


# Methane and Nitrous Oxide Emissions From an Anthropogenically Transformed Lake (Lake Licheńskie, Poland)

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## RESEARCH ARTICLE

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### Key Points:

- Lake Licheńskie (Poland) has been highly transformed by long-term discharge of the effluents from of a power plant
- Lake Licheńskie shows lower diffusive emissions of CH<sub>4</sub> than natural lakes
- Greenhouse gas emissions from Lake Licheńskie are more strongly related to a very high flushing rate than to thermal pollution

### Supporting Information:

Supporting Information may be found in the online version of this article.

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## Methane and Nitrous Oxide Emissions From an Anthropogenically Transformed Lake (Lake Licheńskie, Poland)

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**Abstract** For over 50 years Lake Licheńskie (LLi), central Poland, has been involved in the cooling system of two power plants (PP). Owing to the discharge of cooling waters the lake was prone to considerable environmental changes which involved its thermal structure, mixing regime and water parameters. In this study we investigated how the man-made transformations affected greenhouse gas emissions (GHG; CH<sub>4</sub> and N<sub>2</sub>O) from the lake. The GHG emissions in Lake Licheńskie were monitored at the deepest site from December 2014 to November 2015 and between March 2022 and February 2023. The values obtained were compared to reference lakes encompassing 10 natural and undisturbed inland and coastal lakes in Poland. Our results revealed that LLi was a net source of CH<sub>4</sub> and N<sub>2</sub>O to the atmosphere but the fluxes were low. The mean annual diffusive fluxes were 0.21–0.38 mmol·m<sup>-2</sup> d<sup>-1</sup> for CH<sub>4</sub> and 4.90–7.40 μmol·m<sup>-2</sup> d<sup>-1</sup> for N<sub>2</sub>O. The CH<sub>4</sub> emissions were significantly lower than in most of reference lakes, while the N<sub>2</sub>O emissions were comparable. Therefore, the human intervention resulted in reduction of CH<sub>4</sub> release from LLi but it had minor effect on the N<sub>2</sub>O. The most likely reason for the low direct fluxes of GHGs from the surface waters was the high flushing rate of the lake and export of dissolved gases to adjacent lakes and canals. Hence, the overall emission from the connected lake and canal system was not mitigated by the man-made changes to the lake system.

**Plain Language Summary** CH<sub>4</sub> and N<sub>2</sub>O are potent greenhouse gases (GHGs). Their emission from lakes is often stimulated by human intervention in the ecosystem. Lake Licheńskie, central Poland, represents a highly disturbed lacustrine system, which, together with a few other lakes, is a part of a cooling system of two electric power plants. Consequently, since 1960s the lake has received considerable discharge of cooling waters which changed lake water chemistry and hydrodynamics. In this study we tried to find out how these multifaceted changes affected greenhouse gas production and emission in the lake. For this purpose we collected water chemistry data and measured diffusive emissions of the GHGs from Lake Licheńskie and a few natural undisturbed lakes in Poland. The latter lakes served as reference lakes. Our data revealed that Lake Licheńskie emitted comparable amounts of N<sub>2</sub>O albeit less CH<sub>4</sub> than natural lakes. This lower emission of CH<sub>4</sub> in Lake Licheńskie was a result of the very high flushing rates of the lake by circulating cooling waters. The GHG emissions were most likely released further downwards in the water receiving canals.

## 1. Introduction

Lakes are prone to a wide array of long- and short-term transformations. Some of them are related to ongoing global climate warming which in lacustrine ecosystems will translate into the increase in surface water temperatures, decrease in duration and thickness of winter ice, decline in lake water levels, reduced vertical circulation as well as more frequent harmful cyanobacterial blooms (Woolway et al., 2020, 2022). One of the most important far-reaching effects of the warming will also be enhanced release of greenhouse gases (GHG) (Bartosiewicz et al., 2019; Cheng et al., 2020; Guo et al., 2020; Tanentzap et al., 2019; Yang et al., 2012). However, in many (if not most) lakes, climate impact is superimposed on direct anthropogenic influences. For GHG production in lakes human-induced delivery of nutrients (i.e., cultural eutrophication) will probably be even more influential than temperature (Beaulieu et al., 2019; Davidson et al., 2015; Sanchez et al., 2019; Sun et al., 2021). In general, it is believed that anthropogenically impacted aquatic systems produce more GHG, CH<sub>4</sub> in particular, than natural lakes (Li et al., 2021; Rosentreter et al., 2021).

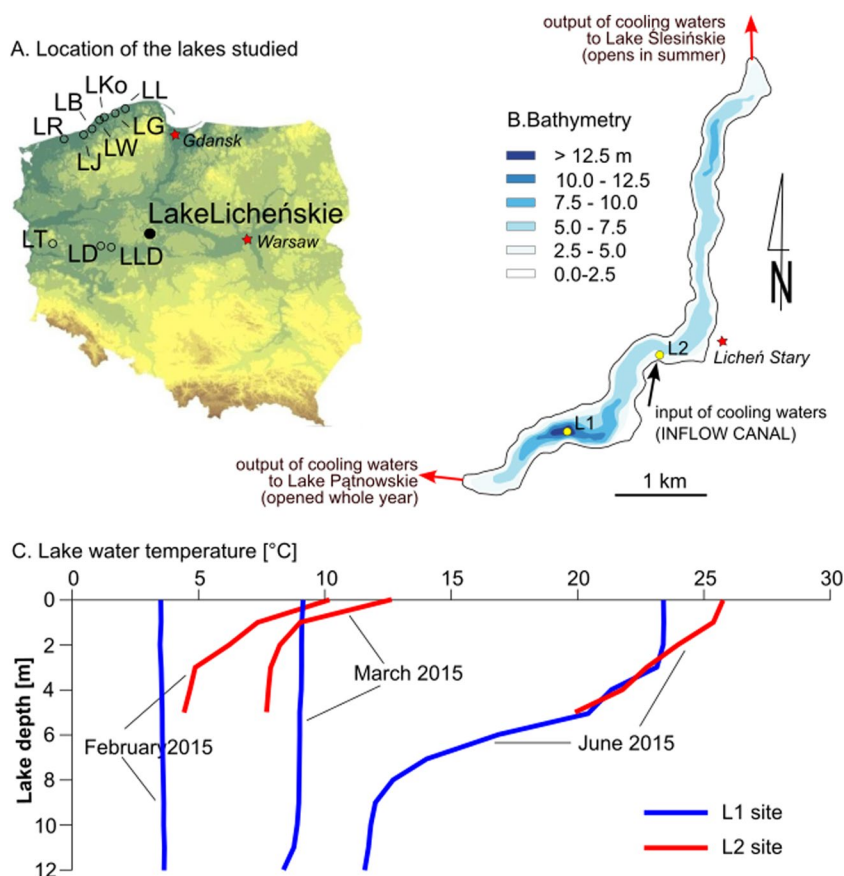
A group of lakes in central Poland (Lake Gosławskie, Pałnowskie, Licheńskie, Wąsosko-Mikorzyńskie and Ślesieńskie, hereafter referred to as Konin lakes) is involved in the cooling system of two nearby electric power plants (PP). In this system, a forced water circulation between the PPs and the lakes is used to ensure effective supply of cold water to electricity generators and to maintain transfer of the heat absorbed to the atmosphere. Because the system has continuously been in operation since 1960s, the lakes have undergone considerable environmental changes. Since the opening of the discharge of warm waters from the PPs, the lakes have become warmer than non-heated lakes in the neighborhood, their mixing regime has been altered, and there were long-term increase in water mineralization as well as deterioration of redox conditions (Dziuba et al., 2020; Pyka et al., 2013; Świątecki et al., 2007). In addition, Socha and Hutorowicz (2009) as well as Dziuba et al. (2020) reported changes in floristic and faunistic assemblages in the Konin lakes. All these changes created a unique aquatic system in which natural biogeochemical cycles have been heavily disrupted, and pushed into new stable states. Among many environmental changes to the lakes, which have already been recognized and empirically proven, some aspects of the system functioning have remained unknown. In the current study we explore biogeochemical processes of production and emission of GHGs in Lake Licheńskie (LLi), acting as the most transformed amidst the group of Konin lakes. Based on the examples of Lake Stechlin (Germany) and Lake Bienne (Switzerland), in which long-term discharge of power plant effluents was accompanied by enhanced thermal stratification of the water column (Kirillin et al., 2013; Răman Vinnă et al., 2017), we hypothesized that similar processes in LLi (and possibly in the other Konin lakes) led to higher emissions of GHG from this lake than from natural lakes. Therefore, we established a two-year-long biogeochemical monitoring of LLi which involved GHG distribution in the lake water column, annual diffusive fluxes of CH<sub>4</sub> and N<sub>2</sub>O as well as chemical composition of inflowing PP cooling waters. The flux values obtained were compared to the GHG emissions from other Polish natural lakes (Lake Łódzko-Dymaczewskie (LLD), Lake Dębno (LD), Lake Trześniowskie (LT) and coastal lakes along S Baltic coast). The main goal of our research was (a) to check if the GHG emissions in a highly transformed lake are different from undisturbed lakes and (b) to identify the drivers of the GHG emissions. In spite of being under the strong anthropogenic influence, LLi seems to release low CH<sub>4</sub> and N<sub>2</sub>O. We believe that this study offers some new insights into the biogeochemistry of human-impacted lakes and contributes to a better understanding of the processes behind production and emission of GHG in aquatic systems.

## 2. Materials and Methods

### 2.1. Study Area

Lake Licheńskie (LLi; 18°20'E; 52°18'N; 80 m asl) is an eutrophicated channel (gutter) lake located in the SE part of the Gniezno Lake District, central Poland (Figure 1a). The lake surface is 1.48 km<sup>2</sup>, its mean water depth is 4.9 m and its deepest point (12.6 m) is located in the SW part of the lake basin (Figure 1b). The lake is situated in an agricultural landscape and, together with five other adjacent lakes, is involved in the Pałnow Power Plant (PPP) and the Konin Power Plant (KPP) cooling system (KPP) (Socha & Hutorowicz, 2009). Because LLi is the smallest lake in system (7.7 mln m<sup>3</sup> of water volume in LLi vs. 11.6–21.5 mln m<sup>3</sup> in other lakes) and the first to receive the inputs from both PPs, it is considered as the most affected by the PPs' effluents. The coolant water inflow of approximately 22 m<sup>3</sup>·s<sup>-1</sup> (Grzybowski, 2003) is from the south while the outflows are located in the westernmost and northernmost sectors (Figure 1b). The outflow to the W (to Lake Pałnowskie) is active throughout the whole year, while the latter (to Lake Ślesieńskie) opens only during summers. The lake water level is artificially maintained at 83.7–84.1 m asl. As a result of lateral heat flow, Lake Licheńskie shows appreciable spatial temperature gradients. The highest temperatures throughout the whole year are observed in the central and west part of the lake, which is under the strongest influence of heated waters from the PPP and KPP, and therefore even during cold winters the ice cover is absent at this location (Brzozowska et al., 2007). The cooling water, while entering the lake, usually spreads over the lake surface in a 1- to 2 m-thick layer. It appears however, that during winters warm water wedge develops in front of the canal delivering cooling waters (Figure 1c). The surface temperature difference in the west part of LLi (c.a. 1 km apart) due to this effect can be as high as 6.7°C (Figure 1c). During spring–autumn the temperature differences are between 1.7 and 3.5°C. Because of lacking ice cover LLi is regarded monomictic (Socha & Hutorowicz, 2009; Stawecki et al., 2013), which is quite unusual for this geographical region. The mixing of the water column occurs between September and April/May while during the warmest season (May–September) the lake becomes thermally and chemically stratified (Stawecki et al., 2013). Owing to flushing by the cooling waters, the lake has a very rapid water exchange rate of 2–9 days (Stawecki et al., 2013).

The distribution of reference lakes of this study is depicted in Figure 1a and their features are summarized in Table 1. The lakes represent medium-size class lakes (1–100 km<sup>2</sup>) and two genetic types (glacial and coastal



**Figure 1.** Location (A), bathymetry (B) and thermal structure (C) of Lake Licheńskie. Black arrow indicate the inflow of cooling waters to the lake and red arrows show outflows from the lake. The Pałnów PP is located W of the lake, and the Konin PP is situated SW of the lake. W part of the lake is heavily affected by the PPs' waters and hardly freezes during winters. Sampling location L1 is at the deepest point. At station L2, located in front of the channel mouth (yellow open circle), CH<sub>4</sub> and N<sub>2</sub>O were measured between December 2022 and February 2023. Locations of reference lakes are shown on the inset map in panel (A) LLD–L. Łódzko-Dymaczewskie, LD–L. Dębno, LT–L. Trzeźniowskie, LL–L. Łebsko, LG–L. Gardno, LKo–L. Kopań, LW–Lake Wicko, LB–L. Bukowo, LJ–L. Jamno, LR–L. Resko. LL, LG, LKo, LW, LB, LJ and LR are referred to as coastal lakes.

**Table 1**  
*Morphometric Features of Lake Licheńskie and Reference Lakes*

Lake	Acronym	Genesis	Depth [m] (mean/max)	Area [km <sup>2</sup> ]	Density stratification	Mixing regime	Trophic state
Lake Licheńskie	LLi	Glacial (gutter)	4.9/12.6	1.48	Stratified	Monomictic	Eutrophic
Lake Łódzko-Dymaczewskie	LLD	Glacial (gutter)	3.6/12.0	1.26	Stratified	Dimictic	Hypertrophic
Lake Dębno	LD	Glacial (gutter)	6.8/11.6	0.25	Stratified	Dimictic	Eutrophic
Lake Trzeźniowskie	LT	Glacial (gutter)	19.3/58.8	1.86	Stratified	Dimictic	Mesotrophic
Lake Łebsko	LL	Coastal lake	1.5/6.3	71.42	Non-stratified	Polymictic	Eutrophic/hypertrophic
Lake Gardno	LG	Coastal lake	1.5/2.6	24.69	Non-stratified	Polymictic	Eutrophic/hypertrophic
Lake Wicko	LW	Coastal lake	2.0/6.1	10.59	Non-stratified	Polymictic	Eutrophic/hypertrophic
Lake Kopań	LKo	Coastal lake	1.9/3.9	7.90	Non-stratified	Polymictic	Eutrophic/hypertrophic
Lake Bukowo	LB	Coastal lake	1.8/2.8	17.47	Non-stratified	Polymictic	Eutrophic/hypertrophic
Lake Jamno	LJ	Coastal lake	1.4/3.9	22.40	Non-stratified	Polymictic	Eutrophic/hypertrophic
Lake Resko Przymorskie	LR	Coastal lake	1.3/2.5	6.87	Non-stratified	Polymictic	Eutrophic/hypertrophic

Note. Lake depth and area reported after Jańczak (1997).

lakes). Two reference lakes (LLD and LD) are very similar to LLi in terms of basin morphometry (Table 1), thermal structure (Figure S1 in Supporting Information S1), high degree of eutrophication as well as catchment characteristics (3.0–3.5° mean slope, low contribution of flowing waters, predominance of open landscape). In addition, both these lakes are under partial protection (they are located within the buffer zone of the Wielkopolski National Park) which eliminates direct anthropogenic influences on biogeochemical processes. LT and a group of coastal lakes (7 lakes altogether) represent contrastive environments. LT is a deep, relatively coldwater and mesotrophic lake (Table 1; Figure S1 in Supporting Information S1) while coastal lakes are shallow, polymictic,  $\beta$ -oligohaline and highly eutrophic/hypertrophic lakes (Table 1; Figure S1 in Supporting Information S1). These lakes were involved in this study to extend the spectrum of possible GHG concentrations and emissions which allowed us to assess the difference between biogeochemical conditions of LLi and natural lakes of its kind. Not without significance was that all the reference lakes were free of ice for the whole sampling period. It made them similar to LLi and enabled obtaining all-year long GHG emission records without any effect of lake ice/ice melt. To the best of our knowledge the lakes involved in this study are the only Polish lakes for which GHG data are available.

## 2.2. Methods

This study uses chemical data deriving from different sources. A large part of measurements were done by the authors during field campaigns in LLi (December 2014–November 2015 and March 2022–February 2023) and in LT, LLD and LD (between July 2019 and July 2020). However, monitoring data from the LLi inflow canal (IC in Figure 1a) were released by the ZE PAK by courtesy of the Management Comitee. All these data has not been published so far. The data from coastal lakes of Southern Baltic were taken from Woszczyk and Schubert (2021). The methods of the study described in detail below refer to the original data from LLi, LT, LLD and LD, while the methods used to analyze water samples from coastal lakes were reported in relevant paper by Woszczyk and Schubert (2021).

### 2.2.1. Water Sampling and In Situ Measurements

The water column of LLi was sampled monthly at the deepest site of the lake (12.6 m-deep) between December 2014 and November 2015. Lake water samples were taken with 1 m resolution from the surface to the near bottom layer. In addition, to check the changes in GHG concentrations and emissions in different years the lake surface was also sampled in the same location each month between March 2022 and February 2023. The samples from reference lakes (LT, LLD and LD) were taken monthly between July 2019 and July 2020, while coastal lakes were sampled between February and October 2015 (Woszczyk & Schubert, 2021). The surface water samples were collected directly at the air-water interface by hand and the deeper water layers were sampled using a Ruttner sampler (KC Denmark A/S). The LLi, LT, LLD and LD samples for  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentration were stored unpreserved in 500 mL HDPE containers and the water for dissolved gases was preserved with KOH powder (min. 85 wt. %; c.a. 1 g) and kept in amber glass 100 mL serum bottles stoppered with butyl septa and crimped with Al seals. Until the measurements the samples were stored in the dark in a cool box (at 4°C).

The LLi, LT, LLD and LD water temperature, pH as well as dissolved  $\text{O}_2$  were determined in situ with a YSI Professional Plus probe, calibrated and checked with certified reference material (Harbor water, NWHAMIL-20.2) beforehand. Ion composition of water was analyzed within 2 days after collection.  $\text{CH}_4$  and  $\text{N}_2\text{O}$  were analyzed within 1–2 weeks after collection.

### 2.2.2. Analytical Methods

The chemical composition of water samples was analyzed after filtration through 0.45  $\mu\text{m}$  membrane disc filters.  $\text{NH}_4^+$  and  $\text{NO}_3^-$  were analyzed with ion-exchange chromatography (ICS2000 Dionex equipped with an IonPac AS18 column). Analytical quality was ascertained with CRMs (Cranberry-05 and NWHAMIL-20.2, Battle-02, Huron-20 and Trois-94). The accuracy of the pH results was 94%–97% and for ions it varied between 93% and 104%. For  $\text{CH}_4$  and  $\text{N}_2\text{O}$  analysis in LLi, LT, LLD and LD a 20%  $\text{N}_2$ -filled headspace volume was created. Then, after initial hand shaking, the samples were left overnight to equilibrate at a constant room temperature and analyzed with a gas chromatograph (GC; Agilent). For the analysis of  $\text{CH}_4$  a Carboxen 1,010 Plot 30m  $\times$  0.53 mm  $\times$  30  $\mu\text{m}$  column (Supelco) and a flame ionization detector (FID) was used. For  $\text{N}_2\text{O}$  a GS-Carbonplot 30m  $\times$  0.32 mm  $\times$  3  $\mu\text{m}$  (Agilent Technologies) column and an electron capture detector (ECD) was used. Concentrations of  $\text{CH}_4$  and  $\text{N}_2\text{O}$  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 (1979) as well as Weiss and Price (1980). For quality control gas standards (CH<sub>4</sub> in N<sub>2</sub> 100.0 ± 1.5 ppm mol and N<sub>2</sub>O in N<sub>2</sub> 100.0 ± 1.5 ppm mol; PanGas; Switzerland) were used. Limit of quantification of our GC measurement was 1 ppm for CH<sub>4</sub> and 0.2 ppm for N<sub>2</sub>O. Analytical error was estimated to ±5%.

### 2.2.3. Data Analysis

Based on water temperature and related density we calculated a stratification stability index ( $W_S$ ; J·m<sup>-2</sup>) (Idso, 1973). This value expresses the work to be done by the wind in order to destratify the lake and is calculated as

$$W_S = \frac{g}{A_l} \int_0^{z_m} (z - z_*) (\rho_z - \bar{\rho}) A_z dz \quad (1)$$

where  $g$  represents acceleration due to gravity (m·s<sup>-2</sup>),  $A_l$ –lake surface area (m<sup>2</sup>),  $A_z$ –surface area at depth  $z$  (m<sup>2</sup>),  $z$ –depth (m),  $z_*$ –depth at  $\bar{\rho}$  (m),  $\rho_z$ –water density at  $z$  (kg·m<sup>-3</sup>) and  $\bar{\rho}$ –mean lake water density in the water column (kg·m<sup>-3</sup>). Lake water density  $\rho_z$  was calculated as a function of temperature, salinity and hydrostatic pressure according to Sun et al. (2008). The higher the  $W_S$ , the stronger is the vertical thermal (and density) stratification of lake waters. The thermocline was defined in this study as at least 1°C temperature difference per 1 m depth change.

Rates of areal accumulation of CH<sub>4</sub> in the hypolimnion (mmol·m<sup>-2</sup> d<sup>-1</sup>) were calculated from the slope of the linear regression line (mmol·d<sup>-1</sup>) relating the total hypolimnetic CH<sub>4</sub> and duration of the stratification period divided by the area of the upper boundary of the hypolimnion (Matthews et al., 2005).

The diffusive fluxes of CH<sub>4</sub> across the metalimnion were approximated with  $D_{CH_4(t,z_m)}$  (mmol·m<sup>-2</sup> d<sup>-1</sup>) (Kaankala et al., 2006) expressed as

$$D_{CH_4(t,z_m)} = K \cdot \frac{[CH_4(t,z_{m-1}) - CH_4(t,z_m)]}{\Delta z} \quad (2)$$

where  $K$ , vertical CH<sub>4</sub> diffusion coefficient, is parametrized with an empirical formula below

$$K = a_k \cdot (N^2)^{-0.43} = 7.06 \cdot 10^{-3} \cdot (A_l)^{0.56} \cdot (N^2)^{-0.43} \quad (3)$$

$a_k$ –empirical parameter related to lake surface area  $A_l$  (km<sup>2</sup>) and

$N^2$ –Brunt-Väisälä stability frequency [s<sup>-2</sup>] calculated from lake water density ( $\rho$ ) for different depths in the water column ( $z$ ) (Lin et al., 2021)

$$N^2 = -\frac{g}{\rho} \cdot \frac{\partial \rho}{\partial z} \quad (4)$$

The CH<sub>4</sub> transfer from the hypolimnion to overlying layers ( $F_{hyp}$ ; mmol·m<sup>-2</sup> d<sup>-1</sup>) due to vertical water mixing was estimated using a two layer lake model with monthly resolution for the period from June to September 2015 (hypolimnion duration period) with Equation (5) given by Matthews et al. (2005).

$$F_{hyp} = v_i \cdot (CH_{4/h} - CH_{4/e}) \quad (5)$$

$F_{hyp}$  was derived as a product of CH<sub>4</sub> concentration difference (mmol·m<sup>-3</sup>) between hypo- ( $CH_{4/h}$ ) and epilimnion ( $CH_{4/e}$ ) and a vertical heat exchange coefficient ( $v_i$ ; m·d<sup>-1</sup>). The latter parameter was calculated from volume ( $V_h$ ) and surface area ( $A_{hyp}$ ) of the hypolimnion, duration of the stratification period (days), average volume-weighted epilimnion temperature ( $T_e$ ; °C) and volume-weighted temperatures of the hypolimnion at the beginning ( $T_{h,i}$ ; °C) and at the end ( $T_{h,s}$ ; °C) of the stratification period as follows (Matthews et al., 2005)

$$v_i = \left[ \frac{V_h}{A_{hyp} \cdot t_s} \right] \cdot \ln \left[ \frac{T_{h,i} - T_e}{T_{h,s} - T_e} \right] \quad (6)$$

The GHG fluxes from the lake surface to the atmosphere ( $F_{surf}$ ;  $\text{mmol}\cdot\text{m}^{-2}\text{d}^{-1}$ ) were calculated from Fick's first law of diffusion

$$F_{surf} = 240 \cdot k \cdot (C_w - C_{eq}) \quad (7)$$

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

Gas transfer velocity  $k$  was calculated as

$$k = k_{600} \cdot \left(\frac{Sc}{600}\right)^{-0.5} \quad (8)$$

where  $Sc_i$  denotes Schmidt number of a gas  $i$  at the temperature and salinity of sample collection and  $k_{600}$  is gas transfer velocity adjusted to  $Sc = 600$ .  $Sc$  values were taken from Ramsing and Gundersen (1994). Since several equations exist to obtain  $k_{600}$ , we calculated this parameter as a function of wind speed  $U_{10}$  at 10 m above water surface ( $\text{m}\cdot\text{s}^{-1}$ ) and lake surface area ( $A_i$ ;  $\text{km}^2$ ) using the following formulas:

$$k_{600} = 0.72 \cdot U_{10} \quad (9)$$

(Crusius & Wanninkhof, 2003; for  $U_{10} < 3.7 \text{ m}\cdot\text{s}^{-1}$ )

$$k_{600} = 4.33 \cdot U_{10} - 13.3 \quad (10)$$

(Crusius & Wanninkhof, 2003; for  $U_{10} \geq 3.7 \text{ m}\cdot\text{s}^{-1}$ )

$$k_{600} = 2.07 + 0.215 \cdot U_{10}^{1.7} \quad (11)$$

(Cole & Caraco, 1998)

$$k_{600} = 0.24 \cdot (4.045 + 2.58 \cdot U_{10}) \quad (12)$$

(Brase et al., 2017) and

$$k_{600} = 2.51 + 1.48 \cdot U_{10} + 0.39 \cdot U_{10} \cdot \log(A_i) \quad (13)$$

(Vachon & Prairie, 2013).

We found, however, that Equation 13 seemed to overestimate the fluxes since the annual emissions of  $\text{CH}_4$  (expressed as a number of moles emitted from the total lake surface during a year) calculated using the method of Vachon and Prairie (2013) surpassed the total amount of methane in the lakes (e.g., in LLi emitted  $\text{CH}_4$  was equivalent to 189% of the total water column  $\text{CH}_4$ ; corresponding values for LLD and LD were 135% and 100%, respectively). This was not the case when the fluxes were calculated with Equations 9–12. Therefore, the  $F$  values obtained using Equation 13 were only reported in Tables 2 and 3 but they were not used in further discussion and the mean monthly diffusive fluxes shown in Figures 3 and 4 were derived from Equations 9–12.

As  $U_{10}$  for LLi we used averaged monthly wind speed values for the town of Koło (23 km SE of LLi) and Powidz (30 km NW of LLi) obtained from <https://en.tutiempo.net/climate/poland.html>. For LLD and LD we used  $U_{10}$  measured in Poznań (15–18 km N/NE of the lakes) while for LT the  $U_{10}$  was from meteorological stations in Słubice and Babimost (50 km W of LT and 40 km SE of LT, respectively). Comparing anemometric data from the rather distant locations showed that the differences between the average monthly wind speeds in Koło and Powidz (c.a. 55 km apart) as well as in Słubice and Babimost (c.a. 85 km apart) during the period of this study were not statistically significant corroborating the use of those values for our study. On the other hand, the coefficient of variability (CV [%];  $\text{CV} = 100 \cdot \text{standard deviation} / \text{arithmetic mean}$ ) for monthly averaged wind speed in the above stations was 10%–35% ( $\bar{x} = 22\%$ ). Therefore adopting these values provides estimations of  $U_{10}$  for the lakes with  $\pm 22\%$  uncertainty.  $C_{eq}$  were calculated on the basis of mean atmospheric concentrations of  $\text{CH}_4$  and  $\text{N}_2\text{O}$  over Europe in 2015 ( $1.859 \cdot 10^{-6}$  and  $3.264 \cdot 10^{-7}$  bar, respectively; [https://www.eea.europa.eu/data-and-maps/daviz/atmospheric-concentration-of-carbon-dioxide-5#tab-chart\\_6](https://www.eea.europa.eu/data-and-maps/daviz/atmospheric-concentration-of-carbon-dioxide-5#tab-chart_6);  $\text{CH}_4$  concentrations reported for 2015 and  $\text{N}_2\text{O}$  concentrations for 2009) and relevant Henry constants ( $K_H$ ). The  $K_H$  values, adopted from Sander (2015) were  $0.0014 \text{ mol}\cdot\text{L}^{-1} \text{ bar}^{-1}$  for  $\text{CH}_4$  and  $0.025 \text{ mol}\cdot\text{L}^{-1} \text{ bar}^{-1}$  for  $\text{N}_2\text{O}$ .

**Table 2**  
Temporal Pattern of CH<sub>4</sub> and N<sub>2</sub>O Fluxes From Lake Licheńskie During 2014/2015

GHG	Unit	12.2014	01.2015	02.2015	03.2015	04.2015	06.2015	07.2015	08.2015	09.2015	10.2015	11.2015
Crusius and Wanninkhof (2003)												
CH <sub>4</sub>	mmol·m <sup>-2</sup> d <sup>-1</sup>	0.37	0.34	0.03	0.41	0.45	0.64	1.08	0.23	0.18	0.18	0.05
N <sub>2</sub> O	μmol·m <sup>-2</sup> d <sup>-1</sup>	14.05	10.69	4.75	18.74	21.11	1.22	1.64	0.90	1.04	3.89	3.33
Cole and Caraco (1998)												
CH <sub>4</sub>	mmol·m <sup>-2</sup> d <sup>-1</sup>	0.24	0.21	0.04	0.32	0.34	0.99	1.14	0.35	0.27	0.24	0.08
N <sub>2</sub> O	μmol·m <sup>-2</sup> d <sup>-1</sup>	8.99	6.48	6.30	14.57	15.90	1.89	1.73	1.37	1.58	5.26	5.12
Brase et al. (2017)												
CH <sub>4</sub>	mmol·m <sup>-2</sup> d <sup>-1</sup>	0.18	0.15	0.03	0.25	0.26	0.80	0.91	0.28	0.22	0.19	0.06
N <sub>2</sub> O	μmol·m <sup>-2</sup> d <sup>-1</sup>	6.77	4.83	5.05	11.30	12.28	1.53	1.37	1.10	1.28	4.21	4.14
Vachon and Prairie (2013)												
CH <sub>4</sub>	mmol·m <sup>-2</sup> d <sup>-1</sup>	0.45	0.38	0.07	0.62	0.65	2.03	2.29	0.71	0.55	0.48	0.16
N <sub>2</sub> O	μmol·m <sup>-2</sup> d <sup>-1</sup>	17.06	12.16	12.74	28.47	30.95	3.87	3.45	2.78	3.22	10.63	10.44

For assessing statistical significance of differences between chemical parameters of LLi and reference lakes we used nonparametric Kruskal-Wallis test supported with Dunn's post hoc test (for more than 2 samples) or Mann-Whitney U test (for 2 samples). The latter was applied to verify hypothesis on the equality of annual fluxes of CH<sub>4</sub> and N<sub>2</sub>O in two study periods (2014/15 vs. 2022/23). The calculations were performed with Past 4.09 program (Hammer et al., 2001).

### 3. Results

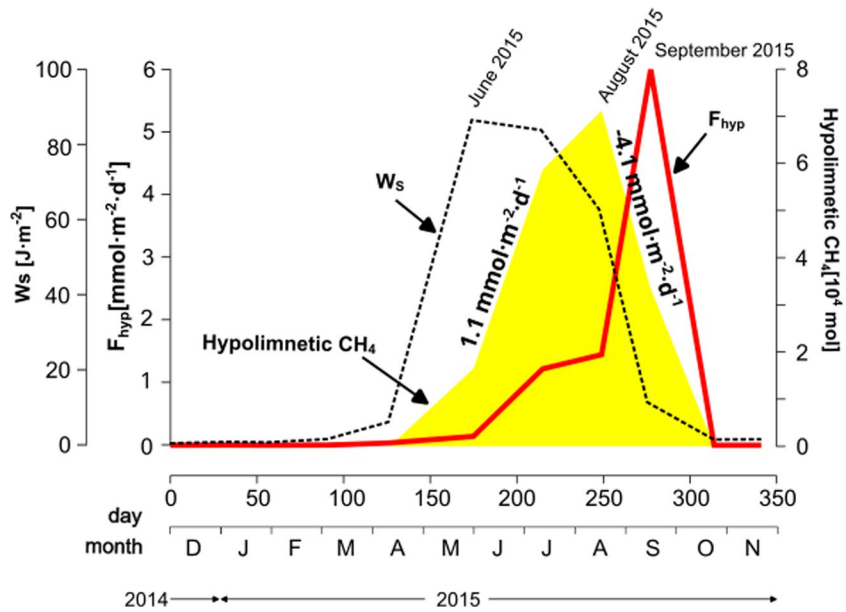
#### 3.1. Bulk Water Parameters

During the study period lake water temperatures varied between 3.5°C in February and 25.2°C in July (Figure S2a in Supporting Information S1). Except of February 2015 the lake water temperatures decreased with depth, however, the thermocline occurred only between April and September 2015. During this period the lake was thermally stratified, as confirmed by  $W_s$  with strongest stratification in June 2015 (Figure 2). The differences in stratification stability ( $W_s$ ) between LLi and LLD and LD were statistically insignificant, but LT differed significantly from all other lakes (for coastal lakes the  $W_s$  was not calculated because these lakes are permanently unstratified). Rapid drop in  $W_s$  between August and September was owing to late summer/early autumn lake overturn. The position of thermocline indicates that the thickness of the epilimnion in LLi varied between 9 m in April and 4 m in July 2015 and the hypolimnion encompassed a 1–7 m-thick water layer in April and June, respectively. LLi showed

**Table 3**  
Temporal Pattern of CH<sub>4</sub> and N<sub>2</sub>O Fluxes From Lake Licheńskie During 2022/23

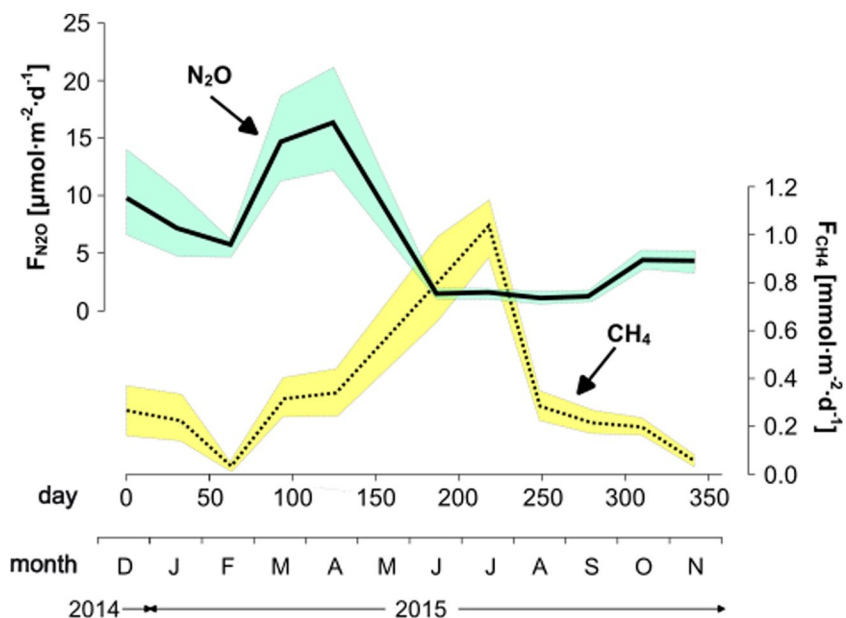
GHG	Unit	03.2022	04.2022	05.2022	06.2022	07.2022	08.2022	09.2022	10.2022	11.2022	12.2022	01.2023	02.2023
Crusius and Wanninkhof (2003)													
CH <sub>4</sub>	mmol·m <sup>-2</sup> d <sup>-1</sup>	0.06	0.18	0.56	0.46	0.26	0.26	0.04	0.06	0.17	0.09	0.13	0.27
N <sub>2</sub> O	μmol·m <sup>-2</sup> d <sup>-1</sup>	2.99	4.52	5.52	-1.03	-1.83	-2.33	7.97	8.94	7.06	14.35	14.52	13.78
Cole and Caraco (1998)													
CH <sub>4</sub>	mmol·m <sup>-2</sup> d <sup>-1</sup>	0.10	0.17	0.86	0.72	0.40	0.43	0.07	0.09	0.26	0.09	0.13	0.20
N <sub>2</sub> O	μmol·m <sup>-2</sup> d <sup>-1</sup>	4.64	4.17	8.45	-1.62	-2.82	-3.80	12.59	14.10	10.97	14.97	13.79	10.19
Brase et al. (2017)													
CH <sub>4</sub>	mmol·m <sup>-2</sup> d <sup>-1</sup>	0.08	0.13	0.69	0.58	0.32	0.35	0.06	0.07	0.21	0.07	0.10	0.15
N <sub>2</sub> O	μmol·m <sup>-2</sup> d <sup>-1</sup>	3.77	3.29	6.82	-1.32	-2.28	-3.10	10.27	11.49	8.91	11.87	10.87	7.86
Vachon and Prairie (2013)													
CH <sub>4</sub>	mmol·m <sup>-2</sup> d <sup>-1</sup>	0.20	0.33	1.74	1.47	0.82	0.88	0.14	0.18	0.53	0.18	0.25	0.38
N <sub>2</sub> O	μmol·m <sup>-2</sup> d <sup>-1</sup>	9.52	8.28	17.21	-3.33	-5.77	-7.85	25.93	29.03	22.49	29.93	27.41	19.79



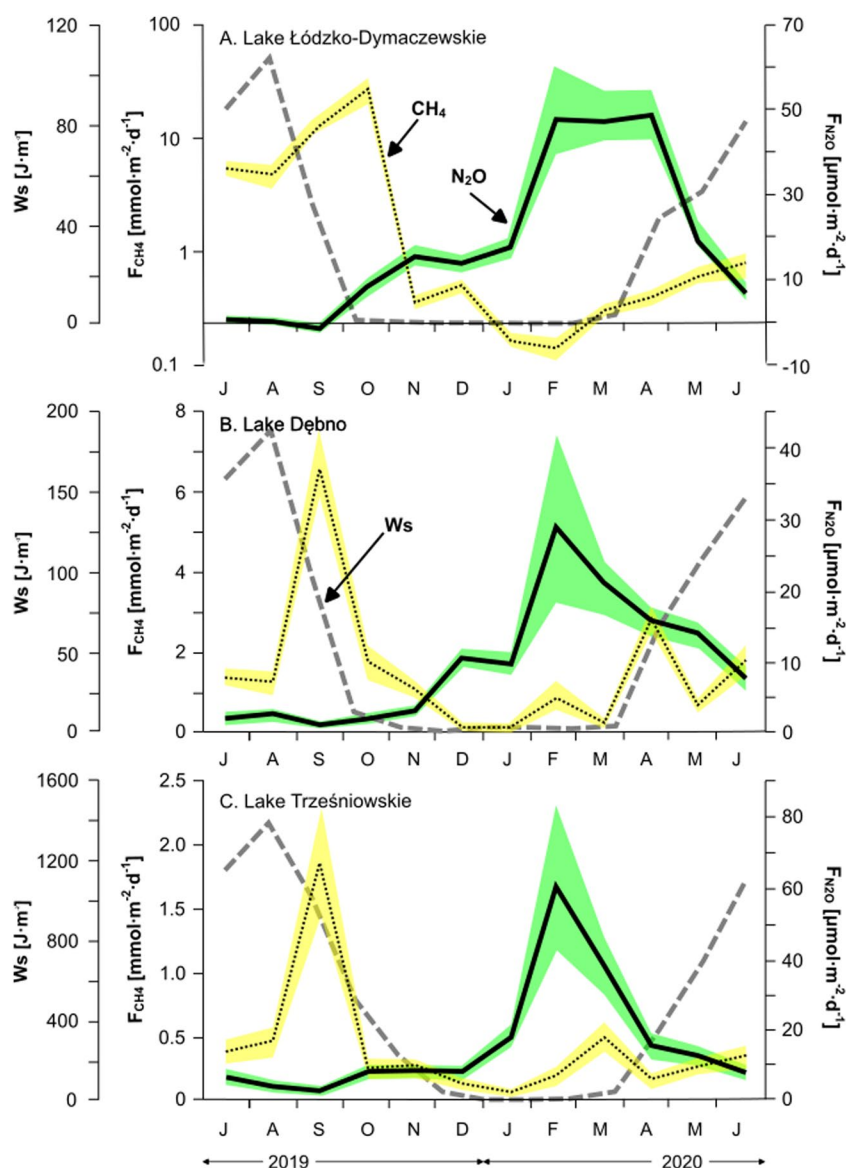


**Figure 2.** Temporal pattern of water column stratification ( $W_s$ ; dotted line), diffusive  $\text{CH}_4$  flux from the hypolimnion, ( $F_{hyp}$ , in red) and accumulation of  $\text{CH}_4$  in the hypolimnion (in yellow) during the period of study. Duration of the study period expressed in days starting from 18/12/2014. Positive and negative values in bold show accumulation and removal rates of hypolimnetic  $\text{CH}_4$ , respectively.

somewhat lower volume of hypolimnion than the reference lakes. On an annual basis, the total volume of hypolimnetic waters in LLI accounted for 6% of the total lake volume. In LD, LLD and LT the share of hypolimnion was 10%, 12% and 29% respectively. Thermal and density stratification of the lake water column was followed by vertical and seasonal hydrochemical changes. Prior to and after the stratification, the lake water was chemically homogenous albeit the values of bulk chemical parameters were different in these two periods. Between December 2014 and April 2015, EC and pH showed minor variations between 623 and 663  $\mu\text{S}\cdot\text{cm}^{-1}$  and from 7.2 to 7.6, respectively while in October and November 2015, EC was 560–570  $\mu\text{S}\cdot\text{cm}^{-1}$  and pH was 7.6–8.2 (Figure S2b in



**Figure 3.** Monthly fluxes of  $\text{N}_2\text{O}$  (green) and  $\text{CH}_4$  (yellow) from Lake Licheńskie between December 2014 and November 2015 calculated with different methods.



**Figure 4.** Monthly fluxes of  $\text{N}_2\text{O}$  (green) and  $\text{CH}_4$  (yellow) from reference lakes, Lake Łódzko-Dymaczewskie (A), Lake Dębno (b) and Lake Trześniowskie (c) between July 2019 and June 2020 calculated with different methods. Note logarithmic scale for the  $\text{CH}_4$  flux from LLD. Logarithmic scaling was used to show the changes in  $F_{\text{CH}_4}$  between November 2019 and July 2020. GHG emissions shown at the background of stratification stability index ( $W_s$ ; gray dotted line).

Supporting Information S1).  $\text{O}_2$  showed an increase from  $9.1\text{--}9.7\text{ mg}\cdot\text{L}^{-1}$  in December 2014 to  $12.3\text{--}13.2\text{ mg}\cdot\text{L}^{-1}$  in March 2015 (Figure S2c in Supporting Information S1). The latter values were the maximum  $\text{O}_2$  concentrations in the lake during the study. In October and November 2015 the  $\text{O}_2$  concentration was  $7.4\text{--}9.5\text{ mg}\cdot\text{L}^{-1}$ . Within the hypolimnion the rapid consumption of  $\text{O}_2$  started already in April and in the near-bottom layer (at 12 m depth) hypoxic conditions (i.e.,  $< 2\text{ mg}\cdot\text{L}^{-1}$ ; Diaz, 2001) developed. The maximum vertical extent of the hypoxic zone occurred in June and July 2015 ( $> 5\text{ m}$  water depth), whereas in August and September in the bottom 4–5 m layer the conditions were strongly hypoxic ( $< 0.5\text{ mg}\cdot\text{L}^{-1}$ ; Diaz, 2001) or even anoxic ( $\sim 0\text{ mg}\cdot\text{L}^{-1}$ ; Diaz, 2001). In 2014/15 the oxygen contents in LLi water were significantly different from LLD and coastal lakes but not from LD and LT. LLD were more  $\text{O}_2$ -depleted and coastal lakes were more oxygenated than LLi.

### 3.2. Nitrates and Ammonium

$\text{NO}_3^-$  concentrations in LLi varied from  $0.03 \text{ mg}\cdot\text{L}^{-1}$  in July 2015 to  $3.5 \text{ mg}\cdot\text{L}^{-1}$  in January 2015 and, except of February 2015, the concentrations were vertically uniform (Figure S3 in Supporting Information S1).  $\text{NO}_3^-$  showed an increase from December 2014 to January 2015 followed by a declining trend until July 2015 and a slight increase in August 2015.  $\text{NH}_4^+$  concentrations in the whole water column were below  $0.2 \text{ mg}\cdot\text{L}^{-1}$  for most of the study period. Only, between June and August 2015 the hypolimnion showed  $\text{NH}_4^+$  concentrations up to  $2.5 \text{ mg}\cdot\text{L}^{-1}$  with maximum values in August. In each month, the  $\text{NH}_4^+$  increased downwards.

### 3.3. $\text{CH}_4$ and $\text{N}_2\text{O}$

Between December 2014 and April 2015 the LLi water column was vertically homogenous with regard to  $\text{CH}_4$ .  $\text{CH}_4$  varied from  $0.05$  to  $0.36 \text{ }\mu\text{mol}\cdot\text{L}^{-1}$  with the lowest concentrations in February 2015 (Figure S4 in Supporting Information S1). During summer the  $\text{CH}_4$  values increased throughout the whole water column, however in the hypolimnion the concentrations were up to three orders of magnitude higher than in the epilimnion and increased with increasing water depth. Maximum  $\text{CH}_4$  ( $434 \text{ }\mu\text{mol}\cdot\text{L}^{-1}$ ) occurred in September 2015. Accumulation of  $\text{CH}_4$  in the hypolimnion commenced shortly after the onset of anoxia and continued in a nearly linear fashion until August with a rate of  $1.1 \text{ mmol}\cdot\text{m}^{-2} \text{ d}^{-1}$  (Figure 3). At the decline of the summer a rapid depletion of the hypolimnetic  $\text{CH}_4$  storage ( $4.1 \text{ mmol}\cdot\text{m}^{-2} \text{ d}^{-1}$ ) until complete removal in October was seen (Figure 2).

$\text{N}_2\text{O}$  changed from  $<5$  to  $27.5 \text{ nmol}\cdot\text{L}^{-1}$  (Figure S5 in Supporting Information S1). The minimum concentrations were measured during summer (June–September) in the meso- and hypolimnion, whereas the highest values occurred in March. Prior to and after the stratification period (April–September) the  $\text{N}_2\text{O}$  showed only minor variability in the water column however, in March and April the near bottom layer differed from the above waters. In March the concentrations at  $>10 \text{ m}$  depth were higher than in the upper layer and in April there was a slight  $\text{N}_2\text{O}$  decline below  $8 \text{ m}$  depth.

$\text{N}_2\text{O}$  concentrations in LLi were statistically significantly different (lower) than in all reference lakes (Figure S6 in Supporting Information S1). As for  $\text{CH}_4$ , the concentrations in LLi were significantly different (lower) than in LLD, LD and LT. Only coastal lakes displayed no significant differences in  $\text{CH}_4$  values compared to LLi (Figure S6 in Supporting Information S1).

### 3.4. GHG Fluxes

In 2014/15 the  $\text{N}_2\text{O}$  and  $\text{CH}_4$  emissions from LLi were positive throughout the period of study and ranged from  $0.90$  to  $21.11 \text{ }\mu\text{mol}\cdot\text{m}^{-2} \text{ d}^{-1}$  and  $0.03$  to  $1.14 \text{ mmol}\cdot\text{m}^{-2} \text{ d}^{-1}$ , respectively (Figure 3; Table 2). However, in 2022/23 we obtained a bit smaller fluxes of both gases ranging from  $-3.10$  to  $14.97 \text{ }\mu\text{mol}\cdot\text{m}^{-2} \text{ d}^{-1}$  for  $\text{N}_2\text{O}$  and from  $0.04$  to  $0.86 \text{ mmol}\cdot\text{m}^{-2} \text{ d}^{-1}$  for  $\text{CH}_4$  (Table 3). On a yearly basis in 2014/15 LLi emitted  $4.90$ – $7.40$  ( $\bar{x} = 6.19$ )  $\mu\text{mol N}_2\text{O}\cdot\text{m}^{-2} \text{ d}^{-1}$  and  $0.30$ – $0.38$  ( $\bar{x} = 0.35$ )  $\text{mmol CH}_4\cdot\text{m}^{-2} \text{ d}^{-1}$  and in 2022/23 the respective values were  $5.70$ – $7.14$  ( $\bar{x} = 6.35$ )  $\mu\text{mol N}_2\text{O}\cdot\text{m}^{-2} \text{ d}^{-1}$  and  $0.21$ – $0.29$  ( $\bar{x} = 0.25$ )  $\text{mmol CH}_4\cdot\text{m}^{-2} \text{ d}^{-1}$  (Table 4). The differences between diffusive fluxes from LLi in 2014/15 and 2022/23 for both gases were statistically insignificant. It seems therefore that the GHG fluxes obtained were not accidental. There were, however, some differences in temporal distribution of fluxes throughout the periods studied. In 2014/15 the  $\text{N}_2\text{O}$  was primarily released during spring while in 2022/23 the culmination of  $\text{N}_2\text{O}$  emissions was during autumn/winter. In both periods during the summer months the  $\text{N}_2\text{O}$  fluxes were at their minima, however in 2022/23 between June and August the  $F_{\text{N}_2\text{O}}$  was slightly negative (Figure 3; Table 3) while in 2014/15 only positive values were obtained.  $\text{CH}_4$  emission peak in 2014/15 season was during mid-summer, while in 2022/23—as early as in spring (Figure 3; Table 3).

GHG emissions from other inland lakes in Poland varied between  $7.53$ – $10.30 \text{ }\mu\text{mol}\cdot\text{m}^{-2} \text{ d}^{-1}$  in LD and  $15.89$ – $20.35 \text{ }\mu\text{mol}\cdot\text{m}^{-2} \text{ d}^{-1}$  in LLD for  $\text{N}_2\text{O}$  (Table 4) and between  $0.38$ – $0.59 \text{ mmol}\cdot\text{m}^{-2} \text{ d}^{-1}$  in LT and  $3.37$ – $4.80 \text{ mmol}\cdot\text{m}^{-2} \text{ d}^{-1}$  in LLD for  $\text{CH}_4$  (Table 4). Coastal lakes, however, displayed different pattern than inland lakes as they released as high as  $13.64$ – $20.45 \text{ }\mu\text{mol N}_2\text{O}\cdot\text{m}^{-2} \text{ d}^{-1}$  while the emissions of  $\text{CH}_4$  were in the range  $0.51$ – $2.14 \text{ mmol CH}_4\cdot\text{m}^{-2} \text{ d}^{-1}$  (Table 4). In all reference lakes the emissions of  $\text{CH}_4$  culminated during the summer/early autumn (July–October) and  $\text{N}_2\text{O}$  peaked in winter/early spring (February–April) (Figure 4). The diffusive emissions of GHG from LLi seem lower than the emissions from reference lakes (Table 4). For  $\text{CH}_4$  statistical test proved significant differences between LLi and LLD, LD and coastal lakes, while the differences between LLi and LT were not significant. For  $\text{N}_2\text{O}$  however, only coastal lakes have significantly different fluxes than LLi.

**Table 4**  
*Atmospheric Fluxes of CH<sub>4</sub> and N<sub>2</sub>O From Lake Licheńskie and Reference Lakes Calculated With Different Approaches*

Lake	Method of calculation	Year/s of sampling	GHG flux (F)	
			CH <sub>4</sub> mmol·m <sup>-2</sup> d <sup>-1</sup>	N <sub>2</sub> O μmol·m <sup>-2</sup> d <sup>-1</sup>
Lake Licheńskie	Crusius and Wanninkhof (2003)	2014/2015	0.36	7.40
	Cole and Caraco (1998)		0.38	6.29
	Brase et al. (2017)		0.30	4.90
	Vachon and Prairie (2013)		0.76	12.34
	Crusius and Wanninkhof (2003)	2022/2023	0.21	6.20
	Cole and Caraco (1998)		0.29	7.14
	Brase et al. (2017)		0.24	5.70
	Vachon and Prairie (2013)		0.59	14.39
Lake Łódzko-Dymaczewskie	Crusius and Wanninkhof (2003)	2019/2020	3.01	13.49
	Cole and Caraco (1998)		4.70	20.35
	Brase et al. (2017)		3.80	15.89
	Vachon and Prairie (2013)		9.49	39.55
Lake Dębno	Crusius and Wanninkhof (2003)	2019/2020	1.13	6.35
	Cole and Caraco (1998)		1.73	9.60
	Brase et al. (2017)		1.39	7.53
	Vachon and Prairie (2013)		3.02	16.34
Lake Trześniowskie	Crusius and Wanninkhof (2003)	2019/2020	0.37	10.52
	Cole and Caraco (1998)		0.59	16.29
	Brase et al. (2017)		0.48	13.00
	Vachon and Prairie (2013)		1.24	33.38
Lake Bukowo	Crusius and Wanninkhof (2003)	2015	1.91	15.66
	Cole and Caraco (1998)		1.09	9.48
	Brase et al. (2017)		0.79	7.17
	Vachon and Prairie (2013)		2.05	19.44
Lake Gardno	Crusius and Wanninkhof (2003)	2015	0.86	14.43
	Cole and Caraco (1998)		0.51	9.67
	Brase et al. (2017)		0.38	7.26
	Vachon and Prairie (2013)		0.97	19.50
Lake Jamno	Crusius and Wanninkhof (2003)	2015	0.96	19.60
	Cole and Caraco (1998)		0.54	11.40
	Brase et al. (2017)		0.39	8.38
	Vachon and Prairie (2013)		1.01	23.76
Lake Kopań	Crusius and Wanninkhof (2003)	2015	1.55	16.80
	Cole and Caraco (1998)		0.88	9.25
	Brase et al. (2017)		0.64	6.74
	Vachon and Prairie (2013)		1.60	15.95
Lake Łebsko	Crusius and Wanninkhof (2003)	2015	0.46	14.12
	Cole and Caraco (1998)		0.28	8.41
	Brase et al. (2017)		0.21	6.20
	Vachon and Prairie (2013)		0.59	19.12

**Table 4**  
Continued

Lake	Method of calculation	Year/s of sampling	GHG flux (F)	
			CH <sub>4</sub> mmol·m <sup>-2</sup> d <sup>-1</sup>	N <sub>2</sub> O μmol·m <sup>-2</sup> d <sup>-1</sup>
Lake Resko Przym.	Crusius and Wanninkhof (2003)	2015	0.69	16.49
	Cole and Caraco (1998)		0.38	9.84
	Brase et al. (2017)		0.28	7.26
	Vachon and Prairie (2013)		0.69	16.82
Lake Wiczo	Crusius and Wanninkhof (2003)	2015	1.80	19.36
	Cole and Caraco (1998)		1.03	11.45
	Brase et al. (2017)		0.75	8.44
	Vachon and Prairie (2013)		1.89	21.18

Note. Data from Woszczyk and Schubert (2021).

### 3.5. Cooling Water Composition

During the study periods the cooling waters were delivered to LLi at constant rate of approximately 22 m<sup>3</sup>·s<sup>-1</sup>. Physical and chemical properties of the waters are depicted in Figure S7 in Supporting Information S1. In both periods studied the temperature values in the channel were similar and ranged from ca. 9.1–10.3°C in winter to 30.7–31.1°C in summer. Among the N species present NO<sub>3</sub><sup>-</sup> was the most abundant (0.27–3.17 mg·L<sup>-1</sup>). The maximum concentrations of NO<sub>3</sub><sup>-</sup> were during winter. NH<sub>4</sub><sup>+</sup> changed irregularly between <0.06 and 0.33 mg·L<sup>-1</sup>. Nitrites occurred at very low levels of <0.05 mg·L<sup>-1</sup>. Translating the above numbers into loads of N species it appears that 2.4·10<sup>5</sup>–3.4·10<sup>6</sup> mol NO<sub>3</sub>-N (equivalent to 3–48 tonnes of N) and 1.9·10<sup>5</sup>–1.1·10<sup>6</sup> mols of NH<sub>4</sub>-N (c.a. 3–15 tonnes of N) were delivered to the lake monthly during both study periods. Unfortunately, the data on CH<sub>4</sub> and N<sub>2</sub>O concentrations in cooling waters are very scarce. We have only analyzed them from December 2022 and February 2023. The values for this period were relatively high and ranged between 0.61 and 4.19 μmol·L<sup>-1</sup> for CH<sub>4</sub> and 17.9–35.4 nmol·L<sup>-1</sup> for N<sub>2</sub>O. The corresponding concentrations in L1 site were 0.12–0.23 μmol·L<sup>-1</sup> and 20.9–29.2 nmol·L<sup>-1</sup> thus indicating that the cooling waters can be an important source of CH<sub>4</sub> to LLi.

## 4. Discussion

### 4.1. Methane

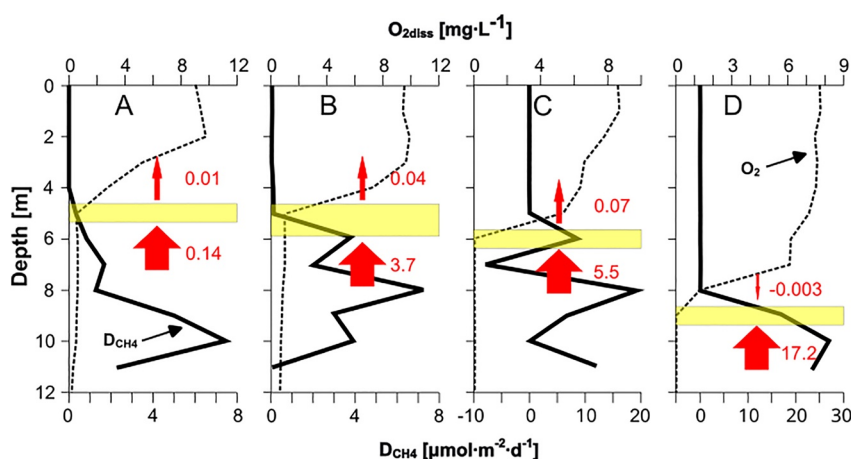
The concentrations of CH<sub>4</sub> in LLi followed typical vertical and seasonal patterns obtained in reference lakes of this study (Figure S4 in Supporting Information S1) as well as was in the other temperate lakes (Casper et al., 2000; Diem et al., 2012; Schubert et al., 2010). The CH<sub>4</sub> showed negative relationship to dissolved O<sub>2</sub> ( $r = -0.57, p < 0.0001$ ) and the highest CH<sub>4</sub> values occurred in hypoxic bottom waters. Compared to most of our reference lakes as well as other eutrophic lakes (Casper et al., 2000; Matthews et al., 2005 and references therein), the concentrations of hypolimnetic CH<sub>4</sub> in LLi (59–434 μmol·L<sup>-1</sup>) were low. Although the water temperature was statistically insignificant for determination of the CH<sub>4</sub> pattern in the lake it was responsible for the enrichment in CH<sub>4</sub> during summer. CH<sub>4</sub> accumulation accompanied thermal stratification of the lake (Figure 2) when rapid O<sub>2</sub> consumption in the hypolimnion occurred thus creating favorable conditions for methanogens, known for being obligate anaerobes (Liu, 2010). In addition, stimulating effect of higher bottom water temperatures (10.4–12.9°C from April to September 2015 vs. 3.6–8.4°C during the rest of the study period) on the rate of methanogenesis has well been established (Avery et al., 2003). However, the rate of the CH<sub>4</sub> accumulation in the LLi hypolimnion of 1.1 mmol·m<sup>-2</sup> d<sup>-1</sup> was lower than in reference eutrophic lakes (Table 5) thus indicating that the production of CH<sub>4</sub> in Lake Licheńskie was weaker than in the other lakes and/or that the CH<sub>4</sub> was consumed anaerobically in the hypolimnion. It is also possible that the inflow of heated waters to the lake induces circulation within the lake such as this described by Nepf and Oldham (1997). Although no research on the lake hydrodynamics has been carried out so far, we believe that such vertical and horizontal water movements can contribute to the erosion of hypolimnion and thus lead to relatively low volume of the hypolimnion in LLi compared to LD and LLD. A progressive destratification of the lake between August and October 2015 resulted in CH<sub>4</sub> removal from the

**Table 5**  
The Rates of Accumulation and Removal of Hypolimnetic CH<sub>4</sub> in Lake Licheńskie and Reference Lakes

Lake	Accumulation rate		Removal rate
	mmol·m <sup>-2</sup> d <sup>-1</sup>		
Lake Licheńskie	April–August 2015		August–October 2015
	1.14		−4.14
Lake Łódzko-Dymaczewskie	July–September 2019	April–July 2020	September–November 2019
	10.0	13.6	−36.2
Lake Dębno	July–September 2019	April–July 2020	September–November 2019
	6.5	3.7	−8.6
Lake Trześniowskie	July 2019–January 2020	April–July 2020	January–March 2020
	0.5	<0.1	−5.6

hypolimnion at a rate of  $-4.1 \text{ mmol}\cdot\text{m}^{-2} \text{ d}^{-1}$  (Figure 2). This value was again lower than in reference eutrophic lakes (Table 5).

A build-up of CH<sub>4</sub> in the hypolimnion and its downward increase indicate a profound role of benthic processes in methane production (Matthews et al., 2005; Schubert et al., 2010). However, steep gradients in CH<sub>4</sub> concentration profiles for June–September 2015 (Figure S4 in Supporting Information S1) suggest oxidation of methane in the water column. Based on the calculated  $D_{\text{CH}_4}$  values and in agreement with previous reports (Schubert et al., 2010; Schubert & Wehrli, 2018; Thalasso et al., 2020; Thottathil et al., 2019) the oxidation zone was located within the metalimnion and below the oxycline at 5–8 m depth. Within this zone the efflux of CH<sub>4</sub> from the hypolimnion ( $D_{\text{CH}_4}$ ) of  $0.14\text{--}17.2 \text{ }\mu\text{mol}\cdot\text{m}^{-2} \text{ d}^{-1}$  was greatly reduced to  $-0.003\text{--}0.07 \text{ }\mu\text{mol}\cdot\text{m}^{-2} \text{ d}^{-1}$  (Figure 5). In total only c.a. 1% of CH<sub>4</sub> diffusing from the hypolimnion into the metalimnion was passed upwards (i.e., 99% was consumed). This is consistent with reports showing that metalimnetic consumption can be very effective in depleting CH<sub>4</sub> yields in lake water columns (Schubert et al., 2010; Thalasso et al., 2020). The cessation of vertical diffusive transfer of methane within the metalimnion is usually related to aerobic CH<sub>4</sub> oxidation (MOX) and in LLi this process was presumably favored by the O<sub>2</sub> concentrations of 0.3 and 30  $\mu\text{mol}\cdot\text{L}^{-1}$ , which were found “optimal” for MOX (ca. 7 and 36  $\mu\text{mol O}_2\cdot\text{L}^{-1}$ ; Thottathil et al., 2019 and references therein).



**Figure 5.** Diffusive fluxes of CH<sub>4</sub> across the water column of LLi ( $D_{\text{CH}_4}$ ; bold lines) calculated for the stratification period (A–June 2015, B–July 2015, C–August 2015, and D–September 2015) during which the CH<sub>4</sub> built up in the hypolimnion and a strong CH<sub>4</sub> gradient between hypo- and epilimnion developed. Positive values indicate upward flux. The yellow bars indicate the location of the major CH<sub>4</sub> consumption zone corresponding to the oxycline. Vertical dissolved O<sub>2</sub> distribution (dotted lines) shown for comparison. In the consumption zone the upward CH<sub>4</sub> fluxes from the hypolimnion are greatly reduced. Large red arrows indicate upward CH<sub>4</sub> fluxes from the hypolimnion to the consumption zone and small red arrows indicate reduced CH<sub>4</sub> efflux out of the consumption zone. On average only 1% of methane inflowing to the consumption zone diffuses upwards.

From the above calculations it follows that the metalimnion acts as an impermeable barrier to hypolimnetic CH<sub>4</sub> in LLi. Consequently, the question arises on the origin of epilimnetic methane, which, given the high rates of consumption in the metalimnion, seems to be disproportionately high in relation to hypolimnetic CH<sub>4</sub>. Our estimations showed that hypolimnetic CH<sub>4</sub> yielded on average 92% of the total CH<sub>4</sub> in the lake and most of this methane has not crossed the anoxic/oxic boundary. On the other hand, the number of moles of CH<sub>4</sub> released from the lake surface to the atmosphere during stratification period (1.11–1.39·10<sup>8</sup> mmol; see Table 3) was equivalent to 62%–77% of hypolimnetic CH<sub>4</sub> (1.8·10<sup>8</sup> mmol). This would indicate that diffusive emissions from the lake are fed by non-hypolimnetic CH<sub>4</sub>. The CH<sub>4</sub> in epilimnion as well as throughout the aerobic lake water column was linked among others to methanogenesis by photoautotrophic microorganisms in O<sub>2</sub>-rich water (Grossart et al., 2011), dissolution of rising bubbles of sediment gas (DelSontro et al., 2015; McGinnis et al., 2006), and advection of CH<sub>4</sub> from littoral/shallow water sediments (Bussuman, 2005; DelSontro et al., 2018; Peeters et al., 2019). Owing to the fact that relevant data are missing altogether the contribution from the first two processes in LLi is difficult to assess. However, provided that the importance of oxidative methanogenesis is still debatable (Peeters & Hofmann, 2021) and that substantial bubble dissolution requires higher water depths than there are in LLi (McGinnis et al., 2006) it appears that these processes are not critical for the CH<sub>4</sub> delivery to surface water in the site studied. Delwiche and Hemond (2017) estimated that in Upper Mystic Lake (US; 24 m max depth) the contribution of bubble dissolution to diffusive CH<sub>4</sub> emission from the lake surface was c.a. 13%. Therefore alternative CH<sub>4</sub> sources should be expected. Since LLi has a wide littoral zone, lateral transport of methane from this zone seems very likely source of epilimnetic CH<sub>4</sub> in the lake. DelSontro et al. (2018) demonstrated that in surface waters of lakes dissolved CH<sub>4</sub> exponentially declines with distance from the shore and pelagial waters often contain only a small fraction of the shallow water CH<sub>4</sub>. From the model developed by DelSontro et al. (2018) it follows that in the central part of a lake with the size of LLi (i.e., with an elongated basin of approximately 1 km<sup>2</sup> surface area) the CH<sub>4</sub> concentrations can be 50%–70% depleted compared to the littoral waters. Given that the epilimnetic CH<sub>4</sub> originates from the bottom sediments lying above the chemocline, the mean benthic methane flux of 0.11 mmol·m<sup>-2</sup>·d<sup>-1</sup> is required to produce the yield of epilimnetic CH<sub>4</sub> during stratification period (June–September; 2.8·10<sup>6</sup> mmol) in LLi. Such value seems low when compared to published reports (Lojen et al., 1999; Peeters et al., 2019; D'Ambrosio et al., 2022). In addition to internal CH<sub>4</sub> sources, LLi might be receiving a considerable CH<sub>4</sub> input from adjacent areas via the inflow canal. Despite that the CH<sub>4</sub> data from the canal were scarce, the analyses performed between December 2022 and February 2023 clearly showed that the cooling waters inflowing to LLi were rich in dissolved CH<sub>4</sub>. The CH<sub>4</sub> concentrations in the canal varied between 0.61 and 4.19 mmol·L<sup>-1</sup> while the corresponding values in LLi water were 1.11–2.61 mmol·L<sup>-1</sup> in front of the channel mouth (L2 site; Figure 1) and 0.12–0.23 mmol·L<sup>-1</sup> in the L1 site. The lake can thus ventilate CH<sub>4</sub> delivered from the catchment.

Since the ratio of diffusive CH<sub>4</sub> emission to hypolimnetic CH<sub>4</sub> in LLi (62%–77%) is higher than in the reference lakes (17%–19% in LLD, 46%–62% in LD and 40%–63% in LT), it appears that the lateral transport of CH<sub>4</sub> in this lake is more important for the surface methane emissions than in other lakes of this study.

#### 4.2. Nitrous Oxide

In contrast to CH<sub>4</sub>, nitrous oxide in LLi water column shifted from supersaturation to undersaturation. The highest levels of oversaturation (160%–340%) accompanied by an evenly distribution of the N<sub>2</sub>O in the water column occurred during the non-stratified period (i.e., between December 2014 and April 2015 and in October–November 2015). The enrichment in N<sub>2</sub>O indicated in situ production in the water column and/or delivery of N<sub>2</sub>O from the catchment. Between June and September 2015, however, the N<sub>2</sub>O saturations were lower. In the epilimnion and metalimnion they varied between 120% and 94%, while in the hypolimnion the gas was below limit of quantification. According to Beaulieu et al. (2015) the decline of N<sub>2</sub>O in the hypolimnion argues for an in situ consumption of the gas.

The changes of N<sub>2</sub>O in LLi were primarily related to O<sub>2</sub> and NH<sub>4</sub><sup>+</sup>. The concentrations of N<sub>2</sub>O and O<sub>2</sub> were highly positively correlated ( $r = 0.87$ ;  $p < 0.001$ ) while relationship between N<sub>2</sub>O and NH<sub>4</sub><sup>+</sup> was negative ( $r = -0.45$ ;  $p < 0.001$ ). Interestingly, reference lakes showed much weaker relationships between N<sub>2</sub>O and O<sub>2</sub>. In coastal lakes and LLD these gases showed positive covariance ( $r = 0.66$  at  $p < 0.001$  and  $r = 0.55$  at  $p < 0.001$ , respectively), whereas in LT the correlation was very weak ( $r = -0.017$ ;  $p = 0.02$ ) and in LD the N<sub>2</sub>O and O<sub>2</sub> were unrelated altogether ( $r = -0.03$ ;  $p = 0.75$ ). High NH<sub>4</sub><sup>+</sup> values in the hypolimnion accompanied complete N<sub>2</sub>O depletion.

Since the conditions in LLi water column were, for the major part of the year, aerobic it seems reasonable to conclude that the most probable mechanism of  $N_2O$  production in the lake was nitrification. This agrees with a growing body of evidence from various shallow and well aerated lentic systems (Beaulieu et al., 2015; Nevison et al., 2003; Priscu, 1997; Xiao et al., 2019) as well as with IPCC estimations on the predominance of nitrification over denitrification in  $N_2O$  production in lakes and rivers (Frame et al., 2017; Hinshaw & Dahlgren, 2013). During nitrification, ammonium is oxidized to nitrate via a few intermediate steps and the  $N_2O$  is a by-product of this process (Massé et al., 2019; Nevison et al., 2003). Both nitrification pathways (i.e., two-step nitrification and comammox) were shown to release  $N_2O$ , however the former mechanism was found to be more effective (Han et al., 2020; Kits et al., 2019). Among many factors that control the rate of nitrification the availability of  $O_2$  and inorganic N species ( $NO_2^-$  and  $NH_4^+$  in particular) are of key importance (Xiao et al., 2019). Indeed, during the  $N_2O$  concentration peak, in March 2015, the epilimnetic  $NH_4^+$  and  $O_2$  were at their maxima of 2.8–5.0  $\mu\text{mol}\cdot\text{L}^{-1}$  and 383–414  $\mu\text{mol}\cdot\text{L}^{-1}$ , respectively. Based on the overall agreement between temporal pattern of  $NH_4^+$  delivery with cooling waters and the epilimnetic ammonium pool in LLi, it appears that the inorganic N, which fuels  $N_2O$  production in the lake, is primarily from external sources. Interestingly, the  $N_2O$  concentration in LLi seems weakly sensitive to temperature which opposes to the well known temperature dependence of microbial N cycling processes (Pfenning & McMahon, 1996; Thamdrup & Fleischer, 1998). Such relationship argues for a stronger control from substrate availability than temperature for  $N_2O$  production as predicted by Davidson et al. (2015) and Beaulieu et al. (2019).

Nitrification is active down to nanomolar  $O_2$  levels, however below 1  $\mu\text{mol}\cdot\text{L}^{-1}$  its rate declines sharply (Bristow et al., 2016). In suboxic and anoxic conditions (at  $< 0.2\text{ mg}\cdot\text{L}^{-1}$ ) alternative pathways of microbial N cycling, such as reduction of  $NO_3^-$  to  $N_2$  (denitrification) or to  $NH_4^+$  (dissimilatory nitrate reduction to ammonium, DNRA), become active (Beaulieu et al., 2015; Dong et al., 2011; Pandey et al., 2020). The latter processes are known to consume  $N_2O$  when  $NO_2^-$  and  $NO_3^-$  concentrations in the water column drop below 50  $\mu\text{gN}\cdot\text{L}^{-1}$  (Beaulieu et al., 2015; Pandey et al., 2020). As the undersaturation of  $N_2O$  in LLi hypolimnetic waters during stratification period coincided with a decrease in  $NO_3^-$  (to 29–9  $\mu\text{gN}\cdot\text{L}^{-1}$  in August) and an enrichment in  $NH_4^+$  (to 23–3,200  $\mu\text{gN}\cdot\text{L}^{-1}$  in August) the shift towards denitrification and DNRA seemed to provide a plausible explanation for the  $N_2O$  decrease in the water column.

### 4.3. GHG Fluxes From LLi

Because we used four different approaches to calculate  $k_{600}$ , the diffusive fluxes of  $CH_4$  and  $N_2O$  from LLi and reference lakes changed broadly (Tables 2 and 3). The  $F_{surf}$  values consistently showed that on an annual basis LLi acted as a net source of the GHGs to the atmosphere during both periods of study (Figure 3). However, the annual fluxes of  $CH_4$  and  $N_2O$  were relatively low compared to reference aquatic systems in Poland (Table 4).  $CH_4$  emissions were indeed similar to the values obtained in a mesotrophic Lake Trześniowskie but compared to other reference inland lakes they were on average 5–12 times lower. Even in highly turbulent and aerated coastal lakes the  $F_{surfCH_4}$  were 4 times higher than in LLi. Despite being up to 3 times lower than in reference Polish lakes, the  $N_2O$  emissions from LLi were within the global average  $N_2O$  fluxes from lakes of  $6.8 \pm 4.3\ \mu\text{mol}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$  (Lauerwald et al., 2019) and were not statistically different from LLD, LD and LT emissions. It was worth noting that in the latter lake the concentrations of  $N_2O$  were statistically different (higher) than in LLi. Interestingly, the  $F_{surfN_2O}$  values obtained in LLi were also similar to the numbers from low N-loaded lakes (McCrackin & Elser, 2011). However, McCrackin and Elser (2011) defined the low N-loaded lakes as receiving  $< 2\text{ kgN}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$  while the N load to LLi from inflowing waters was as high as c.a.  $1,700\text{ kgN}\cdot\text{ha}^{-1}\cdot\text{y}^{-1}$ . Therefore the low  $N_2O$  emissions were definitely unrelated to N deficiency in this case.

Low GHG diffusion fluxes from LLi were undoubtedly associated with low concentrations of  $CH_4$  and  $N_2O$  in the lake water column, as described above, albeit the reasons for this depletion remained hypothetical. The low GHG concentrations and emissions ( $CH_4$  in particular) are definitely surprising in a thermally polluted lake, in which, owing to temperature stimulation of microbial metabolism, we would rather expect enhanced production of  $CH_4$  and  $N_2O$ . On the other hand, as follows from Figure S1 in Supporting Information S1, LLi water column temperatures are not significantly different from natural Polish lakes. This implies that the thermal pollution primarily occurs in the surface water layer of LLi, but its effect on the pore waters of the lake, where  $CH_4$  is produced, seems to be limited. Currently therefore, we incline toward the hypothesis that the low  $CH_4$  and  $N_2O$  concentrations in LLi result from a very high fluxing rate of the lake. Although, the water exchange rates in LLD, LD and



LT are unknown, based on published data, it is clear that even in very small and shallow lakes the horizontal water exchange rates are between 0.13 and 1.1 y (i.e., 47–401 days; Ferencz & Dawidek, 2012). In Lake Gopło (central Poland; 21 km<sup>2</sup>, 16 m max depth), flushed by the Noteć river (SSQ = 1.4 m<sup>3</sup>·s<sup>-1</sup>; Kubiak-Wójcicka, 2021), the water is exchanged every 292 days (Piasecki & Skowron, 2014). Lakes located in NE Poland have median water exchange rates of ca. 350 days ( $\bar{x}$  = 670 days) with very few exceptions (3 out of 32 lakes studied) with an exchange rate of 10 days (Bajkiewicz-Grabowska, 1983). For coastal lakes on the Polish Baltic coast, which are flushed by flowing through rivers, Cieśliński et al. (2016) obtained rates between 38 and 456 days. These numbers consistently show that the horizontal water exchange rate in LLI of 2–9 days is definitely unusually rapid for the lake of its kind. On the other hand, the values are similar to rheolimnic reservoirs, such as the Włocławek Reservoir (central Poland) (Mimier et al., 2018). Owing to the flushing, considerable amounts of GHG are exported from LLI to another lakes and canals involved in the PPP/KPP cooling system. Assuming that the volume of water outflowing from LLI is equal to the inflow (i.e., 22 m<sup>3</sup>·s<sup>-1</sup>) and taking the average annual CH<sub>4</sub> and N<sub>2</sub>O concentrations in the epilimnion (0.27 μmol·L<sup>-1</sup> and 15.21 nmol·L<sup>-1</sup>, respectively), we estimate that approximately 1.9·10<sup>8</sup> mmol of CH<sub>4</sub> and 1.0·10<sup>7</sup> mmol of N<sub>2</sub>O is discharged from LLI yearly thus reducing diffusive fluxes from the lake by about 85%–90% for methane and >90% for nitrous oxide. Retaining such amounts of gases in the system would translate into the CH<sub>4</sub> fluxes of 2.28–2.90 mmol·m<sup>-2</sup> d<sup>-1</sup> and >100 μmol·m<sup>-2</sup> d<sup>-1</sup> for N<sub>2</sub>O. The former values are much closer to the emissions from reference inland lakes (Table 4), but the latter are tremendously high, albeit possible. Comparably high N<sub>2</sub>O fluxes were reported from littorals of highly eutrophic lakes and urban rivers (Wang et al., 2006; Xiao et al., 2019; Zhang et al., 2021). On the other hand, the gas exported from LLI does not necessarily add to the pool of gas dissolved in the waters of adjacent lakes because favorable conditions for evasion of the gases to the atmosphere exist in the canals conveying water from LLI to L. Ślesińskie (c.a. 6.1 km long) and L. Pałnowskie (0.7 km long). In the terminal part of the former canal an artificial spillway exists and the water flow from LLI to L. Pałnowskie is regulated by the weir. By increasing turbulence, both hydrodynamic constructions very likely facilitate degassing of flowing waters as shown by Leibowitz et al. (2017) and Botter et al. (2022).

Despite that there were some differences in monthly patterns of  $F_{surfCH_4}$  and  $F_{surfN_2O}$  during 2014/15 and 2022/23 it was clear that the emissions of CH<sub>4</sub> and N<sub>2</sub>O were decoupled and showed some seasonality. The  $F_{surfCH_4}$  displayed distinct maxima in summer 2015 and spring/early summer 2022 while N<sub>2</sub>O fluxes were high during winters and peaked in spring. Reference lakes showed similar tendencies (Figure 4). Enhanced methane emissions during summer, both in LLI and in reference lakes, can be explained by higher CH<sub>4</sub> production rates in warmer anoxic sediments (Avery et al., 2003) superimposed on decreased gas solubilities at higher temperatures. However, the highest CH<sub>4</sub> emissions in September 2015 were associated with seasonal lake overturn. This process was shown to lift anoxic CH<sub>4</sub>-supersaturated hypolimnetic waters to the lake surface within appreciably short time (in 3–4 weeks during “hot moments of emission” according to Guérin et al., 2016). Fernández et al. (2014) showed that in Lake Mindelsee (Germany), which was similar to LLI in terms of morphometric conditions, autumn mixing accounted for around 80% of annual CH<sub>4</sub> emissions. Indeed, the storage flux of CH<sub>4</sub> in LLI caused a rapid decrease in the yield of hypolimnetic CH<sub>4</sub>. Based on the  $F_{hyp}$  of 6.0 mmol·m<sup>-2</sup> d<sup>-1</sup> (Figure 2) it can be estimated that during this event in September 2015 ca. 3.1·10<sup>7</sup> mmol CH<sub>4</sub>, equivalent to 90% of the hypolimnetic CH<sub>4</sub>, was transmitted from the hypolimnion to overlying waters and finally to the atmosphere. In the reference lakes late summer/early autumn vertical water mixing also played a substantial role in gas transfer. As can be seen in Figures 2 and 4 a coincidence between weakening of vertical density stratification of water (shown by a drop in  $W_s$ ) and rapid increase of  $F_{surfCH_4}$  was evident in each lake. This might indicate that the timing and mechanism of methane emission from LLI is still determined by natural biogeochemical and hydrodynamical processes. On the other hand, it shall be underlined that in 2022 the rapid outgassing did not occurred in LLI and emission culminated in May, shortly after the onset of vertical stratification. Because in 2022/23 we have not monitored CH<sub>4</sub> distribution in the whole water column the reasons for this emission patterns remain unclear.

Temporal patterns of  $F_{surfN_2O}$  were similar in both periods under study (Tables 2 and 3) and followed the changes in inorganic N delivery to the lake. Higher  $F_{surfN_2O}$  values in winter/spring (4.2–10.6 μmol·m<sup>-2</sup> d<sup>-1</sup>) were synchronous with high N influx from the canal of 1.6·10<sup>12</sup>–1.4·10<sup>13</sup> μmol·month<sup>-1</sup> while suppressed emissions in summer/early autumn (0.9–3.5 μmol·m<sup>-2</sup> d<sup>-1</sup>) coincided with diminished N influx of 1.4·10<sup>12</sup>–2.1·10<sup>12</sup> μmol·month<sup>-1</sup>. This shows that the N<sub>2</sub>O emissions from LLI surface were largely controlled by the availability of substrates as proposed by Yang et al. (2015), Kortelainen et al. (2019), and Xiao et al. (2019). Thereby, substrate supply could also be invoked to explain the springtime peak in N<sub>2</sub>O in LLI, because the maximum annual N<sub>2</sub>O emission

coincided with the maximum  $\text{NH}_4^+$  input of  $4.1 \cdot 10^5 \mu\text{mol} \cdot \text{s}^{-1}$ . The springtime culmination of  $F_{\text{surfN}_2\text{O}}$  acted as an interesting biogeochemical feature of LLi.  $\text{N}_2\text{O}$  emission maxima in lakes often overlap with enhanced  $\text{CH}_4$  fluxes (Fernández et al., 2020; Xiao et al., 2019) and thus occur in summer. This is because the  $\text{N}_2\text{O}$  can be produced in the anoxic hypolimnions and sediments via denitrification (Beaulieu et al., 2015) and/or released from littoral sediments (Mengis et al., 1997). Alternatively some authors provided evidence for the enhanced  $\text{N}_2\text{O}$  emissions during cold seasons (Kortelainen et al., 2019; Woszczyk & Schubert, 2021), autumn (Soued et al., 2015), during development or breakdown of water column stratification (Salk et al., 2016) and/or concluded on non-seasonal pattern of  $\text{N}_2\text{O}$  release (Roland et al., 2016). It thus appears that there are considerable differences between lakes with regard to the timing of  $\text{N}_2\text{O}$  emissions. Provided that the  $\text{N}_2\text{O}$  production in LLi is fueled by the very high inorganic N load delivered by the inflow channel, the relatively low  $F_{\text{surfN}_2\text{O}}$  values seem surprising. However, this discrepancy might be explained by the removal of the large part of in situ produced  $\text{N}_2\text{O}$  due to flushing of the lake. Export of the  $\text{N}_2\text{O}$  from the lake makes our estimation of very high potential  $\text{N}_2\text{O}$  flux from LLi at reduced flushing rate possible.

During both periods of the study, the  $\text{N}_2\text{O}$  emission showed minima in summer. These drops coincided with the build-up of density stratification of the lake water column and the development of anoxic conditions in the hypolimnion. Hence, the involvement of  $\text{N}_2\text{O}$  in denitrification and/or DNRA, superimposed on the lower N supply by the inflow, reduced the total  $\text{N}_2\text{O}$  yield in the lake and thus led to a decrease in  $\text{N}_2\text{O}$  emissions.

## 5. Conclusions

In this study diffusive fluxes of  $\text{N}_2\text{O}$  and  $\text{CH}_4$  as well as processes behind their production in heavily anthropogenically impacted Lake Licheńskie were investigated. The study revealed that, contrary to what was expected, both the concentrations and diffusive emissions of these gases from LLi were low, albeit only for  $\text{CH}_4$  they were significantly different from the reference (not disturbed) Polish lakes.

Despite that Lake Licheńskie has been prone to a long-term thermal pollution it is of little importance for the production of  $\text{N}_2\text{O}$  and  $\text{CH}_4$  in the lake because the excess heat does not accumulate in the lake water column. Therefore enhanced vertical stratification and prolonged anoxia creating favorable conditions for GHG production are not observed in the lake. Instead, there seem to be a considerable impact from a very high flushing rate by the water circulating in the cooling system. These waters presumably export GHGs from the lake resulting in reduced methane emissions from the lake surface.  $\text{N}_2\text{O}$  is affected by this effect as well, however, even though large amounts of  $\text{N}_2\text{O}$  are removed from the system, its emissions remain at a level observed in natural lakes. Based on this we came to the conclusion that the flushing prevented the lake from the significant accumulation of this potent greenhouse gas.

Altogether, our data indicate that the human intervention substantially changed the biogeochemical cycle of LLi in a somewhat surprising manner because it resulted in appreciably low GHG emissions from the lake. It does not mean, however, that the accelerated horizontal water exchange rate mitigated the  $\text{CH}_4$  and  $\text{N}_2\text{O}$  release to the atmosphere. Most likely, the enhanced flushing of the lake has shifted the emissions to outside of the lake, that is, to adjacent canals. Further research is required to check if this hypothesis is true. Finally, it should be borne in mind that ebullitive transport of gases has not been considered in our study. Provided that ebullition can account for a significant portion of total emissions of GHGs from lakes, the understanding of biogeochemistry of LLi would also benefit from quantification of this emission pathway.

Our study also has some methodological implications suggesting that thermally polluted lakes not necessarily can be used as sentinels of environmental change in aquatic systems induced by a globally warming climate. Lake Licheńskie shows that local factors can overwhelm the effects of long-term heating.

## List of Symbols and Acronyms

GHG	greenhouse gas
KPP	the Konin Power Plant
LD	Lake Dębno
LLD	Lake Łódzko-Dymaczewskie
LLi	Lake Licheńskie

LT	Lake Trzesniowskie
PPP	the Pątnów Power Plant
ZE PAK	Zarząd Elektrowni Pątnów-Adamów-Konin
$A_{\text{hyp}}$	surface area of the hypolimnion [ $\text{m}^2$ ]
$A_l$	lake surface area [ $\text{m}^2$ ]
$A_z$	bathymetric surface area at depth $z$ [ $\text{m}^2$ ]
$C_{\text{eq}}$	equilibrium concentration of a gas in lake water [ $\text{mmol}\cdot\text{L}^{-1}$ ]
$\text{CH}_4(t, z_m)$	dissolved $\text{CH}_4$ concentration at time $t$ and depth $z = m$ [ $\text{mol}\cdot\text{m}^{-3}$ ]
$\text{CH}_4(t, z_{m-1})$	dissolved $\text{CH}_4$ concentration at time $t$ and depth $z = m - 1$ [ $\text{mol}\cdot\text{m}^{-3}$ ]
$C_w$	actual concentration of a gas in lake water [ $\text{mmol}\cdot\text{L}^{-1}$ ]
$D_{\text{CH}_4(t, z_m)}$	diffusive $\text{CH}_4$ flux across metalimnion [ $\text{mmol}\cdot\text{m}^{-2}\text{d}^{-1}$ ]
$F_{\text{hyp}}$	$\text{CH}_4$ transfer from the hypolimnion to overlying water due to mixing [ $\text{mmol}\cdot\text{m}^{-2}\text{d}^{-1}$ ]
$F_{\text{surf}}$	diffusive flux of GHG from lake surface to the atmosphere [ $\text{mmol}\cdot\text{m}^{-2}\text{d}^{-1}$ ]
$g$	acceleration due to gravity [ $\text{m}\cdot\text{s}^{-2}$ ]
$K$	vertical $\text{CH}_4$ diffusion coefficient [ $\text{m}^2\cdot\text{d}^{-1}$ ]
$k$	gas transfer velocity [ $\text{cm}\cdot\text{h}^{-1}$ ]
$k_{600}$	gas transfer velocity adjusted to $Sc = 600$ [ $\text{cm}\cdot\text{h}^{-1}$ ]
$N^2$	Brunt-Väisälä stability frequency [ $\text{s}^{-2}$ ]
SSQ	average annual mean flow [ $\text{m}^3\cdot\text{s}^{-1}$ ]
$T_e$	volume-weighted epilimnion temperature [ $^{\circ}\text{C}$ ]
$T_{h,i}$	volume-weighted temperature of hypolimnion at the onset of stratification [ $^{\circ}\text{C}$ ]
$T_{h,s}$	volume-weighted temperature of hypolimnion at the end of stratification [ $^{\circ}\text{C}$ ]
$U_{10}$	wind speed at 10 m above ground [ $\text{cm}\cdot\text{s}^{-2}$ ]
$v_t$	vertical heat exchange coefficient [ $\text{m}\cdot\text{d}^{-1}$ ]
$z$	water depth [m]
$\rho$	water density [ $\text{kg}\cdot\text{m}^{-3}$ ]
$\rho_z$	water density at depth $z$ [ $\text{kg}\cdot\text{m}^{-3}$ ]
$\bar{\rho}$	mean water density in a lake water column [ $\text{kg}\cdot\text{m}^{-3}$ ]

## Data Availability Statement

In the paper we used publicly available data on climate parameters in Poland released by Tutiempo Network, S.L. (<https://en.tutiempo.net/climate/poland.html>) as well as atmospheric GHG concentrations over Europe collected by European Environment Agency ([https://www.eea.europa.eu/data-and-maps/daviz/atmospheric-concentration-of-carbon-dioxide-5#tab-chart\\_6](https://www.eea.europa.eu/data-and-maps/daviz/atmospheric-concentration-of-carbon-dioxide-5#tab-chart_6)). The LLi water chemistry as well as  $\text{CH}_4$  and  $\text{N}_2\text{O}$  fluxes from LLi, LLD, LD, and LT data used in the study values are available at PANGAEA repository under the URL: <https://doi.pangaea.de/10.1594/PANGAEA.961315>.

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