



## RESEARCH ARTICLE

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# Dynamics of Greenhouse Gases (CH<sub>4</sub> and CO<sub>2</sub>) in Meromictic Lake Burgsee, Germany

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### Key Points:

- In the urban meromictic Lake Burgsee, methane production potentials in the sediment are similar to eutrophic holomictic lakes
- At its deepest site, it contains one of the highest methane concentrations (>5 mmol L<sup>-1</sup> CH<sub>4</sub>) ever reported for a natural freshwater lake
- Lake Burgsee emits up to >3 mmol m<sup>-2</sup> d<sup>-1</sup> CH<sub>4</sub> to the atmosphere above the sinkhole and <1 mmol m<sup>-2</sup> d<sup>-1</sup> CH<sub>4</sub> at a near-by shallow site

### Supporting Information:

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

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**Abstract** Extraordinary amounts of greenhouse gases can be stored within the monimolimnion of meromictic lakes, that is, in the water body which is excluded from mixing events. Lake Burgsee (Thuringia, Germany) is a shallow (depth <5 m) lake with a approximately 24 m deep sinkhole, which is fed by underground brine sources and has formed such a monimolimnion. We investigated the carbon dioxide and methane dynamics in this meromictic lake, from production potentials in the sediment via concentrations in the monimolimnion and mixolimnion to emissions to the atmosphere. In the monimolimnion, we found one of the highest methane concentrations (up to >5 mmol L<sup>-1</sup>) ever reported for a natural freshwater lake, while carbon dioxide concentrations in the water and methane production rates in the sediments were rather ordinary and within the range of holomictic eutrophic lakes. At the thermocline, gas concentrations accumulated to approximately 100 μmol L<sup>-1</sup> CH<sub>4</sub> and 80–230 μmol L<sup>-1</sup> CO<sub>2</sub>. Estimated fluxes to the atmosphere reached considerable 3.5 mmol CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> and 1.5 mmol CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> above the sinkhole and 0.8 mmol CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> and 0.4 mmol CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> above the near-by shallow lake center in 2018. Our results demonstrate that lakes in natural brine areas may provide significant storages and releases of greenhouse gases and require further investigation.

**Plain Language Summary** In meromictic lakes, the deepest water layer, the monimolimnion, is stagnant and not included in seasonal water circulation. Organic matter continuously sinks down into the oxygen-free monimolimnion, where it is decomposed into the final gaseous products carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>). Lake Burgsee is a meromictic shallow (depth <5 m), brine-fed lake with a approximately 24 m deep sinkhole. At the bottom of the narrow sinkhole, salinities are as high as in brackish water and cause a chemical stratification of the water body—a monimolimnion—in approximately 18 m depth. CH<sub>4</sub> concentrations above the sediment reach >5 mmol L<sup>-1</sup>, which is more than one order of magnitude higher than at the water surface and among the highest CH<sub>4</sub> concentrations found in freshwater lakes worldwide. Further, emissions of CH<sub>4</sub> and CO<sub>2</sub> from the water to the atmosphere were considerable in 2018, and about four times higher above the sinkhole than above the shallow lake center. These results demonstrate, that lakes in natural brine areas may store and release significant amounts of greenhouse gases and require further investigation.

## 1. Introduction

Methane formed in freshwater lakes is emitted to the atmosphere by different pathways, mainly by diffusion, ebullition, or plant-mediated release (Bastviken et al., 2011). However, gases may be trapped or accumulate during the ascension due to floating macrophytes (Attermeyer et al., 2016), ice-covers (Greene et al., 2014), thermoclines (Donis et al., 2017), or chemical gradients found in volcanic (Descy et al., 2012) and other meromictic lakes (Bohrer et al., 2017). In meromictic lakes, that is, permanently stratified lakes, chemical stratification causes a nonrecirculating monimolimnion that prevents the release of gases and nutrients into the upper water layers, and thus, to the atmosphere. The water body above the chemocline, the mixolimnion, may stratify into epilimnion and hypolimnion and may recirculate seasonally (Bohrer et al., 2017; Bohrер & Schultze, 2008). Due to the lack of mixing, oxygen may get depleted in the deeper layers of the hypolimnion of holomictic and meromictic lakes at the end of the summer stratification, and is usually depleted in the monimolimnion of meromictic lakes. Under anoxic conditions, anaerobic decomposition processes dominate, with carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>) being key products. In temperate latitudes, CO<sub>2</sub> and CH<sub>4</sub> concentrations reach on average < 1 mmol L<sup>-1</sup> in the hypolimnion of holomictic lakes (Juutinen et al., 2009), whereas these gases may accumulate to enormous

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concentrations in the monimolimnion of meromictic lakes. The most prominent example is the meromictic Lake Kivu (Rwanda/Democratic Republic of the Congo); extreme gas concentrations originating from the nearby volcano Mount Nyiragongo (last eruption: May 2021) are stored in the deep water layers (ca. 85–100 mmol L<sup>-1</sup> CO<sub>2</sub> and ca. 16–19 mmol L<sup>-1</sup> CH<sub>4</sub> dissolved in 450 m depth, Boehrer et al., 2019), and the increasing population in the catchment results in eutrophication and a continuous accumulation of biogenic methane (2.8 ± 1.8 mol C<sub>CH4</sub> m<sup>-2</sup> yr<sup>-1</sup>) (Nayar, 2009; Pasche et al., 2011). This resource is used to generate electricity via the KivuWatt Power Station, with 26 MW installed and 75 MW planned (Contour Global, [www.contourglobal.com](http://www.contourglobal.com); Rwanda energy group, [www.reg.rw](http://www.reg.rw), May 2021).

The occurrence of meromixis depends on (a) the morphometry of a lake, (b) its wind fetch, and (c) sufficient accumulation of ions in the deep water body to assure stable density gradients, leading to a chemical stratification. Regarding lake morphometry, the lake needs to have a large maximum depth relative to the fetch length, that is, the horizontal distance or direction over which the wind blows. Sinkholes caused by the collapse of cover material into subterranean cavities are one potential reason for a morphometry causing meromixis. The area of Thuringia in central Germany experiences sudden sink falls regularly, due to cavities originating from natural processes, such as the dissolution of ground material of the former Zechstein Sea, and from anthropogenic activities, such as former salt mining.

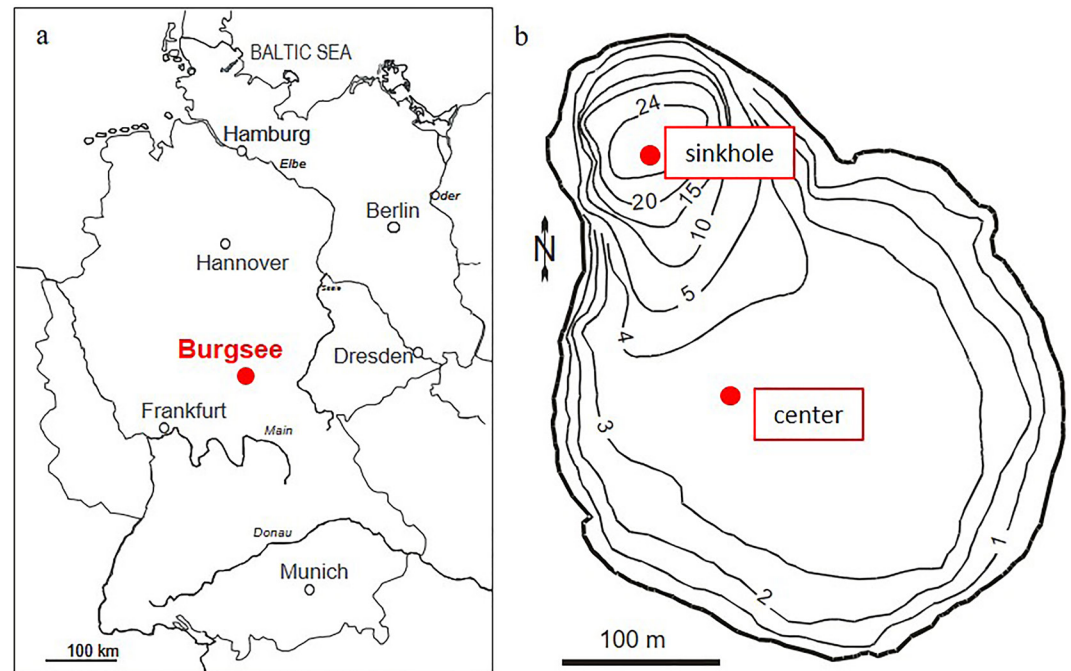
Chemical stratification can be caused by groundwater inflows, among other things, if the ion concentration of the groundwater is exceptionally high and its exfiltration occurs in the deep areas of the lake. For example, water-filled former mining pits tend to become meromictic (Boehrer & Schultze, 2008). The absence of clogging layers in these young lakes facilitates the seepage of high ion concentrations from oxidized sediments into the bottom waters and the formation of intense chemical gradients. These ion-rich (high salinity) bottom waters have a much higher density than fresher water and remain permanently close to the lake bottom. Recently, Horn et al. (2017) described for the mining pit lake Vollert-Sued (Germany) ebullitive release rates of approximately 10 mmol m<sup>-2</sup> d<sup>-1</sup> CH<sub>4</sub> from supersaturated, deep waters into the atmosphere, and Boehrer et al. (2016) reported 2.5 l of gas being dissolved in 1 L of water in the deep layers of the Guadiana pit lake in Southwest Spain. The most common examples for meromictic lakes, however, are found in volcanic craters, where CO<sub>2</sub> originates from a mix of mantle fluids and thermometamorphic reactions with limestone (Cabassi et al., 2013). In the volcanic lakes Nyos and Monoun (both Cameroon), limnic eruptions released vast amounts of accumulated CO<sub>2</sub> to the atmosphere and tragically caused the death of approximately 1,800 people, making these case studies globally well-known disasters (ISSA et al., 2013).

Meromictic lakes can contain the highest greenhouse gas concentrations in lakes worldwide, and the release of greenhouse gases to the atmosphere via limnic eruptions is far more impactful than the emission by diffusion, ebullition, and gas release during lake overturn. To the best of our knowledge, carbon dioxide and methane accumulation in meromictic lakes has mainly been studied in volcanic, mining, or tropical and subtropical lakes, whereas natural, nonvolcanic lakes in temperate regions have received little attention. The aim of the present study is to investigate and understand the carbon dioxide and methane dynamics in the meromictic Lake Burgsee (Thuringia, Germany), a naturally formed water-filled sinkhole. Furthermore, Lake Burgsee is an urban lake with a long eutrophication history and exposed to high loads of organic matter input, which intensified the accumulation of greenhouse gases in its monimolimnion. For that purpose, we determined the concentrations of the greenhouse gases methane and carbon dioxide in the water column, as well as the methane production potential in the sediment and the methane emissions to the atmosphere.

## 2. Material and Methods

### 2.1. Study Site

Lake Burgsee is a small (surface area 10.3 ha), circular, eutrophic lake located in the spa town Bad Salzungen in Thuringia, Germany. While more than 80% of the lake is shallow (less than 4.3 m depth), there is an approximately 24 m deep sinkhole in the north-western part. The lake was formed approximately 10,000–15,000 years ago, but <sup>14</sup>C dating indicates that the sinkhole is much younger (Bauriegel, 2004). Local folktales suggest that the strong earthquake in Lisbon in 1755 caused the ground to collapse on the north-western shore line of Lake Burgsee (Bauriegel, 2004; Ruck, 2017), and thus created the lake's sinkhole, but we could not find any formal evidence to confirm this. However, the area of Thuringia is prone to collapsing grounds and experiences 5–50



**Figure 1.** Location of Lake Burgsee in Germany (a) and bathymetric map of the lake (b). The positions of the sampling sites are marked within the lake map.

sinkholes per year, due to the subsidence of the prehistoric Upper Permian Zechstein by groundwater (<https://www.planet-wissen.de/natur/landschaften/erdfaele/erdfaele-thueringen-100.html>). In Bad Salzungen, a rock salt layer lies in 130–150 m depth and feeds the local spa (Bauriegel, 2004). Lake Burgsee has no permanent inflows or outflows, except for several rain water drains, which end in the lake, and an above-ground outflow, which is almost always dry. The salinity gradient in combination with the shape and depth of the lake established a monimolimnion in the sinkhole and a meromictic water body.

In earlier times, wastewater from the spa laundry and wastewater from a large slaughterhouse were discharged directly into Lake Burgsee. Poor water quality (eutrophy) and unpleasant odors emitted under certain weather conditions from the lake have long been a nuisance due to the lake's central location within the city, particularly to the adjacent spa resorts. In order to improve water quality, external phosphate elimination using polyaluminum chloride (PAC) and iron(III) chloride sulfate (Ferrifloc) was carried out from 2000 to 2002. Water from the sinkhole with its high chloride concentrations was pumped into the elimination plant, treated to remove P and returned into the epilimnion. Thus, most of the chemical gradient, that is, most of the monimolimnion was destroyed. Only the lowest approximately 0.5 m of the monimolimnion remained. Since 2002, phosphate (SRP—soluble reactive phosphorus) and chloride ( $\text{Cl}^-$ ) concentrations above ground increased again (SRP: from  $17,650 \pm 328 \mu\text{g L}^{-1}$ ,  $n = 5$  in 1999–2000, to  $311 \pm 36 \mu\text{g L}^{-1}$ ,  $n = 2$  in 2002 to  $11,278 \pm 700 \mu\text{g L}^{-1}$ ,  $n = 5$  in 2011–2018;  $\text{Cl}^-$ : from  $754 \pm 57 \text{ mg L}^{-1}$ ,  $n = 2$  in 1999–2000 to  $>103 \text{ mg L}^{-1}$ ,  $n = 1$  in 2002 to  $397 \pm 31 \text{ mg L}^{-1}$ ,  $n = 5$  in 2011–2018; in 23 m depth, own measurements), thus re-establishing the chemocline and the monimolimnion.

## 2.2. Sampling and Analytics

Preliminary gas analyses of water samples from the sinkhole have been performed in September 2017, and subsequently a more detailed investigation of the  $\text{CH}_4$  dynamics in Lake Burgsee was conducted in September 2018. While the main investigation concentrated on the dynamics in the sinkhole in both years, some additional samples were taken in 2018 at a shallow site (approximately 3.3 m depth) in the center of the lake (Figure 1).

Water samples were taken by different methods:

1. A submersible pump (model Geo-Duplo-Plus, Comet, Germany) was attached to a multiprobe (YSI 6600, Yellow Springs Instrument Inc., OH, USA), lowered to the desired water depths (indicated by the pressure

sensor of the YSI probe) and used to pump the water upwards through a 50 m long gas-tight Tygon tube ( $W_{\text{pump}}$ ).  $W_{\text{pump}}$  samples were taken between 0 and 24.2 m depth in 2017 and until 23.6 m depth in 2018, in 2 m increments until 16 m depth and with increasing sampling depth resolution close to the sediment (1 m increments until 20 m depth, 0.5 m increments until 23 m depth, 0.2 m increments until 24.2 m depth). The first three dead volumes of the tube (2.5 L each) retrieved by the pump were discarded before taking samples for further analyses.

2. A water sampler (LIMNOS, Finland) was used to collect samples without pumping ( $W_{\text{samp}}$ ).  $W_{\text{samp}}$  samples were only taken in 20 and 23 m depth in 2017, and in more detail in 2018 (5 m increments until 20 m depth, 1 m increments until 23 m depth, 23.5 and 23.7 m).
3. For the analysis of  $\text{CH}_4$ , a third method was applied in 2018, using the M-ICOS system (Gonzalez-Valencia et al., 2014; Martinez-Cruz et al., 2020). This method also involved gentle pumping, followed by the passage of the water through an equilibrator (gas-liquid exchange membrane, MiniModule 1  $\times$  5.5 liqui-cel, 3M Wuppertal, Germany) and continuous gas-measurements using a new generation ultraportable greenhouse gas analyzer (UGGA 30P, Los Gatos Research Inc., California, USA), while lowering the tube toward the lake bottom ( $W_{\text{M-ICOS}}$ ).

Temperature, pH, dissolved oxygen (DO), conductivity, chlorophyll *a* (chl *a*) and blue-green algae phycocyanine (BGA) concentrations were measured by the aforementioned YSI probe. The lake water level was 243.2 m above sea level on 29 September 2017 and 242.6 m at 25 September 2018, that is, there was a difference of 60 cm. The variability of the water volume takes place in the upper water body due to precipitation onto and evaporation from the lake surface, due to rain water drainage tubes and surface runoff entering the epilimnion, and due to an aboveground outflow of epilimnetic water. Thus, the thickness of the monimolimnion is not affected, and all water depths of 29 September 2017 were recalculated as if the water level was 242.6 m above sea level.  $W_{\text{pump}}$  and  $W_{\text{samp}}$  samples (except samples for TP analyses) were filtered on-site immediately after collection using syringe filters (0.45  $\mu\text{m}$ , cellulose acetate). To avoid a loss of ammonium and dissolved metals, the corresponding samples were acidified with 2 M HCl to a pH of approximately 2. Samples were cooled until chemical analyses. Chloride ( $\text{Cl}^-$ ), nitrate ( $\text{NO}_3^-$ ), and sulfate ( $\text{SO}_4^{2-}$ ) were measured by ion chromatography (Dionex ICS2000, Thermo Fisher Scientific GmbH, Germany, DIN EN ISO 10304-1). Sodium was measured by inductively coupled plasma optical emission spectrometry (iCAP 6000, Thermo Fisher Scientific, Germany, DIN EN ISO 11885). Ammonium and soluble reactive phosphorus (SRP) were determined photometrically by a segmented flow analyzer (SANplusSystem, Skalar Analytic GmbH, Germany, ammonium: EN ISO 11732, SRP: DIN EN ISO 6878). Total phosphorus (TP) was measured as SRP after digestion at 121°C and 0.12 MPa using peroxydisulfate.

### 2.3. Gas Analyses

For gas analyses,  $W_{\text{pump}}$  and  $W_{\text{samp}}$  samples from each water depth were filled in duplicate into 20 mL vials (triplicates at the water surface) and sealed air-free and gas-tightly with crimp aluminum caps. In 2017,  $\text{ZnCl}_2$  (final concentration 75 mM) was injected through the septum at the sampling site as a fixative, to inhibit further microbial activities, while in 2018 it was added in the laboratory within 6 hr after sampling. Vials were stored upside down at 5°C in the dark until analysis. Helium (99.999%) was used to create headspaces in the water-filled vials, which were analyzed twice by a gas chromatograph (GC2014, Shimadzu, Japan) using a flame ion detector (FID) and a thermal conductivity detector (TCD) for  $\text{CH}_4$  and  $\text{CO}_2$ , respectively. The gas dissolved in water ( $c_w$ , in  $\text{mol m}^{-3}$ ) was calculated from the partial pressure of gas in the headspace ( $p_{\text{gas}}$ , in Pa), taking into account the gas-water-equilibrium described by Henry's law (Equation 1). Partial pressures ( $p_{\text{gas}}$ ) were calculated (Equation 2) on gas concentrations ( $c_{\text{gas}}$ , in  $\text{mol m}^{-3}$ ) in the vial headspace, the temperature ( $T$ , in K) during measurement, and the gas constant  $R$  ( $8.314 \text{ Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1}$ ).

$$c_w = H^{cp} \cdot p_{\text{gas}} \quad (1)$$

$$p_{\text{gas}} = c_{\text{gas}} \cdot T \cdot R \quad (2)$$

Henry's Law solubility constants ( $H^{cp}$ , in  $\text{mol m}^{-3} \text{ Pa}^{-1}$ ) were calculated (Equation 3) with Bunsen solubility coefficients ( $\beta$ ) for  $\text{CH}_4$  and  $\text{CO}_2$ , respectively, at standard temperature  $T_{\text{STD}}$  (273.15 K). Bunsen solubility coefficients were calculated based on the salinity, the temperature during measurement (gas chromatograph set to 50°C), and the constants A1, A2, A3, B1, B2, and B3 as described by Yamamoto et al. (1976) for  $\text{CH}_4$  and by

Weiss (1974) for CO<sub>2</sub> (Equation 4). The salinity ( $S$ , in ppt) in Lake Burgsee was calculated based on the dominant chloride concentrations ( $c_{Cl^-}$ , in ppm) (Equation 5).

$$H^{cp} = \beta \cdot (1/RT_{STD}) \quad (3)$$

$$\ln \beta = A_1 + A_2(100/T) + A_3 \cdot \ln(T/100) + S [B_1 + B_2(T/100) + B_3(T/100)^2] \quad (4)$$

$$S = c_{Cl^-} \cdot (M_{NaCl}/M_{Cl^-}) \quad (5)$$

UGGA data were recorded at high resolution (1 Hz frequency), and subsequently corrected for the delay time (transport time through the tube length), and the response time (nonlinear gas-stripping time of the membrane), as described in Gonzalez-Valencia et al. (2014). Concentrations in surface water samples analyzed by gas chromatography were taken as a reference to correct the M-ICOS gas concentration profiles in the water column.

To assess whether a limnic eruption, that is, a sudden eruption of dissolved gases from deep lake water, can occur in the near future in Lake Burgsee, we compared whether the sum of partial pressures of CO<sub>2</sub> and CH<sub>4</sub> (Equation 1) above the lake bottom is close to the absolute pressure  $p$  (in Pa, Equation 6) in that depth  $h$  (Boehrer et al., 2017).

$$p = p_0 + \rho \cdot g \cdot h \quad (6)$$

The water density ( $\rho$ ) in the water column of Lake Burgsee, calculated from temperature and salinity, varied from 999.2 to 1000.5 kg m<sup>-3</sup> from top to bottom. For the acceleration due to gravity ( $g$ ), we used 9.81 m s<sup>-2</sup>.  $p_0$  is the atmospheric pressure of 1013.5 hPa.

#### 2.4. Gas Production Rates

In 2018, sediment samples were taken at both sites using a sediment corer (Uwitec, Austria). In the boat, overlying water in the sediment cores (6 cm inner diameter) was carefully removed using a syringe, and sediments were gently pushed out from the bottom using a piston. Sediment was sliced into layers 0–2, 2–4, 4–6, 6–10, 10–15, 15–20, and 20–25 cm depth. Sediments were stored cool and dark in zip-lock bags, from which air was removed as best as possible. CH<sub>4</sub> production potentials were determined from sediment samples of two replicate cores. Four milliliter homogenized sediment was taken using a cut-off syringe and transferred into 20 ml vials containing 4 ml autoclaved lake water (121°C, 20 min). The sediment slurry was then degassed with N<sub>2</sub> until no more methane could be detected. To determine gas production rates, headspace gas concentrations were measured after 0, 1, 4, 5, 7, 8, 11, and 12 days by injecting 500 µl subsamples into a gas chromatograph (GC14A, FID, Shimadzu, Japan). Vials were shaken vigorously before headspace samples were taken. Between measurements, vials were stored upside down in the dark at 4°C. Methane production rates were calculated from the increase of CH<sub>4</sub> in the headspace over time during the exponential phase, and related to the wet weight content of the sediment.

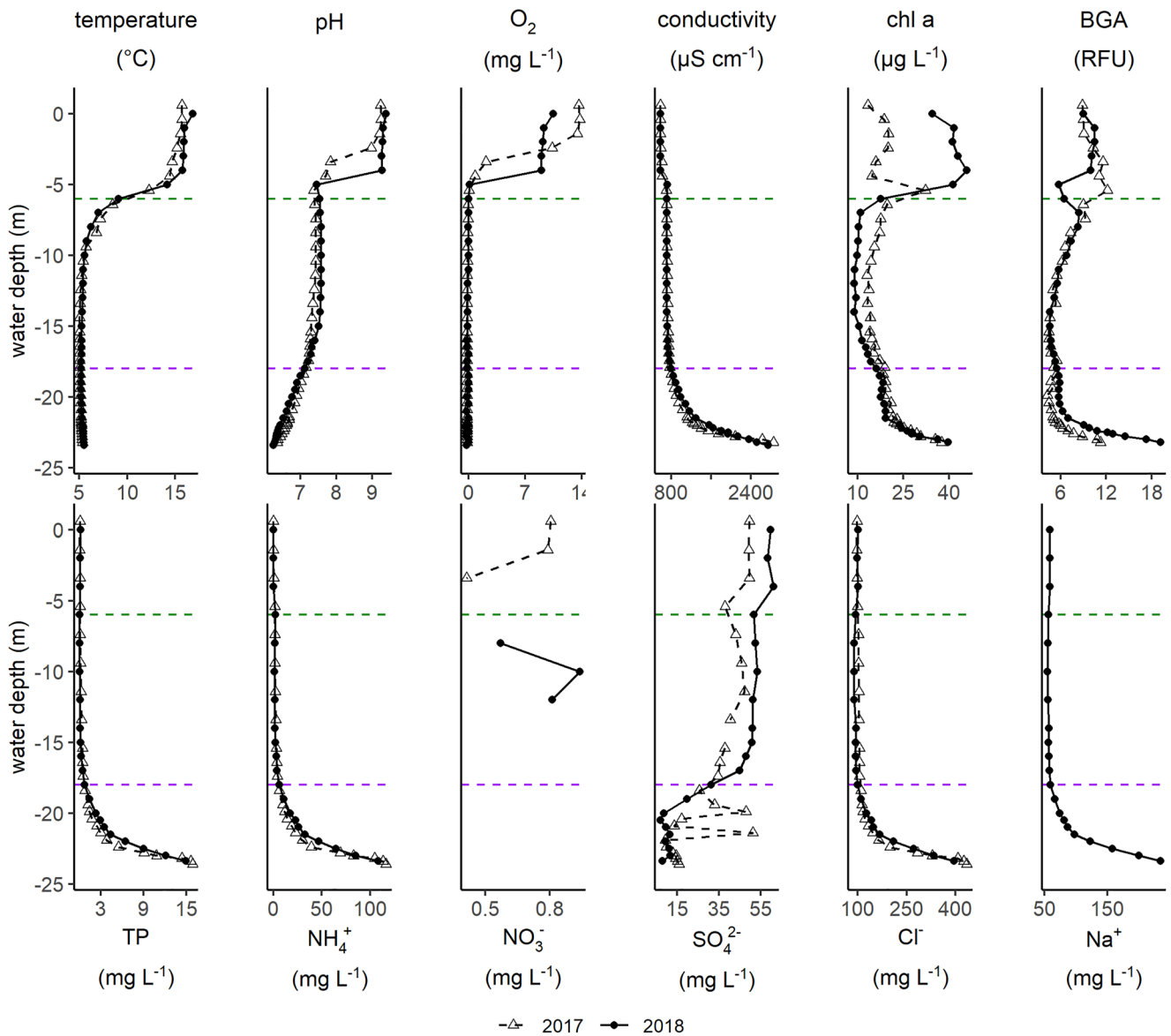
Remaining sediments were dried at 105°C until weight constancy to determine the water content. Dried sediments were then further combusted at 550° and 900°C to determine organic matter and calcium carbonate (CaCO<sub>3</sub>) contents by the loss on ignition (LOI).

#### 2.5. Diffusive Fluxes

Diffusive fluxes ( $F_{gas}$ , in mol m<sup>-2</sup> h<sup>-1</sup>) to the atmosphere at the thin boundary layer (TBL) were calculated (Equation 7) based on the partial pressures of CH<sub>4</sub> and CO<sub>2</sub> at the water surface ( $p_{water}$ , in mol m<sup>-3</sup>) and in the air ( $p_{air}$ , in mol m<sup>-3</sup>, based on water samples from the surface in 2017 and on surface M-ICOS measurements in 2018), and the wind speed dependent gas exchange coefficient ( $k_x$ , in m h<sup>-1</sup>), as described by Cole and Caraco (1998). Schmidt numbers were taken from Wanninkhof (1992) to calculate the gas exchange coefficients of CH<sub>4</sub> and CO<sub>2</sub>. Wind speed was very low and taken from a nearby weather station ([www.michaelreissig.de/wetter.htm](http://www.michaelreissig.de/wetter.htm)).

$$F_{gas} = k_x * (p_{water} - p_{air}) \quad (7)$$

In 2017, only the sinkhole site was investigated, while in 2018, surface water gas concentrations were measured at both sites.



**Figure 2.** Conditions and concentrations in the water column at the sinkhole site of Lake Burgsee on 29 September 2017 (hollow triangles) and 25 September 2018 (filled circles). Temperature (temp), pH, oxygen ( $O_2$ ), electrical conductivity (cond), chlorophyll *a* (chl *a*), blue-green algae phycocyanine (BGA), total phosphorus (TP), ammonium ( $NH_4^+$ ), nitrate ( $NO_3^-$ ), sulfate ( $SO_4^{2-}$ ), chloride ( $Cl^-$ ), and sodium ( $Na^+$ ). Values below the detection limit are excluded. Horizontal dotted lines highlight the depths of the thermocline (green) and the chemocline (purple).

### 2.6. Data

All graphs and statistics were performed using R (R Core Team, 2021), applying the packages *tidyverse* (Wickham et al., 2019), *ggpubr* (Kassambara, 2020), *gridExtra* (Auguie, 2017), and *egg* (Auguie, 2019). M-ICOS response times were calculated based on saturation curves measured above the sediment of Lake Burgsee's sinkhole, using the *solver* function in Excel.

### 3. Results

Although the summer 2018 had been extraordinarily dry and hot, water temperatures in September were similar in 2017 and 2018, with a maximum of approximately 15°C at the water surface and thermal stratification in 4–7 m water depth (Figure 2). Depth profiles of oxygen, conductivity, and pH confirmed a separation into epilimnion and hypolimnion at 6 m depth. Chlorophyll *a* and phycocyanine pigment concentrations indicated the presence

of a phytoplankton bloom in the epilimnion in 2017, while in 2018 peaks of chl *a* and especially phycocyanine pigments were observed at the lower border of the thermocline, where oxygen concentrations became low. Anaerobic conditions ( $<0.5\%$  O<sub>2</sub> saturation) were reached in 5–6 m depth and extended over the entire hypolimnion and below, while pH values decreased to  $<7.0$  in 19 m depth. Further electron acceptors, such as nitrate, occurred only in the upper 4 m in 2017 (max. 0.8 mg NO<sub>3</sub><sup>-</sup> L<sup>-1</sup> in 0 m) and in 8–14 m depth in 2018 (max. 0.9 mg NO<sub>3</sub><sup>-</sup> L<sup>-1</sup> in 10 m), while sulfate decreased in the water column from  $>50$  mg SO<sub>4</sub><sup>2-</sup> L<sup>-1</sup> at the water surface to about 12 mg SO<sub>4</sub><sup>2-</sup> L<sup>-1</sup> in 23.6 m depth (Figure 2).

An additional, chemical, stratification was observed at 16–18 m depth, separating the hypolimnion from the underlying monimolimnion. SRP, TP, NH<sub>4</sub><sup>+</sup>, and Cl<sup>-</sup> increased strongly below 18 m depth and reached extremely high values (about 15 mg SRP L<sup>-1</sup>, 15 mg TP L<sup>-1</sup>, 113 mg NH<sub>4</sub><sup>+</sup>-N L<sup>-1</sup>, and 415 mg Cl<sup>-</sup> L<sup>-1</sup> in 23.6 m depth; Figure 2). Chloride concentrations resulted in an increasing salinity gradient within the water column, reaching 0.4‰ (still freshwater) in 23 m depth.

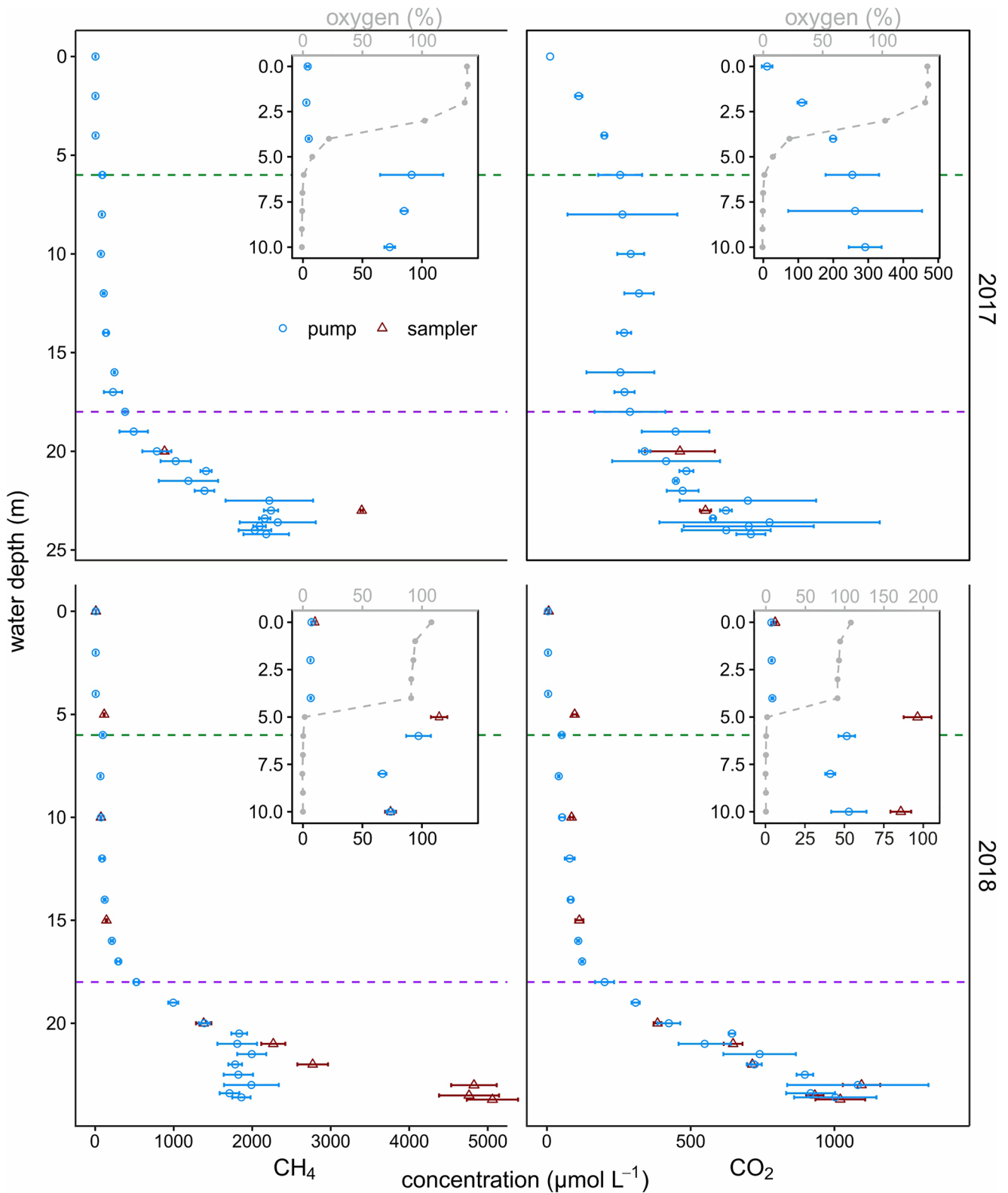
CH<sub>4</sub> concentrations (Figure 3) in the water column (W<sub>pump</sub>) increased 10- to 100-fold across the thermocline and oxycline (from 0.8 and 6.5 μmol L<sup>-1</sup> in 4 m to 105.4 and 66.0 μmol L<sup>-1</sup> in 8 m in 2017 and 2018, respectively), with a distinct peak in 6 m depth (2017: 115.0 μmol L<sup>-1</sup>; 2018: 96.0 μmol L<sup>-1</sup>). In contrast, CH<sub>4</sub> concentrations increased more gradually across the chemocline, reaching CH<sub>4</sub> concentrations of  $>2$  mmol L<sup>-1</sup> in 22.5 m (2017) and 21 m (2018, W<sub>sample</sub>; Table S1) water depth, respectively. Until 20 m depth, dissolved CH<sub>4</sub> concentrations in the sinkhole gave similar results for W<sub>pump</sub> and W<sub>sample</sub> (1.4 mmol L<sup>-1</sup> each in 20 m depth, in 2018), but deviated increasingly with further depth, reaching 1.8 and 2.3 mmol L<sup>-1</sup> in 21 m depth, respectively, as well as 2.0 and 4.8 mmol L<sup>-1</sup> in 23 m depth, respectively (in 2018). At the center site, CH<sub>4</sub> concentrations were only measured by W<sub>M-ICOS</sub> and showed steady concentrations of 1.4–1.7 μmol L<sup>-1</sup> throughout the water column (Figure S1 in Supporting Information S1).

CO<sub>2</sub> concentrations increased gradually with depth in 2017 without any distinct peaks (Figure 3), reaching maxima of 0.3 mmol L<sup>-1</sup> in the epilimnion, 0.5 mmol L<sup>-1</sup> in the hypolimnion, and 1.0 mmol L<sup>-1</sup> in the monimolimnion. In 2018, CO<sub>2</sub> concentrations were very low in the epilimnion ( $<0.06$  mmol L<sup>-1</sup>), reached 0.2 mmol L<sup>-1</sup> in the hypolimnion, but started to increase below the chemocline to a maximum of 1.5 mmol L<sup>-1</sup> in the monimolimnion. In contrast to CH<sub>4</sub>, CO<sub>2</sub> concentrations were similar for W<sub>pump</sub> and W<sub>sample</sub> in all depth layers (e.g., both 1.1 mmol L<sup>-1</sup> in 22 m depth in 2018). At the thermocline, 0.146 mmol CO<sub>2</sub> L<sup>-1</sup> were measured in 5 m depth by W<sub>sample</sub> and 0.079 mmol CO<sub>2</sub> L<sup>-1</sup> in 6 m depth by W<sub>pump</sub> in 2018, showing a steep peak comparable to the one of CH<sub>4</sub>. Center site CO<sub>2</sub> concentrations ranged from 1.1 to 1.4 μmol L<sup>-1</sup> in 2018 (W<sub>M-ICOS</sub>; Figure S1c in Supporting Information S1).

Based on water volume data per depth layer of the sinkhole, a total of 1.9 t CO<sub>2</sub> and 1.0 t CH<sub>4</sub> (W<sub>pump</sub>) or 3.3 t CO<sub>2</sub> and 1.8 t CH<sub>4</sub> (W<sub>sample</sub>), respectively, were stored in the sinkhole in 2018 (Figure 4). The CH<sub>4</sub>:CO<sub>2</sub> compositions were around 2:1 in the epilimnion, 1:1 in the hypolimnion, and 3:1 in the monimolimnion (average W<sub>pump</sub> and W<sub>sample</sub>), with a 5:1 ratio measured by W<sub>sample</sub> above the ground in 23.7 m depth. Due to different pH values, the CH<sub>4</sub>:CO<sub>2</sub> ratio will differ from the CH<sub>4</sub>:DIC ratio among meromictic lakes. Since we measured CO<sub>2</sub> by gas chromatography (TCD) and not DIC, we cannot provide the CH<sub>4</sub>:DIC ratio. However, at pH 6.3 in the monimolimnion of Lake Burgsee, roughly two thirds will be present as HCO<sub>3</sub><sup>-</sup>, that is, DIC will be three times higher than the measured CO<sub>2</sub>.

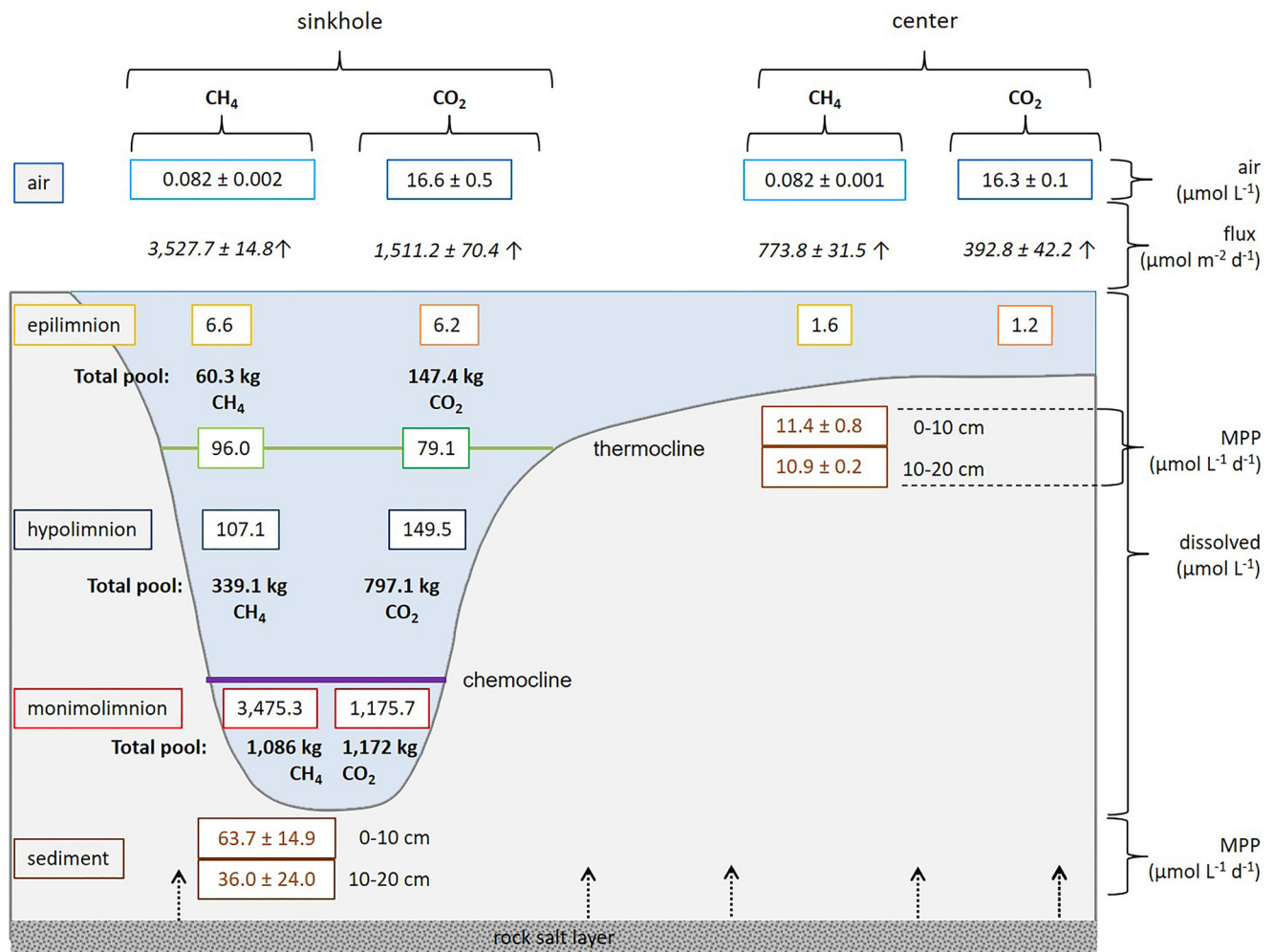
Combined, the partial pressures of the measured greenhouse gases CO<sub>2</sub> and CH<sub>4</sub> (max. 2.9 bar in 23.7 m depth, W<sub>sample</sub>) remained below the absolute pressure (3.3 bar in 23.7 m depth; Figure S2 in Supporting Information S1). When assuming the presence and partial pressure of 0.78 bar for N<sub>2</sub>, the total partial pressure of gases would exceed the absolute pressure at the bottom of the monimolimnion. The very high CH<sub>4</sub> concentrations at the bottom of the monimolimnion and the high sum of partial pressures may indicate an overestimation of the gas concentrations in the monimolimnion, however, we are not aware of any errors or inaccuracies made during the sampling, processing, or analyses. As we observed visually degassing during sampling from depth below 20 m, we assume that ebullition might occur frequently.

Diffusive gas fluxes from the water to the atmosphere, at the thin boundary layer, estimated an emission of  $3.53 \pm 0.01$  mmol CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> and  $1.51 \pm 0.07$  mmol CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> above the sinkhole, and  $0.77 \pm 0.03$  mmol CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> and  $0.39 \pm 0.04$  mmol CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> at the lake center in 2018 (Figure 4). In 2017, gas fluxes were



**Figure 3.** Profiles of  $\text{CH}_4$  and  $\text{CO}_2$  (mean  $\pm$  SD, in  $\mu\text{mol L}^{-1}$ ) in the water column at the sinkhole site in 2017 and 2018, measured by pumping ( $W_{\text{pump}}$ , blue circles) and water sampler ( $W_{\text{samp}}$ , red triangles). Horizontal dashed lines highlight the thermocline (green) and the monimolimnion (purple) depths. Inserted plots zoom into the increase of gas concentrations and decrease of oxygen saturation (gray dashed lines, second x-axis on the top) across the thermocline.





**Figure 4.** Summary of CH<sub>4</sub> and CO<sub>2</sub> concentrations (μmol L<sup>-1</sup>, numbers in regular font), pools (kg, numbers in bold), and fluxes (μmol m<sup>-2</sup> d<sup>-1</sup>, numbers in italics) in Lake Burgsee in 2018. Concentrations are measured by M-ICOS (air), W<sub>pump</sub> (epilimnion and thermocline at the sinkhole site), W<sub>samp</sub> (hypolimnion and monimolimnion at the sinkhole site), and W<sub>M-ICOS</sub> (epilimnion at the center site). Methane production potentials (MPP, μmol L<sup>-1</sup> d<sup>-1</sup>, numbers in brown) are given as averages of the upper 10 cm of sediment and the subjacent 10 cm below. Fluxes across the water-air interface are estimated from concentration differences at the thin boundary layer.

estimated only above the sinkhole and were significantly lower for CH<sub>4</sub>, with  $0.15 \pm 0.01$  mmol CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup>, and higher for CO<sub>2</sub>, with  $5.26 \pm 2.3$  mmol CO<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup>.

Furthermore, in 2018, we measured the methane produced in the sediments, as well as the sediment characteristics, and compared them between the sinkhole and the center of the lake. Sediment characteristics differed between the two sites, showing no drastic changes with depth for the sinkhole sediments but clear gradients at the central site sediments (Table 1). Sediments had a very high water content (>94%) in the top 6 cm of both sites. The water content decreased with depth in the center sediments, but only marginally in the sinkhole sediments. Sinkhole sediments contained a higher content of organic matter (mostly >50%) and organic carbon (mostly >25%) than center sediments, especially below 10 cm depth (Table 1). The content of CaCO<sub>3</sub> was more than five times higher in the center than in the sinkhole sediments (Table 1).

Methane production potentials (MPP) were calculated after 8 days of incubation, as the exponential phase reached its peak during that time for almost all sediment samples. MPP were highest at the sediment-water interface (0–2 cm sediment depth) at both sites, with on average six times higher rates in the sinkhole than in the center sediments. In the center sediments, MPP were steadily around  $0.011 \pm 0.001$  mmol CH<sub>4</sub> L<sup>-1</sup> wet sediment d<sup>-1</sup> (average ± SD) until 25 cm depth. In the sinkhole sediments, MPP decreased strongly below 15 cm sediment depth, although organic matter and organic carbon content decreased only slightly below 15 cm depth.

**Table 1**  
*Sediment Characteristics and Methane Production Potentials (MPP) in Different Sediment Depths at the Lake Center and Sinkhole in 2018*

Site	Depth (cm)	WC (% of WW)	OM (% of DW)	CaCO <sub>3</sub> (% of DW)	Porosity (cm <sup>3</sup> -IW/cm <sup>3</sup> -WS)	MPP <sup>a</sup> (μmol L <sup>-1</sup> WS d <sup>-1</sup> )
Center	0–2	96.1 ± 0.3	36.3 ± 0.2	24.4 ± 0.1	1.00 ± 0.0002	12.6 ± 0.004
Center	2–4	95.2 ± 0.1	38.2 ± 1.3	14.1 ± 1.7	1.00 ± 0.0003	11.3 ± 0.6
Center	4–6	94.3 ± 0.04	48.9 ± 18.0	10.8 ± 7.6	0.99 ± 0.0022	10.8 ± 0.3
Center	6–10	93.6 ± 0.4	35.5 ± NA	15.3 ± 9.9	1.00 ± 0.01	10.8 ± 0.1
Center	10–15	91.1 ± 0.2	31.5 ± 0.3	8.0 ± 0.2	0.98 ± 0.0036	11.0 ± 0.7
Center	15–20	89.4 ± 0.01	29.9 ± 0.3	8.8 ± 0.1	0.97 ± 0.01	10.7 ± 0.3
Center	20–25	87.7 ± 0.1	23.0 ± 0.9	9.5 ± 0.3	0.96 ± 0.0029	10.9 ± 0.9
Sinkhole	0–2	95.8 ± 0.5	55.6 ± 2.9	5.3 ± 2.1	1.00 ± 0.0011	78.4 ± 85.3
Sinkhole	2–4	94.9 ± 0.4	48.6 ± 1.4	5.2 ± 0.8	1.00 ± 0.0004	43.3 ± 36.1
Sinkhole	4–6	95.5 ± 0.1	57.2 ± 0.5	6.4 ± 0.6	1.00 ± 0.0001	64.1 ± 63.7
Sinkhole	6–10	94.5 ± 0.04	52.3 ± 0.8	7.4 ± 0.6	0.99 ± 0.0019	68.9 ± 66.5
Sinkhole	10–15	94.9 ± 0.2	55.8 ± 0.4	5.4 ± 0.9	0.99 ± 0.0003	53.0 ± 58.7
Sinkhole	15–20	94.9 ± 0.6	52.1 ± 2.8	5.2 ± NA	0.99 ± 0.0019	19.1 ± 19.0
Sinkhole	20–25	93.3 ± 1.0	39.0 ± 0.6	7.1 ± 0.1	0.99 ± 0.01	4.0 ± 0.3

Note. DW, dry weight; IW, interstitial water; NA, not available; OM, organic matter; WC, water content; WW, wet weight; WS, wet sediment (mean ± SD,  $n = 2$ ).

<sup>a</sup>Sediment characteristics were determined from sediment core 1 and 3, while MPP were measured from two subsamples per depth in sediment core 2.

Additionally, MPP differed largely between the replicate sediment cores taken in the sinkhole, with one of them showing 0.139 mmol CH<sub>4</sub> L<sup>-1</sup> wet sediment d<sup>-1</sup> in 0–2 cm depth, and the other one 0.018 mmol CH<sub>4</sub> L<sup>-1</sup> wet sediment d<sup>-1</sup> in the same depth.

#### 4. Discussion

The chemical dynamics in Lake Burgsee are largely determined by the sodium and chloride ions seeping or diffusing in from the underground rock salt source while precipitation and other waters dilute the surface water. Thus, there are strong upwardly decreasing gradients in the sinkhole's water column (Figure 2). Moreover, a strong decrease of sulfate concentrations with depth in the deep water of the sinkhole indicates a high activity of sulfate-reducing bacteria and suggests the production of toxic H<sub>2</sub>S in the anoxic environment. Sulfate-reducing bacteria may outcompete methanogens for the same substrates (Martens & Berner, 1974). Yet, methane production in the meromictic sinkhole sediments of Lake Burgsee ranged in the same magnitude as in the sediments of holomictic meso-to eutrophic lakes (e.g., 137.5 μmol L<sup>-1</sup> d<sup>-1</sup> and 20.9 μmol L<sup>-1</sup> d<sup>-1</sup> in the eutrophic lakes Haussee and Dagow, respectively; Casper, 1992). Highest MPP (78.4 μmol L<sup>-1</sup> d<sup>-1</sup> in 0–2 cm) in Lake Burgsee occurred at the immediate sediment-water interface in response to freshly settled material. Similarly, in meromictic lakes, MPP was highest in the sediment surfaces of Knaack Lake (18.2 μmol L<sup>-1</sup> d<sup>-1</sup>; Winfrey & Zeikus, 1979) and ice-covered Lake Shunet (484.3 μmol L<sup>-1</sup> d<sup>-1</sup>; Savvichev et al., 2005), while it increased with sediment depth in the Antarctic Lake Untersee (0.39 μmol L<sup>-1</sup> d<sup>-1</sup> in 0–5 cm of sediment and 0.88 μmol L<sup>-1</sup> d<sup>-1</sup> in 10–15 cm depth; Wand et al., 2006) and ice-covered Lake Shira (0.008 μmol L<sup>-1</sup> d<sup>-1</sup> in 0–2 cm to 0.025 μmol L<sup>-1</sup> d<sup>-1</sup> in 25–30 cm depth; Savvichev et al., 2005), and no methane production was detected in the sediments of the pit lake Cueva de la Mora (Wendt-Potthoff et al., 2012). At the shallow center site of Lake Burgsee, oxygen availability in the overlying water as well as lower organic matter contents led to lower MPPs.

The content of calcium carbonate was distinctly lower in the sinkhole sediments (5%–7% of DW) than in the center site sediments. Calcite precipitation occurs in lakes due to a shift of the carbonate equilibrium toward CaCO<sub>3</sub>, often induced by the intense CO<sub>2</sub> uptake of massive phytoplankton blooms in summer, and subsequently settles to the lake bottom (Fuchs et al., 2016; Kasprzak et al., 2017). Decreasing pH values in the sinkhole of Lake

**Table 2**  
Maximum CO<sub>2</sub> and CH<sub>4</sub> Concentrations in the Monimolimnion of Meromictic Lakes Presented in Literature

Lake	Country	Meromixis	Max. depth (m)	CO <sub>2</sub>	CH <sub>4</sub>	Reference
Albano	Italy	Volcanic	167	<b>1.9 mmol L<sup>-1</sup></b>	0.4 mmol L <sup>-1</sup>	Cabassi et al. (2013)
Alverno	Italy	Volcanic	33	<b>5.2 mmol L<sup>-1</sup></b>	1.1 mmol L <sup>-1</sup>	Cabassi et al. (2013)
Kivu	Rwanda/DR Kongo	Volcanic	485	<b>&gt;85 mmol L<sup>-1</sup></b>	>15 mmol L <sup>-1</sup>	Tietze (1978)
Kivu	Rwanda/DR Kongo	Volcanic	485		~12–19 mmol L <sup>-1a</sup>	Schmid et al. (2005)
Kivu	Rwanda/DR Kongo	Volcanic	485	<b>92–94 mmol L<sup>-1</sup></b>	17–18 mmol L <sup>-1</sup>	Boehrer et al. (2019)
Monticchio Grande	Italy	Volcanic	35	<b>4.9 mmol L<sup>-1</sup></b>	0.4 mmol L <sup>-1</sup>	Cabassi et al. (2013)
Monticchio Piccolo	Italy	Volcanic	38	<b>14.1 mmol L<sup>-1</sup></b>	5.0 mmol L <sup>-1</sup>	Cabassi et al. (2013)
Monoun	Cameroon	Volcanic	99	<b>146.3–157.2 mmol kg<sup>-1</sup></b>	2.7–3.9 mmol kg <sup>-1</sup>	Kling et al. (2005)
Monoun	Cameroon	Volcanic	99	88–153 mmol kg <sup>-1</sup>		Yoshida et al. (2010)
Monoun	Cameroon	Volcanic	99	<b>152.1 mmol kg<sup>-1</sup></b>	4.0 mmol kg <sup>-1</sup>	Issa et al. (2013)
Nyos	Cameroon	Volcanic	210	<b>363.8 mmol kg<sup>-1</sup></b>	2.4 mmol kg <sup>-1</sup>	Kling et al. (2005)
Nyos	Cameroon	Volcanic	210	338–359 mmol kg <sup>-1</sup>		Yoshida et al. (2010)
Nyos	Cameroon	Volcanic	210	<b>369.3 mmol kg<sup>-1</sup></b>	2.4–3.7 mmol kg <sup>-1</sup>	Issa et al. (2013)
Pavin	France	Volcanic	92	1.0 mmol L <sup>-1</sup>	<b>4.1 mmol L<sup>-1</sup></b>	Lehours et al. (2005)
Quilotoa	Ecuador	Volcanic	256	22.7 mmol kg <sup>-1</sup>		Aguilera et al. (2000)
Cueva de la Mora	Spain	Mining pit lake	40	40 mmol L <sup>-1</sup>		Wendt-Potthoff et al. (2012)
Guadiana	Spain	Mining pit lake	68	113.6–125.0 mmol L <sup>-1</sup>		Boehrer et al. (2016)
Vollert-Sued	Germany	Mining pit lake		~1.1 mmol L <sup>-1b,c</sup>	<b>~2.6 mmol L<sup>-1b</sup></b>	Horn et al. (2017)
Dendre	Belgium	Stone pit lake	30		0.9 mmol L <sup>-1</sup>	Roland et al. (2017)
Knaack	Wisconsin, USA	Saline	22		4.0 mmol L <sup>-1</sup>	Winfrey and Zeikus (1979)
Mono	California, USA	Saline	48		0.025–0.057 mmol L <sup>-1</sup>	Miller et al. (1993)
Sakinaw	British Columbia, Canada	Saline	20–140 (transect)		3.0–3.2 mmol L <sup>-1</sup>	Vagle et al. (2010)
Untersee	Dronning Maud Land, Antarctica	Saline	105	~3.8 mmol L <sup>-1c</sup>	<b>21.8 mmol L<sup>-1</sup></b>	Wand et al. (2006)
Burgsee	Germany	Brackish	24	1.5 mmol L <sup>-1</sup>	<b>5.0 mmol L<sup>-1</sup></b>	This study
Shira	Khakassia, Russia	Brackish	23		0.5 × 10 <sup>-3</sup> mmol L <sup>-1</sup>	Savvichev et al. (2005)
Shunet	Khakassia, Russia	Brackish	3		31.3 × 10 <sup>-3</sup> mmol L <sup>-1</sup>	Savvichev et al. (2005)
La Cruz	Spain	Ferric, karstic	24	11.1 mmol L <sup>-1</sup>		Rodrigo et al. (2001)
La Cruz	Spain	Ferric, karstic	24		2.2 mmol L <sup>-1</sup>	Oswald et al. (2016)
Matano	Indonesia	Ferric	>590		1.4 mmol L <sup>-1</sup>	Katsev et al. (2010)
Matano	Indonesia	Ferric	>590	<1 mmol L <sup>-1</sup>	<b>1.4 mmol L<sup>-1</sup></b>	Crowe et al. (2011)
Lugano	Switzerland/Italy	Eutrophic	288		0.1–0.2 mmol L <sup>-1</sup>	Lehmann et al. (2015)

Note. Original values were transformed into mmol L<sup>-1</sup> when possible. The dominant greenhouse gas is indicated in bold when both gases were measured.

<sup>a</sup>Below 450 m, 1974 and 2004; estimated from figure 4 in Schmid et al. (2005). <sup>b</sup>In 21 m depth, estimated from figure 6 in Horn et al. (2017) using WebPlotDigitizer (<https://automeris.io>). <sup>c</sup>DIC converted to CO<sub>2</sub> using PHREEQC.

Burgsee probably redissolve CaCO<sub>3</sub> before it reaches the sediment and simultaneously increase CO<sub>2</sub> concentrations in the monimolimnion (max. concentration 1.0–1.5 mmol CO<sub>2</sub> L<sup>-1</sup>, Figure 3, Table S1 in Supporting Information S1). Enhanced CO<sub>2</sub> concentrations in the monimolimnion have also been observed in the karstic Lake La Cruz (>11 mmol CO<sub>2</sub> L<sup>-1</sup>, Table 2) (Rodrigo et al., 2001). In the former mining lake Guadiana, extraordinary amounts of CO<sub>2</sub> (>110 mmol CO<sub>2</sub> L<sup>-1</sup>, Table 2) are produced and stored in the monimolimnion due to the dissolution of carbonates from rocks at low pH values (Sánchez-España et al., 2014). As saline waters in Lake Burgsee

are derived in unknown quantity from deep underground brines of unknown chemical composition, it is possible that leached carbonates reach the monimolimnion via that route as well.

In addition, dissolved  $\text{CO}_2$  concentrations in the monimolimnion most likely derive from biogenic sources. Lake Burgsee is situated in the center of a small city, with an adjacent small recreational park and a subsurface outflow that is usually dry. Hence, organic matter from the catchment accumulates in the lake, and has accumulated due to former misuse of the lake as a recipient of wastewater. High chlorophyll *a* and phycocyanine concentrations above the sediment indicate that settled phytoplankton from summer blooms accumulates in the sinkhole (Figure 2). The funnel-like morphometry of the lake further promotes the transport of sinking particles towards the sinkhole, accumulating in the small volume at the bottom and fueling the decomposition processes in the permanently separated monimolimnion. Accordingly,  $\text{CO}_2$  and  $\text{CH}_4$  accumulate in the lowest water layers of the sinkhole, with  $\text{CH}_4$  reaching extraordinarily high concentrations compared to lakes that have a “normally” shaped, more voluminous bottom layer and/or experience regular mixing.

Among meromictic lakes (Table 2), the  $\text{CO}_2$  concentrations found in Lake Burgsee are quite low. Usually,  $\text{CO}_2$  is by far the dominant greenhouse gas, due to abundant supplies from, for example, volcanic sources or geochemical interaction (Boehrer et al., 2021). This is not the case in Lake Burgsee, where  $\text{CH}_4$  concentrations dominate and are comparatively high. Only few studies, such as Lehours et al. (2005), Wand et al. (2006), Horn et al. (2017), and Crowe et al. (2011), reported a higher concentration of  $\text{CH}_4$  than of  $\text{CO}_2$  in the monimolimnion of a lake. However, the  $\text{CH}_4$ :DIC ratio may differ largely in these lakes, as well as in Lake Burgsee, due to different pH values. In anoxic environments, hydrogenotrophic methanogens can transform  $\text{CO}_2$  to  $\text{CH}_4$ , which is the dominant methanogenic pathway in the monimolimnion of the natural meromictic lakes Shira, Shunet, and Untersee (Savvichev et al., 2005; Wand et al., 2006). In Lake Burgsee,  $\text{CH}_4$  almost reaches its solubility maximum above the lake bottom (Table S1 in Supporting Information S1), and even in the epilimnion  $\text{CH}_4$  concentrations are high. The partial pressures of greenhouse gases in the lake are only slightly below the absolute pressure, that is, close to posing a risk of eruption. It is likely, that ebullition occurs frequently. However, recent preliminary data (Figure S3 in Supporting Information S1) show that the monimolimnion in Lake Burgsee receded in 2020 and 2021, thus reducing the likelihood of an uncontrolled gas release and the risk for the local population. Lake Vollert-Sued has a maximum total gas pressure of 2.6 bar at the bottom of the monimolimnion, similar to the maximum partial pressure of the greenhouse gases at the bottom of the sinkhole in Lake Burgsee in 2018, and experiences high ebullitive gas release (Horn et al., 2017). However, Horn et al. (2017) stated that the gas release of  $\text{CH}_4$  and  $\text{N}_2$  was not as violent as from  $\text{CO}_2$ -dominated limnic eruptions, and did not endanger the public. The increase of  $\text{CO}_2$  concentrations in Lake Burgsee between the 2 years of measurements in our study indicated the development of an increasing gas depot in the monimolimnion of the lake until 2018. Similarly, the so-called killer lakes Nyos and Monoun, which erupted in the 1980s, reached alarming concentrations again 15–20 years later, due to continuous  $\text{CO}_2$  recharge originating from magma (Halbwachs et al., 2004). Since 2001 and 2003, respectively, Lake Nyos and Lake Monoun are degassed in a controlled manner, but Kling et al. (2005) found that while  $\text{CO}_2$  concentrations in these lakes were lowered,  $\text{CH}_4$  concentrations continued to increase, and attributed this to biogenic  $\text{CH}_4$  production exceeding the gas release.

In holomictic lakes,  $\text{CH}_4$  concentrations in the hypolimnion are determined primarily by oxygen concentrations, organic carbon content, and the release of microbially produced methane from the sediment into the water column (Juutinen et al., 2009). The hypolimnetic  $\text{CH}_4$  concentrations in meromictic lakes are not directly linked to  $\text{CH}_4$  production in bottom sediments, but are derived from diffusive fluxes from the monimolimnion and lateral sediments instead. During lake overturn in autumn and winter or after ice-melt in spring, very large amounts of  $\text{CH}_4$  that accumulated in the anoxic hypolimnion during stratification are oxidized (Rudd & Hamilton, 1978) or released into the atmosphere (Michmerhuizen et al., 1996). This storage flux can amount to approximately 20% of the total  $\text{CH}_4$  emission from a lake of the surface size of Lake Burgsee (Bastviken et al., 2004). A total of 0.3 t  $\text{CH}_4$  and 0.7 t  $\text{CO}_2$  (based on  $W_{\text{pump}}$ ) could potentially be released from the epilimnion and hypolimnion of the sinkhole of Lake Burgsee during overturn, if not oxidized, transformed or released in advance.

$\text{CO}_2$  and  $\text{CH}_4$  concentrations in Lake Burgsee decrease strongly from the sediment to the chemocline, and less strongly but continuously toward the thermocline. Distinct  $\text{CO}_2$  and  $\text{CH}_4$  peaks indicated an accumulation of gases below the thermal density border at very low oxygen concentrations. Recently, cyanobacteria have been found to produce  $\text{CH}_4$  under oxic and anoxic conditions (Bižić et al., 2020), and may have contributed to the metalimnetic  $\text{CH}_4$  peaks in Lake Burgsee. During stable stratification, multiple phytoplankton species,

including cyanobacteria, may thrive in the metalimnion or upper hypolimnion and form deep chlorophyll maxima (Selmečzy et al., 2016). However, with  $\sim 100 \mu\text{mol L}^{-1}$  at the thermocline,  $\text{CH}_4$  concentrations in Lake Burgsee are far higher than those reviewed in Tang et al. (2016;  $0.02\text{--}5 \mu\text{mol L}^{-1}$ ).

Oxidation may reduce methane concentrations by up to 99% during its diffusive ascension from the sediment towards the water surface (Bastviken et al., 2008; Frenzel et al., 1990). This leads to a decoupling of anaerobic methane production in sediments and emission across the water-atmosphere interface (Li et al., 2021). Frequently,  $\text{CH}_4$  oversaturation—relative to atmospheric  $\text{CH}_4$  concentrations—is detected at the water surface of freshwater lakes. In Lake Burgsee,  $\text{CH}_4$  concentrations reached approximately  $7 \mu\text{mol L}^{-1}$  at the water surface above the sinkhole in 2018, similar to values observed in small ponds (summarized by Holgerson, 2015), and were oversaturated relative to the air above the lake (approximately  $0.08 \mu\text{mol L}^{-1}$ ). In consequence, the diffusive  $\text{CH}_4$  transport is directed from the water to the atmosphere (Schilder et al., 2013) and expressed as positive flux, estimated to reach  $0.15 \text{ mmol CH}_4 \text{ m}^{-2} \text{ d}^{-1}$  in 2017 and  $>3 \text{ mmol CH}_4 \text{ m}^{-2} \text{ d}^{-1}$  in 2018 above the sinkhole. In summer 2018, large parts of Europe experienced an extended period of high air temperatures without any or with very little rainfall. This may have increased organic matter decomposition rates and lateral transport of  $\text{CH}_4$  towards the sinkhole, and/or triggered  $\text{CH}_4$  production by phytoplankton communities within the sinkhole. It is also possible that low atmospheric pressure or a vertical mixing event might have triggered a short-term increase in emissions. In the meromictic Lake Vollert-Sued, Horn et al. (2017) measured ebullitive fluxes of  $11.0\text{--}27.4 \text{ mmol CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ , depending on daily changes in air pressure. The authors also reported that the released gas derived from deeper, monimolimnetic waters.

Lake Burgsee presents an extreme case of spatial variability in emission rates, showing that an emission hotspot can exist above a significantly deeper lake area. Although both sites are within a few hundred meters distance to each other, the gas concentrations and fluxes across the water-atmosphere interface are much higher above the sinkhole than at the center site. On average, diffusive fluxes from lakes reach  $0.6 \text{ mmol CH}_4 \text{ m}^{-2} \text{ d}^{-1}$  in temperate regions (Bastviken, 2009), which is below the estimated flux of  $0.8 \text{ mmol CH}_4 \text{ m}^{-2} \text{ d}^{-1}$  at the center of Lake Burgsee. In the shallow center location, the presence of *Aphanothece* colonies in sediments may contribute additional  $\text{CH}_4$  (Bižić et al., 2020), increasing the emission beyond the mere diffusive flux of  $\text{CH}_4$  produced in the sediment from organic matter. As there is no thermocline or chemocline barrier hindering the release of  $\text{CH}_4$  from the shallow sediments at the lake's center site,  $\text{CH}_4$  may be emitted directly to the air, only reduced by oxidation during the short passage through the shallow water body.

In summary, Lake Burgsee is a naturally slightly saline meromictic lake that contains and probably releases impressive amounts of greenhouse gases that are unaccounted for. While volcanic and former mining meromictic lakes receive a certain degree of attention toward the analyses of their water chemistry and occasionally their content of greenhouse gases, naturally formed saline meromictic lakes are rarely investigated. The Zechstein Sea, which provides the brine source for Lake Burgsee, extended over vast parts of middle to northern Europe, and especially in salt mining and spa areas the occurrence of saline meromictic lakes is increased. The amount of greenhouse gases stored and released from naturally meromictic lakes is unknown, and there is no program to monitor their development or to assess their hazardous potential. Especially pollution and eutrophication accelerate greenhouse gas formation in meromictic lakes. In addition, climate change will in general increase water temperatures, biological activities, and thus, methane production rates, emphasizing the need to investigate natural meromictic lakes as potential source of greenhouse gases.

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#### Data Availability Statement

The data used in this study are available in the Freshwater Research and Environmental Database (FRED) repository via doi: 10.18728/igb-fred-761.0 under the Open Data Commons Attribution License.

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