]

(5)

where

\(x_i\) – length of the radial i for the site modelled
\(\alpha_i\) – angle between the radial i and the wind direction.

3.4. Statistics

Statistical treatment of the data was performed using R and Statistica 12.5. We tested statistical significance of differences between mean GHGs concentrations in SW and BW (\(\Delta CSW-BW\)) using Wilcoxon signed-ranked test. The Wilcoxon test was chosen as an alternative for t-Student test due to the small sample size and the inability to presume normality of the \(\Delta CSW-BW\) distribution.

4. Results

4.1. Lake water chemistry

The composition of coastal lake waters was in general uniform throughout water column yet displayed considerable variability in time and space (Suppl. data; Table S2). pH was appreciably low in all lakes in February 2015 (7.16 ± 0.21; \(\bar{x} \pm \sigma\)) while in May, July and October 2015 the values were higher albeit with some differences between the lakes (8.90 ± 0.27, 8.88 ± 0.40 and 8.59 ± 0.49, respectively). The coastal lake waters were highly oxygenated throughout the study period, however during winter the \(O_2\) concentrations reached maximum values (14.10 ± 0.86 mg·L⁻¹) and the minima were found in summer (8.54 ± 1.48 mg·L⁻¹). A similar trend was displayed by nitrates, which changed from 5.32 ± 2.13 mg·L⁻¹ in January 2015 to 0.18 ± 0.07 mg·L⁻¹ in July 2015. Changes in salinity and TOC were spatial rather than seasonal i.e. the differences between lakes were higher than temporal changes in those parameters in each lake. Lake Resko Przymorskie had the highest salinities (2.6–3.9‰) while the lowest occurred in Lake Jamno and Wicko (0.2‰). The average salinity for the whole study period was 1.34 ± 1.25‰. The highest TOC values were obtained in Lake Kopań (12.0–19.0 mg·L⁻¹) and the lowest were in Lake Gardno (4.4–6.2 mg·L⁻¹).

4.2. Concentrations of GHGs

CH₄ varied seasonally between 25.6 and 1066.8 nmol·L⁻¹ (Suppl. data; Table S3, Fig. S1). The lowest concentrations of CH₄ in most sites studied occurred in February, while the maxima were measured in July. In each season, the site BUK6, located in the most wind-protected part of Lake Bukowo, showed the highest CH₄ values. On the other hand, the most CH₄-depleted sites in each season were different (e.g. BUK 3 and BUK 8 in February, RP5 in May, LEB4 in July, BUK 3 and BUK8 in October) and the minimum CH₄ concentrations occurred in open-water stations. The \(\Delta CSW-BW\) for CH₄ was minor and statistically insignificant throughout the sampling periods, however, BW usually had slightly higher CH₄ values than SW.

The N₂O concentrations ranged between 7.60 and 39.44 nmol·L⁻¹ (Suppl. data; Table S3, Fig. S2). The concentrations showed a clear decrease from February to July followed by a slight increase in October. In May and July spatial variability of N₂O within lakes and between lakes was minor and the differences got higher in February, and lessened in October. \(\Delta CSW-BW\) for N₂O were insignificant.

CO₂ varied greatly from 1.67 nmol·L⁻¹ to 1.54 mmol·L⁻¹ (Suppl. data; Table S3, Fig. S3). In February, the CO₂ concentrations were by far the highest throughout the study period and on average one order
of magnitude higher than during the rest of the sampling campaigns. In May, July and October the CO₂ was relatively low and largely similar although the minimum values in most sites were reached in July and a slight increasing trend from May–July to October was observed. Spatial variability of CO₂ was appreciably high, however, the highest concentrations were usually noted in BUK6 while the lowest values occurred predominantly in GAR2 and GAR4 sites. The CO₂ gradients in the water column (ΔC₅₅BW) were very weak and statistically insignificant but in SW the concentrations were slightly higher than in BW.

4.3. Stable carbon isotopic composition of CH₄ (δ¹³C₄CH₄)

δ¹³C₄CH₄ values ranged from −60.4 to −28.9‰ (Suppl. data; Table S3) and showed appreciable spatial variability between lakes and within each lake. In terms of average values, δ¹³C₄CH₄ slightly increased from February to October, albeit this trend was accompanied by the increase in spatial variability of δ¹³C₄CH₄. For example in July 2015 both minimum and maximum δ¹³C₄CH₄ for the period of study were obtained. δ¹³C₄CH₄ changes were thus quite irregular. The water column of coastal lakes were uniform with regard to the isotopic composition of CH₄ with the exception of Lake Jamno, in which δ¹³C₄CH₄ in surface waters was usually higher (4.9 to 16.1‰) than in bottom waters.

4.4. GHG fluxes

Throughout the study period the fluxes of CH₄ (FCH₄) were positive at each site. The highest FCH₄ occurred in July (54.9 ± 53.6 mg CH₄ m⁻² d⁻¹; ± 1σ) and the lowest values (4.2 ± 3.8 mg CH₄ m⁻² d⁻¹) occurred in October (Table 2; Suppl. data; Table S3; Fig. S4). Lakes with highest CH₄ emissions were Bukowo and Wicko (on average 34.3 and 32.5 mg CH₄ m⁻² d⁻¹ respectively) while the lowest FCH₄ was measured in Lake Lebsko and Resko Przymorskie (on average 8.2 and 12.4 mg CH₄ m⁻² d⁻¹ respectively) (Table 2; Suppl. data; Table S3).

N₂O fluxes (FN₂O) displayed a relatively low level of spatial variability. During the study period the highest values of FN₂O occurred in February and May (1.3 ± 0.4 and 1.1 ± 0.1 mg N₂O·m⁻²·d⁻¹ respectively) (Table 2; Suppl. data; Table S3). In July and October the FN₂O varied within the same range of 0.2 ± 0.1 mg N₂O·m⁻²·d⁻¹. Except of one record (BUK6), the FN₂O was positive throughout the study period. Highest emissions of N₂O were calculated for Lake Kopań (0.9 mg N₂O·m⁻²·d⁻¹), and the lowest from Lake Lebsko (0.62 mg N₂O·m⁻²·d⁻¹) (Table 2; Suppl. data; Table S3).

The CO₂ flux (FCO₂) demonstrated a considerable variability throughout the study period. The yearly course of FCO₂ displayed highly positive values in February (51.1 ± 28.3 g CO₂·m⁻²·d⁻¹; ± 1σ), negative fluxes in May (−0.4 ± 0.8 g CO₂·m⁻²·d⁻¹) and July (−1.0 ± 0.7 g CO₂·m⁻²·d⁻¹) as well as negative/positive values in October (0.7 ± 1.3 g CO₂·m⁻²·d⁻¹) (Table 2; Suppl. data; Table S3; Fig. S6). Highest CO₂ emissions were measured for Lake Kopań (22.5 g CO₂·m⁻²·d⁻¹), however, the most CO₂ productive site was BUK6 (Table 2; 4). In the latter location FCO₂ was positive throughout the study period and the flux was between 122.1 g CO₂·m⁻²·d⁻¹ in February and 0.4 g CO₂·m⁻²·d⁻¹ in July 2015 (Table 2; Suppl. data; Table S3).

5. Discussion

5.1. Controls over GHGs distribution and emissions from coastal lakes

5.1.1. Methane

Measured CH₄ concentrations, although displaying a great degree of variability, were in the upper part of the range of estuaries and lagoons and were rather low compared to freshwater lakes (Middelburg et al., 2002; Bange, 2006; Bastviken et al., 2004, 2008;
Borges and Abril, 2012; Martinez-Cruz et al., 2015; Saarela et al., 2020). The dissolved CH4 in the water column was 13C-enriched with most samples having δ13CCH4 > −50‰ (Table S3). Such high values indicate considerable CH4 oxidation (Whiticar, 1999; Bastviken et al., 2008; Schubert et al., 2010; Lecher et al., 2017; Saarela et al., 2020).

As concluded by Borges and Abril (2012) the largest amounts of CH4 are delivered to estuarine waters from bottom sediments, while CH4 production in the water column is minor. However some CH4 can also originate from river input, wetlands adjacent to estuaries/lagoons and resuspension of littoral sediments (Middelburg et al., 2002; Bussmann, 2005; Saarela et al., 2020). Yang et al. (2015) compared CH4 emissions from a number of Nordic lakes and concluded that the lakes representing higher trophic status released significantly more CH4 than low-productivity lakes. The reason for these differences is related to a higher availability of easily degradable autochthonous organic matter in the sediments of productive lakes, acting as a substrate for microbial metabolism. Given the fact that the sediments of the lakes studied are largely similar in terms of abundance in phytoplankton-derived organic matter (TOC between 9.8 and 20.6%; TOC/N < 10; δ13C-TOC < −24‰; Woszczyk et al., 2016) and that microbial CH4 is found in each site (Woszczyk et al., 2016) the CH4 distribution in the water column seems not to be controlled by the availability of substrates for methanogenesis. On the other hand, since the information on in situ methanogenesis in the sediments is missing altogether the influence of benthic processes on lake water composition cannot be assessed quantitatively. However, the overall positive relationship between CH4 and water temperature (Fig. 2A) clearly shows that seasonal variability of CH4 in coastal lakes can be related to fluctuations in the rates of methanogenesis within the bottom sediments because the latter process is strongly temperature-controlled and CH4 production increases exponentially with temperature (Avery et al., 2003). Exponential increase in mean/median CH4 concentrations in coastal lakes (Fig. 2A) certainly reflects this broad tendency.

From our data it emerged that CH4 concentrations in coastal lake waters showed negative relationships with lake water salinity (Fig. 2B), depth (Fig. 2C) and FW of the predominant winds (Fig. 3A). A CH4 decrease with increasing salinity was reported from many estuaries (Middelburg et al., 2002; Borges and Abril, 2012; Bange et al., 2019) and was related to inhibiting effects of salinity (SO42− concentrations in particular) on methanogenesis and/or enhanced anaerobic oxidation of CH4 with sulphates within estuarine sediments. Maltby et al. (2018) established that methanogenesis ceased above 1 mmol SO42−·L−1 and Caldwell et al. (2008) found considerably high CH4 oxidation even below 2 mmol SO42−·L−1. Given that the concentrations of SO42− in the pore waters within the top 20 cm of coastal lake sediments were between 0.4 and 4.6 mmol SO42−·L−1 in Lake Gardno, 0.4 and 8.1 mmol

![Fig. 2. Relationships between concentrations of CH4 and (A) lake water temperature, (B) salinity, and (C) lake depth. Note, that to show the trends of change in panels B and C the average CH4 concentrations were shown in larger scales.](image)

![Fig. 3. Relationships between WSW wind fetch (FW) and (A) CH4 and (B) CO2 concentrations in lake waters. The decrease in CH4 concentrations accompanying FW increase occurred throughout the whole period of study while CO2 demonstrated the overall relationship with the FW only during February 2015.](image)
SO\textsubscript{4}\textsuperscript{2-} \cdot \text{L}^{-1} in Lake Bukowo and 4.4–10.4 mmol SO\textsubscript{4}\textsuperscript{2-} \cdot \text{L}^{-1} in Lake Resko (data not shown), the conditions for methanogenic bacteria in the lakes were rather unfavourable. In such circumstances, the methanogenic zone is usually shifted towards deeper sediment layers while within the top sediments CH\textsubscript{4} is exposed to oxidation which thus reduces CH\textsubscript{4} flux from pore waters to the lake water column (Whiticar, 1999). From Fig. 2B it appears that the decrease in CH\textsubscript{4} accompanying oxidation increase is not monotonous because there is a secondary peak in concentration at salinities of 3–4%. At this stage, the reasons for this “disruption” remain unclear. We relate it, however, to some local factors rather than the whole system peculiarity, because the samples are largely derived from one location. The highest concentrations in CH\textsubscript{4} were measured exclusively in the shallowest sites (<100 cm) of the lakes and showed an overall decrease with increasing water depths (Fig. 2C). Similar tendencies were reported by Bastviken et al. (2008), Borges and Abril, 2012, DeSontro et al. (2016) and Humborg et al. (2019) and explained with oxidation of CH\textsubscript{4} as it diffuses from the pore waters to the atmosphere via an oxygenated water column. The oxidation of CH\textsubscript{4} increases with the thickness of oxygenated water column albeit even in very shallow waters (1–2.5 m depth) the share of oxidized CH\textsubscript{4} can be high (20–40%) (Bastviken et al., 2008). Highly turbulent conditions in lakes further strengthen CH\textsubscript{4} oxidation (Zhu et al., 2018). Sturm et al. (2016) provided evidence that high O\textsubscript{2} concentrations in lake waters (>1.92 mg O\textsubscript{2}·L\textsuperscript{-1}; >120 μmolO\textsubscript{2}·L\textsuperscript{-1}) inhibit CH\textsubscript{4} oxidation. Because coastal lake waters were very rich in O\textsubscript{2} throughout the study period (Table S2) it might be that major part of CH\textsubscript{4} oxidation occurred within the topmost layer of surface sediments.

Relationship between CH\textsubscript{4} and F\textsubscript{CH4} displays a sharp decrease in CH\textsubscript{4} with increasing F\textsubscript{CH4} (Fig. 3A) thus reflecting the impact of hydrodynamic forces on the gas concentrations. F\textsubscript{CH4} values control the depth of wind-driven water mixing (Woszczyk et al., 2017) which in turn acts for aerating the lake water column (Chiba and Baschek, 2010; Liang et al., 2011) and creates favourable conditions for CH\textsubscript{4} oxidation (Zhu et al., 2018). On the other hand, decreased surface roughness of lake waters compared to terrestrial areas causes acceleration of wind currents over lakes (Samuelsson and Tjernström, 2001) and in this way enhances gas exchange between lake and atmosphere via an increase in piston velocity k\textsubscript{piston} (Eqs. (3) and (4)).

5.1.2 Nitrous oxide (N\textsubscript{2}O)

In contrast to CH\textsubscript{4}, N\textsubscript{2}O is often produced in lake water columns while its benthic release is restricted to the top sediment layers (Senga et al., 2000). Estuaries are also known to have some external N\textsubscript{2}O inputs from inflowing rivers and terrestrial runoff (Bange et al., 1998; Harley et al., 2015). N\textsubscript{2}O is an intermediate product of denitrification (reduction of NO\textsubscript{3} to N\textsubscript{2}) and by-product of nitrification (oxidation of NH\textsubscript{3} to NO\textsubscript{2}) and its formation is closely related to O\textsubscript{2}, NO\textsubscript{3} and/or NH\textsubscript{4} concentrations (Walter et al., 2006; McCrackin and Elser, 2011; Yu et al., 2013) albeit the dependence between N\textsubscript{2}O and O\textsubscript{2}/NO\textsubscript{3}/NH\textsubscript{4} can be different in different locations (e.g. Senga et al., 2002; Walter et al., 2006; Beaulieu et al., 2015; Harley et al., 2015; Xiao et al., 2019).

It is clear however, that denitrification is limited to <0.2 mg O\textsubscript{2}·L\textsuperscript{-1}, and thus is highly unlikely in well-oxygenated waters, while nitrification requires >1 mg O\textsubscript{2}·L\textsuperscript{-1} and seems the predominating N\textsubscript{2}O production pathway in oxic waters (Beaulieu et al., 2015).

N\textsubscript{2}O production in coastal lakes of the South Baltic region seems to be a very complex process. On one hand, N\textsubscript{2}O concentrations show an overall positive dependence on O\textsubscript{2} and NO\textsubscript{3} in lake waters (Fig. 4A, B), which would suggest that it is produced via nitrification in the water column. On the other hand, however, a negative relationship between N\textsubscript{2}O and temperature (Fig. 4C) conflicts with the above interpretation because both nitrification and denitrification rates accelerate with higher temperatures (Palacín-Lizarbe et al., 2018; Norton and Ouang, 2019). Unfortunately our data are insufficient to investigate N\textsubscript{2}O formation in more detail, however coinciding culminations of N\textsubscript{2}O, NO\textsubscript{3} and O\textsubscript{2} at low temperatures let us to hypothesize that terrestrial input of denitrification/nitrification substrates (e.g. inorganic and organic N species) and/or N\textsubscript{2}O itself to large degree determines seasonal changes in N\textsubscript{2}O in coastal lakes. Wielgat-Rychert et al. (2015) and Cieśliński (2016) demonstrated that Lake Gardno and Lake Lebsko, the largest coastal lakes on the Polish coast, received much of their N loads via the river inflows during winters and estimated that 80% of this N was lost via denitrification (Wielgat-Rychert et al., 2015). The delivery of N\textsubscript{2}O to coastal lakes from their catchments was not investigated so far, however widespread occurrence of wet soils (e.g. peat soils and peat-muck soils) in the vicinity of coastal lakes (Moczek, 1978), in which denitrification produces large N\textsubscript{2}O yields (Beaulieu et al., 2011), might be supportive for the hypothesis. Yang et al. (2015) argued for a role of atmospheric NO\textsubscript{3} deposition for N\textsubscript{2}O production in boreal lakes. However, given that vertical water exchange is negligible compared to horizontal exchange in coastal lakes (Cieśliński et al., 2016) and that atmospheric NO\textsubscript{3} deposition is relatively low on the Baltic coast in Poland (Grodzińska-Jurczuk and Godzik, 1999; Wielgat-Rychert et al., 2015) river input of N species seems to be more important for N\textsubscript{2}O than rain. Interestingly, in July 2015 concentrations of N\textsubscript{2}O and CH\textsubscript{4} were strongly negatively correlated (Fig. 5). We believe that such feature reflects contrasting conditions of N\textsubscript{2}O and CH\textsubscript{4} formation. As it was mentioned earlier decreasing concentrations of CH\textsubscript{4} in coastal lakes were largely owing to oxidation in the water column. Bodíel and Frenzel (1999) showed that methanotrophic bacteria significantly contribute

![Fig. 4. Relationships between concentrations of N\textsubscript{2}O and (A) dissolved O\textsubscript{2}, (B) nitrates, and (C) lake water temperature.](image)
5.1.3. Carbon dioxide (CO₂)

Average concentrations of CO₂aq in the coastal lakes studied are very high in comparison to other inland lakes (Sobek et al., 2005) and fit in the upper range of the estuarine/lagoon range (Borges and Abril, 2012). However, the CO₂ displays diametrical seasonal changes and after very high values in winter for the major part of the year, the concentrations remain low even falling below saturation level. When plotted against temperature, CO₂ shows a sharp decline between 0–5 and 5–10 °C and only minor changes above 10 °C (Fig. 6). Such a trend can easily be explained by enhanced consumption of CO₂ due to primary production in the lakes accompanying temperature increase. On the other hand, tremendously high CO₂ concentrations during winter imply that the production of the gas due to degradation of organic matter, terrestrial input of CO₂ and/or release of CO₂ from the sediments (or a combined effect of these factors) were not balanced by photosynthetic fixation of CO₂. Xiao et al. (2020a) argued that such imbalance resulted in high CO₂ emissions from anthropogenically polluted small urban lake in China. Bastien et al. (2011) showed that high CO₂ emissions from some estuaries were largely owing to ventilation of terrestrially-derived CO₂ in the fresh- saltwater mixing zone and Maberly et al. (2013) demonstrated that emissions of CO₂ from lakes echoed catchment productivity as CO₂ concentrations/efflux were strongly positively correlated to net primary productivity in the catchment.

In February 2015 spatial distribution of CO₂aq throughout the coastal lakes were controlled by wind fetch (Fig. 3B), and the CO₂aq concentrations in open-water sites were lower than in wind-protected sites presumably due to enhanced water turbulence in the former stimulating CO₂ escape to the atmosphere. During July CO₂aq was negatively related to O₂ (Fig. 7B), which clearly showed production of CO₂aq via heterotrophic processes in the water column.

5.2. Emission of GHGs from coastal lakes

On the basis of calculated fluxes of GHGs coastal lakes of the South Baltic coast act as net sources of CO₂, CH₄ and N₂O. Mean FCH₄, FCO₂ and FN₂O for the whole system of coastal lakes were estimated to 21.7 ± 36 mg CH₄·m⁻²·d⁻¹, 12.7 ± 26.5 g CO₂·m⁻²·d⁻¹ and 0.7 ± 0.7 g N₂O·m⁻²·d⁻¹, respectively.}

**Fig. 5.** Relationship between concentrations of N₂O and CH₄ for July 2015. In the remaining sample sets (from February, May and October 2015) the gases were mutually unrelated.

In February 2015 CO₂aq showed an overall positive correlation with TOC in lake waters (Fig. 7A) which might suggest that the CO₂aq was produced from oxidation of organic matter. Highly oxic conditions in the lakes in February 2015 could indeed favour microbial respiration of organic matter (Bastviken et al., 2004) but, on the other hand, owing to a strong temperature control on this process (Carignan et al., 2000), its intensity at around 2 °C was expected to be low. Alternatively, the relationship between CO₂aq and TOC can be explained by the origin of both species from inflowing rivers, which contribute to 44–75% of the water budget of the lakes (Cieliński et al., 2016) and display wintertime outflow maxima (Szymczak and Piekarek-Jankowska, 2007). Borges and Abril (2012) also showed that high CO₂ emissions from some estuaries were largely owing to ventilation of terrestrially-derived CO₂ in the fresh- saltwater mixing zone and Maberly et al. (2013) demonstrated that emissions of CO₂ from lakes echoed catchment productivity as CO₂ concentrations/efflux were strongly positively correlated to net primary productivity in the catchment.

In February 2015 spatial distribution of CO₂aq throughout the coastal lakes were controlled by wind fetch (Fig. 3B), and the CO₂aq concentrations in open-water sites were lower than in wind-protected sites presumably due to enhanced water turbulence in the former stimulating CO₂ escape to the atmosphere. During July CO₂aq was negatively related to O₂ (Fig. 7B), which clearly showed production of CO₂aq via heterotrophic processes in the water column.

**Fig. 6.** Relationship between concentrations of dissolved CO₂ (CO₂aq) and lake water temperature.

**Fig. 7.** Relationship between concentrations of dissolved CO₂ (CO₂aq) and lake water TOC for February 2015 (A) and dissolved O₂ in July 2015 (B). In the remaining sample sets the species were mutually unrelated. In February 2015 the CO₂aq and TOC showed an overall positive correlation however two samples (marked with open circles) were out of this trend. Note that, for sake of clarity, CO₂ concentrations in July were shown in logarithmic scale.
0.6 mg N₂O·m⁻²·d⁻¹, respectively (Table 2) which was equivalent to 7.9 ± 13.1 g CH₄·m⁻²·y⁻¹, 4.6 ± 9.7 kg CO₂·m⁻²·y⁻¹ and 270 ± 203 mg N₂O·m⁻²·y⁻¹. CH₄ and N₂O are released from the lake waters to the atmosphere throughout the year. CO₂, however, is predominantly emitted during winter, while during the warm season the lakes become autotrophic and thus absorb CO₂ from the ambient air which is evidenced by negative FCO₂ values. Autotrophic character of coastal lakes between spring and autumn, inferred from FCO₂, is in line with the results obtained by Wielgat-Rychert and Rychert (2008) showing that during the same period the gross primary production in the lakes is in excess of the total C respiration.

Spatial and temporal changes in average annual fluxes followed the gas concentration patterns. Consequently, the considerably higher fluxes of CH₄ were observed in wind-protected sections of coastal lakes than in open-waters sites (e.g. 87.9 vs 7.1 mg CH₄·m⁻²·d⁻¹ in Lake Bukowo, 29.5 vs 8.2 mg CH₄·m⁻²·d⁻¹ in Lake Jamno and 13.3 vs 5.1 mg CH₄·m⁻²·d⁻¹ in Lake Łębsko; Table S3). FCH₄ was also related to salinity and water depth at the sampling sites and showed a tendency to decline with increase in both parameters. In contrast to FCH₄, FCO₂ was unrelated to salinity and water depth. Likewise, the protection against the wind seemed not to be crucial factor for FCO₂, however, the highest emissions occurred from the well-sheltered BUK6 site. FCO₂ showed overall decrease with increasing wind fetch and salinity.

Interestingly, CH₄ and CO₂ fluxes showed an overall increase with decreasing ratio of catchment to lake area as well as lake surface area itself, however, statistical significance of these relationships was low (CA/LA; Fig. 8A and B). Because CA/LA determines the flushing rate of lakes (the higher CA/LA the more rapid the water exchange; Kalff, 2001), it appears that CH₄ and CO₂ emissions are stimulated by longer water retention time (WRT). As shown by Groeger and Kimmel (1984) lakes with low WRT tend to have high loading with allochthonous and refractory organic matter in dissolved form while in lakes with long WRT autotrophic and more biodegradable particulate OM (which acts as substrate for microbial processes) is more abundant. For N₂O the relationship with CA/LA is very weak (Fig. 8A) implying that the relationship between N₂O flux and WRT is unimportant. The decrease in GHG emission fluxes with increasing lake surface area, albeit of low statistical significance (Fig. 8B), is in agreement with Juutinen et al. (2009) and Holgerson and Raymond (2016).

The results obtained clearly show the transitional lacustrine/estuarine biogeochemical character of coastal lakes. In Table 3 we collected data illustrating the annual emissions of GHGs from different types of aquatic systems. From this list, it appears that CH₄ emissions from coastal lakes are high when compared to estuaries and rather low when compared to lakes. CO₂ emissions from the coastal lakes seem high in relation to average emissions from freshwaters and are in the upper range compared to estuaries. N₂O emissions are relatively low compared to estuaries and high when compared to lakes (Table 3).

Diffusive emission of GHG acts as of the most important mechanism of gas transfer from water to the ambient air. However in some cases ebullition is equally or even more effective. While for N₂O and CO₂ ebullition is less significant (Gao et al., 2013; Sapulveda-Jauregui et al., 2015) for CH₄ ebullitive transport is often more efficient than diffusion, especially in shallow lakes (Bastviken et al., 2004; DelSontro et al., 2016). Hence, our assessment of GHGs emissions from coastal lakes (methyl CH₄ in particular) is minimum values.

### 6. Conclusions and outlook

Results of this study clearly demonstrate that coastal lakes act as net sources of CH₄, CO₂ and N₂O to the atmosphere; however, the differences within each lake and between lakes are appreciably high. Despite this many questions regarding the production of the gases and their cycling in the system still remain unanswered, it seems that emissions of CO₂ and N₂O are, at least to some degree, controlled by terrestrial input of C and N species. In contrast, CH₄ flux is largely regulated by intrinsic processes of CH₄ production and oxidation in lakes.

This study represents a first step towards understanding the biogeochemical processes in coastal lakes; however, the results presented here are not complete. Further studies could profit from higher resolution analyses, longer timescales, and the quantification of GHGs emission (CH₄ in particular) via ebullition.

Coastal lakes are located in a very dynamic environment and do show appreciable sensitivity to the ongoing accelerated sea level rise.

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**Fig. 8.** Relationships between CH₄, CO₂ and N₂O fluxes and (A) the ratio of catchment area to lake area (CA/LA) and (B) lake area. In each case a decreasing trend was found. The relationships provide evidence for increase in GHG fluxes with decrease in lake area and increase in water retention time.
However, future directions of GHG production in the system are difficult to predict because, as shown by our data, GHG emissions are dependent not only on the direct effects of sea level increase (and enhanced salt water ingressions) on lake water chemistry but also concomitant changes in lake surface area, morphometry as well as catchment processes and management. Therefore the projection of biogeochemical changes in coastal lakes would definitely benefit from monitoring catchment productivity, nutrient export accompanying changes in lake level/surface area, and hydrochemistry.

CRediT authorship contribution statement

Michał Woszczyk – grant beneficiary, field expeditions and sample collection, stable C isotope analyses, preparing manuscript (with tables, figures and Supplementary data), correspondence with the journal, revision of the text. Carsten Schubert – CH4 and N2O analyses; revision of the text.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.143500.

Table 3

| CH4, CO2 and N2O fluxes from estuaries: global and regional parametrisations and selected case studies. |
|-------------------------------------------------|-----------------|-----------------|-----------------|-----------------|
| Flux | g CH4·m⁻²·y⁻¹ | g CO2·m⁻²·y⁻¹ | g N2O·m⁻²·y⁻¹ |
| Coastal lakes (5 Baltic area) | | | |
| Global freshwater lakes | | | |
| Freshwater lakes (diffusive flux) | 7.9 | 0.069 | |
| High N-loaded lakes | 0.41 | 1.211 | |
| Low N-loaded lakes | 1.49 | 0.121 | |
| European estuaries | 3.75 | 1301–1886 | |
| European estuaries | 0.41 | 231.1 | |
| Low N-loaded lakes | 1.49 | 450.4 | |
| European estuaries | 1.49 | 3967 | |
| European estuaries | 0.41 | 203–122.06 | |
| Inland water lakes | 0.47–17.75 | 677–2072 | |
| European shelf areas | 0.06–0.12 | | |
| European estuaries | 1.81–3.94 | | |
| Small deltas and estuaries | | | |
| Tidal system and embayments, Lagoons | | | |
| Nordic boreal lakes | 9.928–24.76 | 198.3–485.5 | |
| Tay estuary | 1.36 | 1328 | |
| Elbe estuary | | | |
| Hudson estuary | 2.04 | 257–578 | |
| Pearl river estuary (China) | | | |
| River Colne estuary (UK) | | | |
| Yangtze estuarine wetland (China) | | | |
| Lake Taihu (China) | | | |

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