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Key Points:

- The stored mass of methane at the end of the stratified period is strongly linked to the autochthonous primary production during the season
- The interannual variability of methane emissions during overturn is mainly triggered by the seasonal magnitude in primary production
- Climate warming and higher nutrient loadings are expected to increase the contribution of lakes to global methane emissions

Supporting Information:

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

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Interannual Variability of Methane Storage and Emission During Autumn Overturn in a Small Lake

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Abstract Methane emissions from freshwater systems, and especially from small lakes, source a significant proportion of naturally produced atmospheric methane. In small temperate lakes, storage flux, that is, the diffusive emission of methane that was stored in anoxic waters during the seasonal overturn of the water column, can contribute a large fraction of annual methane emissions. Here, we use an extensive field data set to quantify methane storage in anoxic deep water and identify as well as quantify the sources and losses of this methane. The comparison of measurements from 4 years in a small temperate lake (Illmensee) shows that methane storage can differ substantially between years. In 2012 and 2018, the annual maximum of the methane stored in the entire water column was around twice as high (5,350 and 5,822 kg) as in 2013 and 2017 (2,722 and 2,295 kg). A methane mass balance approach suggests that the variability of methane storage in the anoxic water between the years was not caused by the methane flux at the anoxic–oxic water interface, but rather was related to changes in the methane source from the anoxic sediments. The interannual differences in sediment flux could not be explained by sediment temperature, but rather by the differing supply of organic matter. Our findings suggest that phytoplankton blooms promote methane storage within the same year and thus cause interannual variability in emissions during autumn overturn.

Plain Language Summary Methane emissions from lakes are a major natural source of atmospheric methane. Small, temperate lakes that form an anoxic deep water layer during stratified conditions can store huge amounts of methane that can be suddenly released to the atmosphere during overturning. Our study provides evidence that and why within a lake methane storage and emission during autumn overturn can differ substantially between years. The interannual variability is affected not only by the overturn dynamics but also by the stored mass of methane at the end of the stratification period. The latter is strongly linked to the autochthonous primary production during that period for two reasons: the degraded biomass (a) affects the duration and extent of anoxic conditions in the deep water and thus the duration of methane accumulation and the area of the sediment surface at which methane fluxes from sediments are not oxidized and (b) leads to an increase in methane production and therefore in the source of methane in anoxic waters. Thus, ecosystem productivity and its interannual variability are major modulators of methane emissions from lakes. In consequence, lakes that experience higher nutrient loadings and climate warming are expected to increase their contribution to global methane emissions.

1. Introduction

Methane is one of the most potent greenhouse gases, whose atmospheric concentration has increased by a factor of 2.5 since preindustrial times (IPCC, 2014). Lakes, especially small lakes, are an important source of methane (Bastviken et al., 2004). In lakes, methane is mainly produced in anoxic sediments by anaerobic methanogenic archaea and diffuses from the pore water to the sediment surface (Rudd & Hamilton, 1978). Recent studies, however, suggest that the sediment flux comprises two parts: the diffusive transport of methane through the pore water of the sediment and the flux of methane that is generated within the fluffy sediments, which is typically considered as a layer enriched in organic material at the top of the sediments (Grasset et al., 2018; Yan et al., 2017).

At oxic sediment–water interfaces (SWIs), a large proportion of the methane transported from the sediments to the water is oxidized; whereas, under anoxic conditions in the overlying water column, methane can accumulate in the anoxic water layer during summer stratification to high concentrations (up to 20 mmol L^{−1}; Encinas Fernán-dez et al., 2014; Schmid et al., 2005). In the latter case, methane oxidation typically takes place at the anoxic–oxic

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water interface (AOI; Rudd et al., 1976). However, recent studies show that methane oxidation can also occur under anoxic conditions in sediments (Martinez-Cruz et al., 2018; Winkel et al., 2019) and in the hypolimnion of lakes (Eller et al., 2005; Schubert et al., 2010). Anaerobic oxidation of methane (AOM) should reduce the rate of accumulation of methane in the anoxic hypolimnion. The estimates of the AOM rates in the anoxic hypolimnion of lakes have an extremely wide range with mean AOM rates per lake ranging from 0.03 to 1,584 $\mu\text{mol L}^{-1} \text{ day}^{-1}$ (Cabrol et al., 2020; Milucka et al., 2015). Most of the lakes, where AOM was investigated, are characterized first by meromixis and second by extreme conditions such as high alkalinity, acidity, salinity, or nutrient content or formed by thawing permafrost or from volcanic activity (Iversen et al., 1987; Thalasso et al., 2020; Van Grinsven et al., 2021). Taking into account only lakes with a seasonal development of anoxic deep water (at least periodically), AOM rates range from 0.04 to 0.33 $\mu\text{mol L}^{-1} \text{ day}^{-1}$ (Oremland et al., 1993; Oswald, Milucka, et al., 2016; Oswald et al., 2015). The rate of methane storage is according to Vachon et al. (2019) substantially affected by changes in the turbulent diffusive flux of methane across the AOI. A stronger summer stratification, which is associated with a lower turbulent vertical diffusivity K_z at the AOI, can potentially increase the proportion of stored methane (Vachon et al., 2019).

The sediment flux of methane is dependent on the methane production rate and the AOM rate, which is typically about 1–2 orders lower than the methane production rate in the sediments (D'Ambrosio & Harrison, 2021; Zehnder & Brock, 1980). The methane production rate is driven by two main factors: temperature and the availability of organic material. Methanogenesis is exponentially dependent on temperature, showing the highest production rates at around 30°C (S. Schulz et al., 1997; Thebrath et al., 1993). In the hypolimnion, however, temperature sensitivity and temperature changes are small, resulting in only moderate changes in methanogenesis (Duc et al., 2010; Fuchs et al., 2016). Methane is typically formed in deep sediments and depends there on the standing stock of organic material, that is, in the study of Isidorova et al. (2019), 35%–39% of the methane was formed in the sediments older than the transition age of 6–12 years (9–23 cm), where a low and stable background methane formation was reached. The highest methane formation rates, however, are typically measured in young sediments (e.g., 1 year) and decrease with sediment age (Isidorova et al., 2019; Schwarz et al., 2008). The fluffy layer on the sediment surface, enriched in organic material, which can be formed at times of high sedimentation rates, that is, after a phytoplankton bloom, is therefore discussed to strongly affect methane formation rates. Several studies simulating algal deposition showed that at constant temperatures methane production rates in sediment cores increased significantly by added algal biomass on top of the sediments (S. Schulz & Conrad, 1995; Schwarz et al., 2008; Yan et al., 2017). Algal blooms, such as cyanobacteria blooms, are therefore discussed to play an important role as a facilitator in methane production in the sediments (Bertolet et al., 2020; Li et al., 2020; Yan et al., 2017, 2019).

In addition to methane fluxes into/from the anoxic deep water, methane accumulation in the hypolimnion is affected by the area of the sediment in anoxic water and the duration over which anoxic conditions prevail. Furthermore, the volume of the anoxic water body determines the increase in methane concentration with the accumulation of stored methane and thus affects the concentration gradient of methane and thus the diffusive flux out of the anoxic water body. As a proxy for anoxia, the anoxic factor can be used, representing the integral of the anoxic sediment area over time and normalized by the surface area of the lake (number of days that a sediment area equal to the surface area of the lake is overlain by anoxic water; Nürnberg, 1995).

In summary, the expected key drivers for methane storage in the anoxic hypolimnion are the influx of methane into the anoxic water body at the anoxic SWI, the outflux of methane from the anoxic water body at the AOI by diffusion, and the methane consumption by AOM in the anoxic water body. Aerobic methane consumption by oxidation takes only place in oxic water, at and above the AOI, and anaerobic methane oxidation in sediments outside the anoxic water body and therefore both do not directly affect the methane stored in the anoxic water body. Additional parameters affecting the methane accumulation are the duration of the time period with anoxic conditions, which is typically related to the duration of the stratified period, and the volume of anoxic water. The latter influences the methane concentration developing in response to methane accumulation and thus affects the concentration gradient of methane at the AOI and hence diffusive fluxes across.

Methane release from lakes to the atmosphere can take place through three different emission pathways: diffusive flux, ebullition, and plant-mediated flux (Bastviken et al., 2004). One part of the diffusive flux is the so-called “storage flux,” that is, the diffusive emission of the methane stored in anoxic deep water during strong mixing events in autumn (Encinas Fernández et al., 2014; Schubert et al., 2012; Vachon et al., 2019) or in spring

Figure 1. Study site. Bathymetric map of Illmensee including the sampling station of the vertical profiles at the deepest point of the lake M1 (red asterisk), the eddy covariance station (purple triangle), and the sampling stations of the transects in 2013 (yellow triangles), the transect in 2018 (green triangles), the surface distribution in 2013 (blue dots), and inflow (southeast) and outflow (northwest).

after ice break-up (Greene et al., 2014; Karlsson et al., 2013; López Bellido et al., 2009). Here, we focus on the diffusive methane emission, in particular the diffusive methane emission during autumn overturn. Intense vertical mixing during autumn overturn redistributes the dissolved methane, which had accumulated in anoxic deep water over the summer months. This process leads to enhanced methane concentrations at the water surface and thus results in increased diffusive methane fluxes, which can contribute up to 80% to the annual diffusive methane emissions (Encinas Fernández et al., 2014). The total diffusive methane emissions and ebullition are discussed to be the main contributors to the total methane emissions, ranging between 23% and 75%, and 27% and 62%, respectively (Bastviken et al., 2004; DelSontro et al., 2018; Sanches et al., 2019). Interannual variability in methane storage may have an impact on the methane emission during the autumn overturn and therefore on the annual total methane emissions. How much of the stored methane is emitted during the overturn is mainly influenced by the oxidation rate (Schubert et al., 2012) during the overturn and the mixing dynamics (Vachon et al., 2019). Studies indicate that between 54% and 94% of the methane is oxidized during the autumn overturn (Encinas Fernández et al., 2014; Kankaala et al., 2007; Rudd & Hamilton, 1978; Schubert et al., 2012; Utsumi et al., 1998).

While the key drivers for methane storage have been identified to our knowledge only a few studies have investigated the relative contribution of these drivers to methane storage (Bartosiewicz et al., 2015; Sanches et al., 2019; Vachon et al., 2019). The latter study focused only on physical parameters and how they can influence the fate of methane produced in the hypolimnetic sediments but did not investigate the relative contribution of other key drivers for methane storage such as the input of organic material or the duration and extent of anoxia. In the present study, we investigated the mass balance of methane in a small, dimictic, and meso-/eutrophic lake for 2 years (2013 and 2018) during summer stratification and autumn overturn. Additional measurements were done in 2012 and 2017. We calculated the diffusive methane flux at the AOI using vertical profiles of methane and K_z determined from the heat budget technique. Sediment fluxes were obtained by closing the mass balance for the methane in the anoxic water column. Diffusive methane

emissions at the lake surface were calculated by different wind models and were compared with methane fluxes measured with an eddy covariance (EC) system.

We investigated the relative importance of several factors influencing methane storage, that is, of sediment temperature, biomass input, duration of the stratification period, anoxic volume, and turbulent diffusivity, on the total methane stored before autumn overturn and on the methane emission during autumn overturn. We hypothesized that lake productivity by regulating methanogenesis and thus sediment flux as observed in previous studies will have the greatest impact on methane storage and thus also on its methane emission. We speculate that the interannual variability in the methane source from the sediment should therefore be the main factor causing interannual variability in methane storage and emission.

2. Material and Methods

2.1. Study Site

Illmensee is a small meso-/eutrophic dimictic lake, which is located in Southwest Germany (47°51.317'N, 9°22.817'E). The surface area of the lake is 710,000 m² and the maximum depth is 16.5 m. The lake is composed of two basins that are well connected. The main inflow and outflow is the Andelsbach, which feeds the Illmensee with a volume of 37 L s⁻¹ on its southeastern shore and runs off on the northwest bank (Figure 1).

2.2. Sampling and Analyses

Measurements were conducted in Illmensee during the years 2012, 2013, 2017, and 2018 at station M1, which is at the deepest location of the lake (Figure 1). In 2013 and 2018, measurements were carried out from April to December, in 2017 from October to December, and in 2012 from September to November. Temperature and oxygen concentration profiles were measured by an optode chain (miniDOT logger, Precision Measurement Engineering [PME]; Vista, CA, USA) with a vertical resolution of 1–3 m and a temporal resolution of 1 min. In addition, in 2013, spatially high-resolution temperature and oxygen profiles were taken with a CTD probe once a month to twice a week during the stratified period and the mixing period, respectively.

Vertical profiles of water samples for dissolved methane concentrations were taken at M1 during 2012, 2013, 2017, and 2018. The temporal resolution varied between once a month to twice a week during the stratified and the mixing period, respectively, and the vertical resolution ranged between 0.5 and 5 m but was most of the time 1 m. Spatially resolved surface distributions of methane were measured before and during summer stratification and after the overturn in 2013 and along a transect during the overturn in 2018 (Figure 1). In order to measure dissolved methane concentrations of the lake water, 122 mL serum bottles were filled with an oversaturated sodium chloride solution, capped gas-tight, and evacuated in the lab as described in Hofmann et al. (2010). Water samples were taken with a 2-L water sampler (Limnos, Finland). About 50 mL of the sample was transferred with a syringe into the serum bottles. Because of the oversaturated solution of sodium chloride in the serum bottles, nearly all of the methane from the water sample was degassed into the remaining headspace. Gas chromatography with a flame ionization detector (GC-FID; Shimadzu, Kyoto, Japan) was used to measure the methane concentration in the headspace. For each water sample, four to eight replicates were taken. The GC data were calibrated using gas standards of 10, 50, 100, 1,000, and 10,000 ppm (Air Liquide). After every five water samples, the calibration was repeated and was used for the subsequent samples. The methane concentration measurements of the replicates varied on average by ~5% (Hofmann et al., 2010).

During and shortly after the autumn overturn period, the dissolved methane concentration was additionally measured by a methane sensor (HydroCTM/CH₄, CONTROS Systems & Solution GmbH, Kiel, Germany) at 2 m water depth. The sensor uses IR, and since 2018 laser absorption spectrometry for the measurement of methane. The probe has a response time of <1 hr, depending on the methane concentration in the lake. Measurements were done once a day at noon for 2–4 hr to reach near 100% actual concentration. Only the mean of the last 10 min of the sampling period was used as daily methane concentration. Gaps in the time series of the probe were caused by insufficient battery supply. The probe was calibrated with the dissolved methane concentrations of the water samples at the same depth.

In 2018, measurements of the methane flux from the water to the atmosphere were conducted by using an EC system that was located at the end of the land tongue (Figure 1). The EC system consists of an open-path CH₄ gas analyzer LI-7700 (LI-COR Inc., Lincoln, USA), a closed path CO₂/H₂O gas analyzer LI-7200 (LI-COR Inc.), and a WindMaster Pro ultrasonic anemometer (Gill Instruments Ltd, UK), installed at about 3 m above the lake level (± 0.5 m due to seasonal changes in water level). The measurement frequency was 10 Hz and the averaging period of the output 30 min. The data were processed using the software EddyPro as described in Van Den Berg et al. (2016) and quality flagged using the system from Mauder and Foken (2004). Moreover, we considered only data with quality flag 0 and periods during which the airflow was from the lake toward the station (wind direction 90°–290°). Note that we obtained some negative outliers in the flux data that can be considered as noise indicating the limits of the methane flux measurement of the EC. The fluxes were corrected by setting negative values to NaN. However, using the corrected flux data made only a negligible difference in our final results, suggesting that our results are not sensitive to the correction of negative outliers.

2.3. Methane Emission

The diffusive flux of methane across the water surface to the atmosphere, F_{CH_4} ($\mu\text{mol m}^{-2} \text{s}^{-1}$), was determined for the stratified period and autumn overturn and derived from the EC technique and empirical relations based on wind speed.

The diffusive flux of methane F_{CH_4} at the lake surface was determined from empirical models based on wind speed utilizing the relation (Liss & Slater, 1974):

$$F_{\text{CH}_4} = k_{\text{CH}_4} \times (C_{\text{CH}_4, \text{w}} - C_{\text{CH}_4, \text{eq}}) \quad (1)$$

where k_{CH_4} is the gas exchange velocity of methane (m s^{-1}), $C_{\text{CH}_4, \text{w}}$ the dissolved methane concentration in the surface water ($\mu\text{mol m}^{-3}$), and $C_{\text{CH}_4, \text{eq}}$ is the dissolved methane concentration in equilibrium with the atmosphere at surface temperature and salinity (Wiesenburg & Guinasso, 1979). The gas exchange velocity of methane k_{CH_4} was estimated using the empirical equation of Liss and Merlivat (1986):

$$k_{\text{CH}_4} = k_{600} \times \left(\frac{Sc}{600} \right)^n, \quad (2)$$

where k_{600} is the gas exchange velocity of carbon dioxide at standard conditions and Sc the Schmidt number of methane for given surface water temperature and salinity (Wanninkhof, 1992). The exponent n can vary from $-2/3$ to $-1/2$ depending on which process dominates diffusion (Jähne et al., 1987). We used $n = -2/3$ for low wind speeds at 10 m elevation $U_{10} \leq 3.6 \text{ m s}^{-1}$ and $n = -1/2$ for $U_{10} > 3.6 \text{ m s}^{-1}$ (Liss & Merlivat, 1986). The gas exchange velocity k_{600} was calculated using several empirical wind models: Cole and Caraco (1998), Livingstone and Imboden (1993), Crusius and Wanninkhof (2003), Guérin et al. (2007), and MacIntyre et al. (2010; $\beta < 0$ cooling, $\beta > 0$ heating, and all β). Using the dissolved methane concentrations obtained from the chemical analysis of the water samples (GC) and the methane sensor (CONTROS), we calculated the diffusive methane flux F_{CH_4} . Additionally in 2018, the diffusive methane flux was compared with the total methane flux measured by the EC system.

2.4. Methane Mass Balance

Dissolved methane concentration profiles at the deepest point of the lake M1 with a spatial resolution of larger than 1 m were linearly interpolated to provide a vertical resolution of 1 m. Higher spatial resolutions, however, were kept. The deepest water sample was always taken as close to the sediment as possible without disturbing the sediment and is considered here to be sampled 0.5 m above the sediment. We assumed that the dissolved methane concentrations were homogenous in the horizontal dimension (Figures S1 and S2 in Supporting Information S1). The mass of dissolved methane stored in the lake was calculated by vertical integration considering the hypsographic curve and the vertical profile of the methane concentration at M1 (Figure S3 in Supporting Information S1). The methane mass stored in the anoxic deep water is the methane mass stored in the water body characterized by dissolved oxygen concentration $C_{\text{O}_2} < 0.2 \text{ mg L}^{-1}$ (Figure S4a in Supporting Information S1). Using the dissolved oxygen concentration measured by the CTD probe instead of the optodes, this limit is slightly increasing from 0.2 to 1 mg L^{-1} due to the high response time of the CTD probe (Figures S4a and S4b in Supporting Information S1). Note that in 2018, we used the optode data with the limit of $C_{\text{O}_2} < 0.2 \text{ mg L}^{-1}$ for the mass balance. In 2013, however we used the CTD data with the limit of $C_{\text{O}_2} < 1 \text{ mg L}^{-1}$, as in 2013 the vertical resolution of the optodes near the AOI was with 3 m too coarse to determine the height of the anoxic water column above maximum depth h_{AOI} accurately enough. For the years 2013 and 2018, we determined the temporal development of the mass of methane stored in the anoxic water starting with the methane measurement date, at which for the first time anoxic conditions in the water column were observed. The height of the anoxic water column above maximum depth h_{AOI} was defined as the height at which the oxygen concentration changes from the anoxic limit to larger concentrations in the water above. In order to determine h_{AOI} , the oxygen data were linearly interpolated in the vertical dimension to provide 0.1 m vertical resolution.

The rate of change of the methane stored in the anoxic hypolimnion, the storage rate dM_{CH_4}/dt (mmol day^{-1}) was calculated by the following mass balance:

$$\frac{dM_{\text{CH}_4}}{dt} = F_{\text{diff, SWI}} \times A_{\text{SWI}} - F_{\text{diff, AOI}} \times A_{\text{AOI}}, \quad (3)$$

where $F_{\text{diff, SWI}}$ ($\text{mmol m}^{-2} \text{ day}^{-1}$) is the diffusive methane flux across the anoxic SWI and $F_{\text{diff, AOI}}$ ($\text{mmol m}^{-2} \text{ day}^{-1}$) is the diffusive methane flux across the AOI. The area of the SWI A_{SWI} was treated as equivalent to the area of the AOI A_{AOI} thereby neglecting the slope of the sediment. AOM within the anoxic hypolimnion was neglected in the mass balance as it is unknown in this study. However, in addition to the main analysis, we carried out an estimate of the mean areal AOM rate in the anoxic hypolimnion by assuming an AOM rate of $0.19 \pm 0.15 \mu\text{mol L}^{-1} \text{ day}^{-1}$

which covers the range of mean AOM rates measured in lakes with a seasonal development of anoxic deep water (Oremland et al., 1993; Oswald, Milucka, et al., 2016; Oswald et al., 2015). The methane flux from the sediment into the water body $F_{\text{diff,SWI}}$ was estimated from the areal methane storage rate $(dM_{\text{CH}_4}/dt) \times (1/A_{\text{AOI}})$ and the diffusive methane flux $F_{\text{diff,AOI}}$ at the AOI:

$$F_{\text{diff,SWI}} = \frac{dM_{\text{CH}_4}}{dt} \times \frac{1}{A_{\text{AOI}}} + F_{\text{diff,AOI}} \quad (4)$$

The diffusive methane flux $F_{\text{diff,AOI}}$ ($\text{mmol m}^{-2} \text{ day}^{-1}$) at the AOI was calculated by Fick's First Law:

$$F_{\text{diff,AOI}} = K_z \times \frac{\partial \text{CH}_4}{\partial z} \quad (5)$$

where K_z is the turbulent diffusivity ($\text{m}^2 \text{ day}^{-1}$) at the AOI and $\partial \text{CH}_4 / \partial z$ is the methane concentration gradient (mmol m^{-1}) at the AOI. The K_z values were determined by the heat budget method (Jassby & Powell, 1975; Quay et al., 1980), using the temperature data of the optode chain. The temperature data were linearly interpolated in the vertical dimension to provide 1 m vertical resolution and 2-day mean values were calculated. K_z values were calculated using time steps of 2 days and space steps of 1 m. $F_{\text{diff,AOI}}$ was calculated between two sampling days by averaging the estimated K_z over the time period between the two sampling days and using the mean methane gradient at the AOI of the two sampling days.

2.5. Phytoplankton

In 2013, 2017, and 2018, the total chlorophyll *a* equivalent (Chl *a*) was measured using the FluoroProbe (bbe Moldaenke GmbH, Schwentinental, Germany). For each measurement day, mean total Chl *a* concentrations were calculated by averaging the values of the concentration profiles, which were then used as a measure of mean, total phytoplankton concentrations.

Additional to the measurements of the FluoroProbe, integrated water samples were taken monthly by the Institute of Lake Research (ISF, Landesanstalt für Umwelt Baden-Württemberg LUBW) in 2012, 2017, and 2018. Integrated water samples were taken from 1 m above the lake bottom to the water surface and were analyzed for different algae classes and taxons. To estimate the concentration of total phytoplankton, 1 mg L^{-1} phytoplankton biomass (wet weight) was equated with 1 $\text{mm}^3 \text{ L}^{-1}$ biovolume, assuming a density of 1 kg L^{-1} . The biovolume was estimated by using a standardized WFD tool which assigns a certain volume to the organisms of each taxon that were found in the microscopically examined sample volume. Note that in the case of the genus *Planktothrix*, a determination after Lugol fixation is difficult, due to the loss of the pink color. Therefore, it is not fully clear whether there are different morphs of *Planktothrix rubescens* or different types of *Planktothrix*.

Mean Chl *a* concentrations in 2013 and 2018 and mean phytoplankton concentrations in 2012, 2017, and 2018 were calculated for the period from the end of May (first common date of all years) to the end of September by interpolating the data linearly to daily time steps, integrating over time and dividing by the time interval. In order to be able to compare all 4 years, the phytoplankton concentrations in 2013 were calculated by using the significant regression fit ($R^2 = 0.83$, $p < 0.01$) of the time-resolved Chl *a* and phytoplankton concentrations of 2017 and 2018 (Figure S5 in Supporting Information S1). From the obtained time-resolved phytoplankton concentrations, we calculated for the period from the end of May to the end of September a mean phytoplankton concentration in 2013.

2.6. Chemical Data

Chemical data such as oxygen (O_2), phosphorus (P), nitrate-nitrogen ($\text{NO}_3\text{-N}$), manganese (Mn), iron (Fe), and sulfate (SO_4^{2-}) were measured monthly along the profile at M1 with a vertical resolution of 2.5 m in the years 2012 and 2017. These data were provided by the ISF.

2.7. Meteorological Data

Wind speed data for the calculation of the diffusive methane emissions were provided by the ISF. The wind speeds were measured on the lake at M1 at a height of 1.75 m and a temporal resolution of 1 hr. Wind speed at 10 m height above the lake surface was estimated from these data assuming a logarithmic boundary layer. We considered a wind speed dependent drag coefficient C_{10} using the method of Wu (1994) and Wüest and Lorke (2003).

3. Results

3.1. Temporal Variation of the Vertical Distribution of Temperature, Dissolved Oxygen, and Methane

During the summer season, Illmensee exhibited a stable thermal stratification in all studied years (Figures 2a and 2b). Water temperatures in the surface layer (0.5–1.5 m water depth) reached maximum values of 27°C and 27.5°C in July 2013 and in August 2018, respectively (Figure S6 in Supporting Information S1). The water temperature ~1 m above the sediment at M1 was 5.3°C and 5.6°C in June 2013 and 2018, that is, at the time of the first simultaneous measurement, respectively, and increased only slightly to 5.7°C and 5.9°C, respectively, in October, that is, at the time of maximum methane storage. In 2013 and 2018, water column temperature became homogenous at the end of October and the beginning of December, respectively, indicating complete mixing.

During summer, stratification oxygen was around saturation in the epilimnion (between 80% and 160%). Metalimnic oxygen was temporally oversaturated, for example, between June and September 2018 (maximum value 1,076 $\mu\text{mol L}^{-1}$). During the same time period in 2013, the metalimnic oxygen concentration reached only a maximum value of 494 $\mu\text{mol L}^{-1}$. In 2018, the high oxygen concentration was related to a metalimnic peak in Chl *a* due to a bloom of *Planktothrix* (Figures 2d and 5a). Below this oxygen peak, oxygen concentration decreased rapidly with increasing water depth (Figure 2). In 2018 anoxic conditions ($C_{O_2} < 0.2 \text{ mg L}^{-1}$) developed already in early May, whereas in 2013 anoxic conditions started more than 1 month later in the middle of June (Figures 2c and 2d; and Figure S7 in Supporting Information S1). In each of the investigated years, autumn overturn led to a complete reoxygenation of the water body (Figures 2c and 2d).

During the stratified period, dissolved methane concentrations in the surface water ranged between 0.5 and 2 $\mu\text{mol L}^{-1}$ in all studied years (Figures 2e and 2f). However, during autumn overturn, the dissolved methane concentration in the surface water reached up to 21 $\mu\text{mol L}^{-1}$ on 10 December 2018 and decreased after the overturn to less than 0.2 $\mu\text{mol L}^{-1}$ (Figure 2f and Figure S14b in Supporting Information S1). During stratified conditions, methane concentration minima occurred in the metalimnion at the thermocline within the zone of methane-oxidizing activity. In the hypolimnion, the dissolved methane concentrations were linearly increasing with increasing depth (Figure S8 in Supporting Information S1), reaching maximum values of 1,084 and 1,546 $\mu\text{mol L}^{-1}$ between October and November in 2013 and 2018, respectively.

3.2. Anoxic Volume and the Duration of the Stratified Period

The thickness of the anoxic water layer varied between years. In 2013 and 2018, the maximum thickness of the anoxic layer was 7.3 and 8 m, respectively (Figure S7a in Supporting Information S1). Correspondingly, the anoxic volume was 33% higher in 2018 than in 2013 (Figure S7b in Supporting Information S1). In 2018, the anoxic conditions started around 1 month earlier than in 2013, that is, on 3 May and 5 June, respectively. The anoxic factor, that is, the number of days a sediment area equal to the surface area of the lake is overlain by anoxic water (Nürnberg, 1995), was in 2013 substantially smaller than in 2018, that is, 49.4 and 63.8 days, respectively.

3.3. Methane Storage

As long as the water above the sediment did not become anoxic, methane storage was very low even under hypoxic conditions ($C_{O_2} < 2 \text{ mg L}^{-1}$). Significant methane accumulation occurred only under anoxic conditions, that is, oxygen concentrations below 0.2 mg L^{-1} (Figure S4a in Supporting Information S1), and started in 2013 at the end of June and in 2018 at the end of May (Figures 2 and 3). As soon as anoxic conditions were established, methane storage in the anoxic deep water and methane storage in the entire water column increased at the same

Figure 2. Temperature, oxygen, and methane. Temporal course of the vertical distribution of (a, b) Temperature ($^{\circ}\text{C}$); (c, d) Dissolved oxygen concentration ($\mu\text{mol L}^{-1}$), and (e, f) Dissolved methane concentration ($\mu\text{mol L}^{-1}$) at the deepest point of the lake (M1) in 2013 and 2018, respectively. Note that the black circles at the top of panel (e) and (f) indicate the sampling dates, the white line in (c)–(f) anoxic conditions ($C_{\text{O}_2} < 0.2 \text{ mg L}^{-1}$), and the ticks for the months correspond to the first of each month.

rate (Figure 3). Maximum methane storage was reached in 2013 at the beginning of November and in 2018 at the beginning of October (Figure 3). At the beginning of October 2018, methane storage in the anoxic deep water (4,300 kg) was lower than the methane storage in the entire water column (5,822 kg) because of a mixing event that had occurred between the end of August and the beginning of October, resulting in a decreased height of the anoxic water column above maximum depth and increased methane concentrations in the surface water (Figure 2f). Between 1 July and 1 October, methane storage in the anoxic deep water increased from 517 to 4,227 kg in 2018 and from 19 to 1,974 kg in 2013 (Figure 3). The average rate of methane increase over the 3 months from 1 July to 1 October was 40.3 and 21.3 kg day^{-1} in 2018 and 2013, respectively, and thus 90% larger in 2018 than in 2013. At the end of October 2013 and 2017, the total mass of dissolved methane stored in the entire water column reached maximum values of 2,722 and 2,295 kg, respectively (Figure 3). In contrast, at the end of September 2012 and 2018, the maximum of the stored methane in the entire water column was 5,350 and 5,822 kg and thus around twice as high as in 2013 and 2017 (Figure 3).

Figure 3. Methane storage. Total mass of dissolved methane stored in the entire water column (dots), and in the anoxic water column (stars) in the years 2012 (magenta), 2013 (black), 2017 (red), and 2018 (green). Note that in 2017 the oxygen concentration profiles measured by the optodes for determining the height of the anoxic water column above maximum depth started later in the year, so no mass of dissolved methane stored in the anoxic water column could be calculated for the first three measurements.

3.4. Chemical Data

Local oxygen maxima in the epilimnion were observed in 2012 (16 April 2012, 11 June 2012, and 10 September 2012) and 2017 (24 April 2017) which were related to phytoplankton blooms (Figures 4a–4d, and see also Section 3.5 for additional results regarding the phytoplankton blooms). Under anoxic conditions in the hypolimnion, the concentrations of dissolved manganese and iron near the lake bed showed maxima approximately 2 months after epilimnetic oxygen maxima (Figures 4i–4l). In 2012, the maximum iron and manganese concentrations at the lake bottom (1,038 and 613 $\mu\text{g L}^{-1}$, respectively) were higher than in 2017 (857 and 437 $\mu\text{g L}^{-1}$, respectively). The initial nitrate-nitrogen concentrations in the epilimnion were 2012 almost twice as high (930 $\mu\text{g L}^{-1}$) as in 2017 (530 $\mu\text{g L}^{-1}$; Figures 4g and 4h). In contrast, hypolimnetic nitrate-nitrogen rapidly decreased, reaching in 2012 lower concentrations (7 $\mu\text{g L}^{-1}$) than in 2017 (59 $\mu\text{g L}^{-1}$). Initial sulfate concentrations were comparable in 2012 (7.3 mg L^{-1}) and 2017 (7.2 mg L^{-1} ; Figures 4m and 4n). In the hypolimnion, sulfate was decreasing faster than in the epilimnion, reaching again lower minimum concentrations in 2012 (0.3 mg L^{-1}) than in 2017 (0.8 mg L^{-1}). Epilimnetic total phosphorus concentrations were comparable and rather constant in both years, ranging between 11 and 34 $\mu\text{g L}^{-1}$ (Figures 4e and 4f). In the hypolimnion, however, phosphorus maxima were detected above the sediment bottom with approximately 2 months delay to the epilimnetic oxic maxima (except for one).

3.5. Autochthonous Primary Production

In 2018, water column mean Chl *a* concentrations and water column mean phytoplankton concentrations showed the same seasonal pattern with maximum values occurring between the beginning of June and the beginning of July (max. 41.6 $\mu\text{g L}^{-1}$, max. 7.5 mg L^{-1} ; Figures 5a and 5b). Mean Chl *a* and phytoplankton concentrations indicate a phytoplankton bloom between June and August in 2018 (max. 41.6 $\mu\text{g L}^{-1}$), whereas during the same time period in 2013 mean Chl *a* concentrations were rather low (max. 12.3 $\mu\text{g L}^{-1}$), but high between August and October (17.4 $\mu\text{g L}^{-1}$; Figure 5b). In summer 2012, the phytoplankton bloom (max. 3.8 mg L^{-1}) was less pronounced than in 2018; however, later in the year another maximum was detected (max. 5.9 mg L^{-1}). In 2017, the phytoplankton bloom was rather weak, the maximum phytoplankton biomass concentration was only 3.5 mg L^{-1} .

Figure 4. Phytoplankton and chemical data. Temporal course of the vertical distribution of (a, b) Average phytoplankton concentration; (c, d) Dissolved oxygen concentration; (e, f) Phosphorus concentration; (g, h) Nitrate-nitrogen concentration; (i, j) Manganese concentration; (k, l) Iron concentration; (m, n) Sulfate concentrations, and (o, p) Dissolved methane concentration during the years 2012 (left) and 2017 (right).

Mean Chl *a* concentrations and mean phytoplankton concentrations were used as a measure of the algal biomass potentially available for sedimentation and thus as a potential organic carbon source for methane production in anoxic deep water. The mean Chl *a* concentrations from the beginning of May to the end of September indicate that the potential biomass input was twice as high in 2018 ($23.1 \mu\text{g L}^{-1}$) compared to 2013 ($11.3 \mu\text{g L}^{-1}$). Considering the mean phytoplankton concentrations of the water samples, in 2018 the potential biomass input (4.8 mg L^{-1}) was almost twice as high as in 2017 (2.8 mg L^{-1}), and more than twice as high as in 2013 (2.3 mg L^{-1}). In 2012, the mean phytoplankton concentration was with 3.8 mg L^{-1} nearly as high as in 2018. In 2012, 2017, and 2018, the phytoplankton community was mainly dominated by cyanobacteria, which made up to 72%, 76%, and 84% of the total biomass, respectively. The by far most abundant cyanobacteria species was with 91%–96% *Planktothrix*.

Figure 5. Temporal course in phytoplankton: (a) Water column mean phytoplankton concentration, measured by integrated water samples (wet weight) in 2012 (magenta), 2017 (red), and 2018 (green) and (b) Water column mean chlorophyll *a* concentration, measured by the Fluoroprobe in 2013 (black), 2017 (red), and 2018 (green). The phytoplankton data and the Fluoroprobe data (dotted line with stars) were provided by the Institute of Lake Research (ISF, Landesanstalt für Umwelt Baden-Württemberg LUBW).

3.6. Methane Mass Balance During the Stratified Period

3.6.1. Areal Methane Storage Rate

The areal methane storage rate was calculated for the time period when the deep water was anoxic, but not yet mixed. The areal mean methane storage rate between 26 June and 30 October 2018 ($11.5 \pm 0.6 \text{ mmol m}^{-2} \text{ day}^{-1}$) was twice as high as between 25 May and 5 October in 2013 ($5.8 \pm 0.3 \text{ mmol m}^{-2} \text{ day}^{-1}$). Maximum areal storage rates of $8.4 \text{ mmol m}^{-2} \text{ day}^{-1}$ (2013) and $22.9 \text{ mmol m}^{-2} \text{ day}^{-1}$ (2018) were observed in both years shortly before the autumn overturn started (Figure 6).

3.6.2. Diffusive Methane Flux at the AOI

During the stratified period, the mean K_z value at the AOI was similar in 2013 ($3.3 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$) and in 2018 ($3.1 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$; Figure S9 in Supporting Information S1). The mean diffusive methane flux at the AOI $F_{\text{diff,AOI}}$ was $0.2 \pm 0.8 \text{ mmol m}^{-2} \text{ day}^{-1}$ in 2013 (26 June to 30 October) and $1.4 \pm 1.6 \text{ mmol m}^{-2} \text{ day}^{-1}$ in 2018 (25 May to 5 October; Table S1 in Supporting Information S1).

3.6.3. Diffusive Methane Flux at the SWI

The mean diffusive methane flux at the AOI is larger in 2013 than in 2018, whereas the mean areal methane storage rate is ~ 2 times larger in 2018 than in 2013. Assuming net-production within the anoxic water layer differences in the sediment flux must be responsible for the differences in the methane storage rate. According to the mass balance, the diffusive methane fluxes at the SWI $F_{\text{diff,SWI}}$ ranged between 2.1 and $8.6 \text{ mmol m}^{-2} \text{ day}^{-1}$ in 2013 and between 8.3 and $23.9 \text{ mmol m}^{-2} \text{ day}^{-1}$ in 2018 (Figure 6). In 2018 the mean diffusive methane flux at the SWI ($12.9 \pm 1.7 \text{ mmol m}^{-2} \text{ day}^{-1}$) was 2 times larger than in 2013 ($6.0 \pm 0.8 \text{ mmol m}^{-2} \text{ day}^{-1}$, Table S1 in Supporting Information S1).

3.6.4. Estimated Anaerobic Methane Oxidation Rate

The estimated mean AOM rates are the same in 2013 and in 2018 ($0.4 \pm 0.3 \text{ mmol m}^{-2} \text{ day}^{-1}$). The AOM rates are 1–2 orders smaller than the storage rates and in a similar order of magnitude as the outflux of methane at the

Figure 6. Methane mass balance. Areal methane rates ($\text{mmol m}^{-2} \text{ day}^{-1}$) calculated by the methane mass balance approach during anoxic conditions (filled markers) in 2013 (black) and 2018 (green): areal methane storage rate (circle), diffusive methane flux at the anoxic sediment–water interface (SWI; triangle), and diffusive methane flux at the anoxic–oxic water interface (AOI; square).

AOI. Taking into account the AOM in the mass balance, the sediment flux is increasing slightly to 6.4 ± 0.9 and $13.3 \pm 1.7 \text{ mmol m}^{-2} \text{ day}^{-1}$ in 2013 and 2018, respectively.

3.7. Diffusive Methane Emission

In 2018, the diffusive methane emissions $F_{\text{diff,WM}}$, estimated from several empirical gas exchange models based on wind speed, and the total emissions $F_{\text{tot,EC}}$, estimated from the eddy correlation technique are shown in Figures S10 and S11 in Supporting Information S1. The emissions estimated from the empirical relations by Guérin et al. (2007), MacIntyre et al. (2010), and Crusius and Wanninkhof (2003) systematically overestimated the total methane flux determined from the eddy correlation technique. The best agreement between the total methane emissions estimated from the eddy correlation technique $F_{\text{tot,EC}}$ and the diffusive methane emissions $F_{\text{diff,WM}}$ was obtained with the wind models by Cole and Caraco (1998) and Livingstone and Imboden (1993) which slightly underestimated $F_{\text{tot,EC}}$ (Figures S10 and S11 in Supporting Information S1). The model by Cole and Caraco (1998) is used in the following to calculate the diffusive methane fluxes.

During the overturn in 2018, the total emitted mass of methane was 2,807 kg which is more than twice as high as in 2017 (1,260 kg) and 3 times higher than in 2013 (760 kg; Table 1 and Figures S11–S13 in Supporting Information S1). The interannual variability of the total emitted methane is only partially explained by the total methane stored in the water body before the overturn. The twice as high methane storage in 2018 (5,822 kg) compared to 2013 and 2017 (2,722 and 2,281 kg) led during the autumn overturn to higher mean methane concentrations in the surface water ($6.5 \mu\text{mol L}^{-1}$ in 2018 compared to 2.9 and $4.5 \mu\text{mol L}^{-1}$ in 2013 and 2017) and methane emissions (2,807 kg in 2018 compared to 760 and 1,260 kg in 2013 and 2017). However, this is not the case comparing only the years with similar low methane storage, 2013 and 2017. Despite slightly higher methane storage in 2013 compared to 2017, the mean methane concentrations and methane emissions during the overturn in 2013 were lower than in 2017. This is because in 2013 only 27.9% of the methane stored in the anoxic water layer was emitted to the atmosphere, whereas it was 55.2% in 2017. In fact, the proportion of emitted methane varied strongly among the years and was found to increase (27.9% in 2013, 48.2% in 2018, and 55.2% in 2017) with increasing mixing speeds, that is, increasing mean gas exchange velocities during the autumn overturn (2.2 cm hr^{-1} in 2013, 2.4 cm hr^{-1} in 2018, and 2.8 cm hr^{-1} in 2017). Higher methane storage has therefore the potential to lead to higher methane emissions, however, can be impacted by the dynamics of the autumn overturn.

Table 1

Temporal Change of Dissolved Methane Stored in the Entire Water Column and the Diffusive Methane Flux to the Atmosphere During the Stratified Period in 2013 and 2018 as Well as During the Overturn in 2013, 2017, and 2018

Time period	Rates			Total mass of methane				Fraction emitted (%)
	Temporal change of stored methane (kg day ⁻¹)	Diffusive methane flux		Water column storage			Emitted methane (kg)	
		(mg m ⁻² day ⁻¹)	(kg day ⁻¹)	Beginning (kg)	End (kg)	Diff (kg)		
07.05.2013 to 30.10.2013	0.1	9.6	6.3	13	2,722	2,710	1,107	
30.10.2013 to 10.12.2013	−66.4	28.3	18.5	2,722	6	2,716	760	27.9
25.10.2017 to 01.12.2017	−61.6	52.0	34.0	2,281	40	2,241	1,260	55.2
27.04.2018 to 05.10.2018	0.2	17.3	11.4	28	5,822	5,794	1,828	
05.10.2018 to 19.12.2018	−77.6	57.1	37.4	5,822	39	5,783	2,807	48.2

Note. The diffusive fluxes were calculated based on the empirical wind model of Cole and Caraco (1998) and the wind data measured in the middle of the lake.

The duration of the overturn differed among the years, the higher the total methane stored in the water body before the overturn, the longer was the duration of the overturn (linear regression model with $n = 3$: $R^2 = 0.93$, $p = 0.17$). While in the years with low methane storage (2017 followed by 2013), the overturn lasted 37 and 41 days, in the year with high methane storage (2018), the overturn period was much longer and lasted in total 75 days. During the overturn, the diffusive methane flux to the atmosphere was around 3–4 times higher than during the stratified period. In total, Illmensee emitted 178 mmol m⁻² methane in 2013 (during 217 days) and 441 mmol m⁻² methane in 2018 (during 236 days).

4. Discussion

This study shows that methane storage and emission of stored methane can be highly variable between years within the same lake. Methane storage was largest in years with the highest amounts of organic matter from autochthonous primary production, suggesting that the production of methane from recently sedimented organic material is an important source of methane in the anoxic hypolimnion.

The amount of methane stored at the end of the stratified period in anoxic waters depends on the duration of anoxic conditions and the storage rate of methane in the anoxic waters. The latter is controlled by (a) the source of methane from the sediments which depends on the sediment area in anoxic water and the production rate of methane and (b) the loss rate of methane toward the overlying oxic water which depends on the concentration gradient, and thus on the concentration of methane in the anoxic water, and the turbulent diffusivity K_z at the AOI. In the following discussion, we compare the different factors controlling the amount of methane stored at the end of the stratified period and demonstrate that the interannual variability in the methane source from the sediment is the main factor causing the interannual variability in methane storage.

4.1. Hypolimnetic Anoxia and Methane Storage

In 2012 and 2018, around twice as much methane was stored in the lake compared to 2013 and 2017 (Figure 3). Focusing on the years 2013 and 2018, the years with the most complete data set, the onset of anoxic conditions occurred earlier in 2018 than in 2013, but the duration of anoxic conditions until autumn mixing was essentially the same in both years (154 days vs. 138 days) because autumn mixing set in earlier in 2018 than in 2013. Hence, the difference in methane storage between these 2 years cannot be explained by a discriminate duration of methane accumulation but requires different methane storage rates.

The thickness of the anoxic hypolimnion was larger in 2018 than in 2013 and therefore also the anoxic sediment area and the anoxic volume (Figure S6 in Supporting Information S1). Assuming the same mean methane concentration in the anoxic water in both years, the anoxic volume just before autumn mixing would explain a 38.5% larger amount of stored methane in 2018 compared to 2013. However, assuming the same sediment flux in both years, the mean methane concentration in 2018 will be lower than in 2013 as the anoxic volume to anoxic area relationship is increasing with increasing height of the anoxic water column above maximum depth. Assuming the same mean sediment flux and the same mean loss rate from the anoxic waters from 2013 for 2018, the difference

in sediment area in anoxic waters would explain only a difference in methane storage of 7.5% between 2018 and 2013. Considering the different duration of methane accumulation between the 2 years, maximum methane storage would be 29.2% larger in 2018 than in 2013.

The differences in anoxic conditions between 2013 and 2018 are at least partially responsible for the differences in methane storage and can be explained by differences in phytoplankton blooms between years. Several studies have shown that settling organic matter especially after phytoplankton blooms can lead to increased sediment oxygen demand, resulting in hypolimnetic oxygen depletion (Beutel, 2003; Grenz et al., 2000; Nürnberg, 1995; Yan et al., 2017). In the study of Beutel (2003) for instance, which compared nine lakes, the annual mean Chl *a* concentration correlated significantly with the sediment and volume-based hypolimnetic oxygen demand as well as with the anoxic factor. Therefore, the higher mean Chl *a* concentrations in 2018 compared to 2013 could explain the larger extent of the anoxic water layer and the higher anoxic factor in 2018 compared to 2013.

However, the differences in anoxic conditions between 2013 and 2018 explain only a minor fraction of the differences in methane storage between the 2 years suggesting that the increase in the area of the anoxic sediment surface and the larger capacity at the same mean concentration of methane are not the main explanation of the differences in methane storage.

4.2. The Source of Methane in the Anoxic Layer and Methane Storage

By applying a methane mass balance approach to the anoxic water body in the deep water of Illmensee, we estimated the differences between 2013 and 2018 in the source of the methane stored in the anoxic water.

Despite the slightly higher mean turbulent diffusivity K_z in 2013 than in 2018, the mean diffusive flux at the AOI was in 2018 ($1.4 \pm 1.6 \text{ mmol m}^{-2} \text{ day}^{-1}$) higher than in 2013 ($0.2 \pm 0.8 \text{ mmol m}^{-2} \text{ day}^{-1}$), because the methane gradient at the AOI was higher in 2018 than in 2013. The differences in the methane gradients were predominantly caused by the difference in methane concentrations in the anoxic water. Because the loss from the anoxic water was much larger in 2018 than in 2013, the source of methane must have been substantially larger in 2018 than in 2013 to explain the larger methane storage in 2018 compared to 2013. Furthermore, the larger methane concentration in combination with the larger anoxic volume enhances the requirement of a substantially larger source of methane in 2018 than in 2013.

The sediment fluxes $F_{\text{diff,SWI}}$ showed a high seasonal and interannual variability but were within the range of other studies (Rudd & Hamilton, 1978; Vachon et al., 2019). In both years, the increase in the sediment flux in the first 3 months of the stratified period (July–September 2013, June–August 2018) was similar. After that period, the observed sediment flux was much higher in 2018 than in 2013. In 2018, the mean sediment flux during the stratified period was twice as high as in 2013 (Table S1). The difference in the overall source of methane in the anoxic layer is even larger because the area of the sediment in the anoxic water is larger in 2018 than in 2013.

Even though physical variables of lakes such as the turbulent vertical diffusivity can influence the fate of methane produced in the deeper sediments (Vachon et al., 2019), during our campaigns only a small fraction of the methane stored in the anoxic hypolimnion was transported across the AOI. Because the diffusive flux at the AOI was comparatively small, the diffusive flux at the SWI was the most important driver for methane storage.

Uncertainties in the calculation of the sediment fluxes from the mass balance approach might be caused by neglecting AOM. To estimate the impact of AOM on our conclusions about the differences in the sediment fluxes between the years, we assumed an AOM rate in the range of $0.04\text{--}0.33 \text{ } \mu\text{mol L}^{-1} \text{ day}^{-1}$, which is given for (at least periodically) monomictic lakes (Oremland et al., 1993; Oswald, Milucka, et al., 2016; Oswald et al., 2015). Considering AOM in the mass balance, the mean sediment fluxes of methane are only slightly increasing about $0.4 \pm 0.3 \text{ mmol m}^{-2} \text{ day}^{-1}$. As a result, the mean sediment flux is in 2018 ($13.3 \pm 1.7 \text{ mmol m}^{-2} \text{ day}^{-1}$) still around twice as high as in 2013 ($6.4 \pm 0.9 \text{ mmol m}^{-2} \text{ day}^{-1}$). Assuming that AOM rates differ between years, AOM still does not affect the differences in sediment fluxes between years. In fact, AOM would need to differ about $6.9 \text{ mmol m}^{-2} \text{ day}^{-1}$ between the years to explain the interannual differences in the sediment fluxes. This would correspond to a mean AOM rate that is $3.2 \text{ } \mu\text{mol L}^{-1} \text{ day}^{-1}$ higher in 2013 than in 2018, which is 1–2 order of magnitude higher than the assumed mean AOM rate. This is very unlikely as mean AOM rates even in meromictic (temperate) lakes typically range only between 0.02 and $1.35 \text{ } \mu\text{mol L}^{-1} \text{ day}^{-1}$ (Blees et al., 2014; Lopes et al., 2011; Milucka et al., 2015; Oswald, Jegge, et al., 2016). Moreover, we assume that the used AOM

rate is probably an overestimation for the dimictic lake Illmensee as there is fewer time for bacteria to build up than in monomictic or meromictic lakes. Additional uncertainties regarding the calculation of the sediment fluxes may also result from the conservative estimation of the AOI. The mean sediment flux of methane was lower in 2013 than in 2018, and this conclusion is insensitive to the exact height of the upper boundary of the anoxic layer. Using h_{AOI} or taking a 1 m higher height of the anoxic water column above maximum depth $h_{\text{AOI}+1 \text{ m}}$, the mean sediment flux of methane is in both cases still around twice as high in 2018 (between 10.1 ± 1.2 and $12.9 \pm 1.7 \text{ mmol m}^{-2} \text{ day}^{-1}$) compared to 2013 (between 4.3 ± 0.2 and $6.0 \pm 0.8 \text{ mmol m}^{-2} \text{ day}^{-1}$; Table S1). This analysis above confirms that the sediment fluxes in 2018 are substantially larger than in 2013 and that the differences in the sediment fluxes are responsible for larger methane storage in 2018 than in 2013.

4.3. Interannual Variation of Methane Production in the Sediments

Interannual variation in sediment fluxes indicates interannual variation in methane production rates in the sediments. The main factors controlling methane production rates under anoxic conditions are temperature (S. Schulz et al., 1997; Thebrath et al., 1993) and organic matter input. However, the maximum mass of stored methane in the lake in the 4 years studied was not significantly correlated to sediment temperatures estimated from temperatures measured 0.25–0.5 m above the lake bed (Figure S15a in Supporting Information S1). In the year with the highest sediment temperatures (2017), the lowest mass of stored methane was measured. However, the sediment temperatures were low and differed only slightly between years (5.7°C – 7.1°C). Under low temperatures, moderate changes in temperatures do not significantly affect methane production rates (Duc et al., 2010; Fuchs et al., 2016). Clearly, the deep water temperature does not explain the differences in methane fluxes from the sediments between the years studied.

Hence, the interannual variability of the available organic matter for methane production is the most likely cause of the observed interannual variability in methane storage. To assess the potential input of biomass into the sediments in the anoxic zone, we used the water column averaged phytoplankton and Chl *a* concentrations as a proxy for the biomass, derived from autochthonous primary production. In the years with high methane storage (2012 and 2018), mean phytoplankton concentrations from the beginning of May to the end of September were higher than in the years with lower methane storage (2013, 2017). Mean Chl *a* concentrations showed the same pattern as the phytoplankton concentrations. In 2018, not only the maximum mass of stored methane was twice as high as in 2013, but also the potential biomass input assessed by the mean Chl *a* concentrations from the beginning of May to the end of September (Figures 3 and 5). These observations suggest that the larger supply of organic matter for methane production in 2018 compared to 2013 was responsible for the differences between these 2 years in sediment fluxes and thus also in the amount of methane stored in the anoxic waters. This conclusion is supported by a study by Bertolet et al. (2019), which compared methanogenesis rates in sediment cores of 14 temperate lakes. They concluded that the lake's primary production (organic matter supplied to sediments) remains the best predictor of methanogenesis. Also, several experiments showed that phytoplankton added on top of sediment cores increased methane production rates in freshwater sediments (Grasset et al., 2018; Liang et al., 2016; S. Schulz & Conrad, 1995; Schwarz et al., 2008; West et al., 2012; Yan et al., 2017). Higher methane production rates, higher methane concentrations, or higher concentrations of the fermentation products acetate and propionate were found in the upper 1–4 cm of the sediment, indicating that the added algae were directly decomposed in the upper layers of the sediment (S. Schulz & Conrad, 1995; Schwarz et al., 2008). An increased amount of added biomass resulted thereby in increased methane production (Yan et al., 2017). Adding phytoplankton on top of sediment cores, methane production maxima were reached after 26–46 days (Yan et al., 2017). In a similar study by Liang et al. (2016), potential methane production rates were reached after 40 days, resulting in the highest methane sediment fluxes and methane concentrations in the overlying water at the same time. In these studies, the phytoplankton biomass was directly added on top of the sediments. In the lake, however, phytoplankton particles have to sediment first from the oxic water to the anoxic lake bed. In the oxic water column, methane may be produced in anoxic microenvironments around organic particles (M. Schulz et al., 2001), leading to a degradation of the organic particles. However, in Lake Illmensee, most of the sinking organic material can be expected to reach the anoxic zone before it is consumed, because during summer stratification the oxic water column is only 8–9 m thick and sinking particles therefore do not spend much time in oxic waters. The cyanobacterium *Planktothrix* was the dominant phytoplankton species in summer that regulates buoyancy by changing its density with their gas vesicles. The sinking velocity of living *P. rubescens* is about 0.6 m day^{-1} (Walsby, 2005; Walsby & Holland, 2006). Assuming the same sinking velocity for dead *P. rubescens* and with a conservatively assumed

peak at 6 m water depth, *P. rubescens* would need 17 days to sink on the lake bottom. Based on the results from the studies that investigated the release of methane from recently sedimented phytoplankton (Liang et al., 2016; Yan et al., 2017), the time period from the onset of sedimentation to degradation and release in methane can be expected to be of about 1.5–2 months.

In Illmensee, a comparatively strong bloom of *Planktothrix* developed from the beginning of June to the beginning of July 2018 (Figure 5). Indeed, around 2 months later from the beginning of August to the beginning of September, the highest methane flux from the sediment and methane storage rate was found (Figures 3 and 6). The comparison of primary production and methane storage of consecutive years, that is, 2012 and 2013, as well as 2017 and 2018, supports the hypothesis, that in Illmensee methane production and thus methane storage is predominantly influenced by the biomass produced within the same year. The high production of biomass in 2012 apparently enhanced the methane accumulation within the same year, but not in the following year 2013, where methane accumulation was low. In 2018, methane accumulation was the highest of all years, although the biomass was low in the previous year. Clearly, the high methane accumulation rate in 2018 was connected to the high production of biomass within the same year. These results are supported by the study of Isidorova et al. (2019) which found that methane formation rates decreased exponentially with sediment age and that the highest methane formation rates occur in the youngest sediments (1-year-old sediments).

These results indicate that the temporal course and magnitude of the primary production within the water column and its degradation in the anoxic sediments affect the methane storage rate within the same year. Interannual variation in biomass production, therefore, causes a similar interannual variability in methane storage.

4.4. Biomass Degradation and Methane Production

In 2012, several oxygen maxima were observed in the epilimnion and could be linked with the mean phytoplankton concentration of the lake (Figures 4a–4d). Organic matter (e.g., from phytoplankton bloom) that settled to the sediments is decomposed by bacteria that always use the energetically most favorable pathway of respiration. Under oxic conditions, oxygen is therefore reduced first, whereas under anoxic conditions first nitrate, then manganese, iron, and sulfate are reduced. This results in a depletion of NO_3^- and SO_4^{2-} and a release of soluble Mn and Fe that diffuse into the water. Maxima of Mn and Fe were found above the lake bed at about 2 months after the epilimnetic oxygen maxima (Figures 4c, 4d and). After the depletion of all alternative electron acceptors (NO_3^- , Mn, Fe, and SO_4^{2-}), methanogenesis occurred, resulting in an accumulation of methane in the anoxic hypolimnion (Figures 4o and 4p). The release of phosphorus from the sediment pore water in the overlying water has also been related to the process of organic matter decomposition and methanogenesis (Bertollet et al., 2019; Sinke et al., 1990; Yan et al., 2017) and is also visible in our data (Figures 4e and 4f).

Our results are in accordance with the above-mentioned studies, which would prognosticate a delay of 1.5–2 months from the phytoplankton peak and the settling of its biomass (Walsby, 2005; Walsby & Holland, 2006) to the methane production maxima (Liang et al., 2016; Schwarz et al., 2008; Yan et al., 2017). In 2012, depletion of NO_3^- and SO_4^{2-} is higher, and also the concentrations of soluble Mn and Fe are higher compared to 2017 (Figure 4). These observations are consistent with the degradation of a larger amount of organic material and the higher methane storage in 2012 than in 2017. Hence, the phenology of the depletion of NO_3^- and SO_4^{2-} and the occurrence of reduced substances as well as the differences between the concentration in 2012 and 2017 supports the link between biomass produced and sedimented within the same year and the methane stored under anoxic conditions in the hypolimnion of lakes.

4.5. Methane Emission

Lake productivity has regulated methane production rates and also the amount of methane stored in the anoxic layer in the hypolimnion, but does larger storage also lead to a larger methane release to the atmosphere? Methane oxidation during the overturn reduces the potential diffusive methane emissions (Encinas Fernández et al., 2014; Schubert et al., 2012). Comparing the diffusive methane emissions during the autumn overturn of three different years (2013, 2017, and 2018), we could show that the fraction of the stored methane emitted to the atmosphere and the oxidation of methane during overturn indeed differed strongly between years (Table 1). The total mass of methane that was emitted during overturn is therefore dependent not only on the methane storage but also on the methane oxidation (see Table 1: fraction emitted). For instance, despite lower methane storage in 2017 compared

to 2013, the mass of methane released during the autumn overturn was higher in 2017 than in 2013, because more methane was oxidized in 2013. However, comparing the year 2018 with 2013 and 2017, we obtained with a double amount of stored methane in 2018 compared to 2013 and 2017, also a methane release during the overturn that was more than twice and 3 times as high as in 2013 and 2017, respectively. The fraction of stored methane that is emitted to the atmosphere seemed to correlate positively with the mean gas exchange velocity during the autumn overturn, which is in accordance with the study of Vachon et al. (2019).

The total diffusive methane emissions of 2013 from May to December (178 mmol m^{-2}) and 2018 from April to December (441 mmol m^{-2}) are comparable with other temperate lakes. Total methane emission estimates for north temperate lakes show an interquartile range of $23\text{--}447 \text{ mmol m}^{-2} \text{ year}^{-1}$ (median $100 \text{ mmol m}^{-2} \text{ year}^{-1}$) and for south temperate lakes of $631\text{--}6,761 \text{ mmol m}^{-2} \text{ year}^{-1}$ (median $1,259 \text{ mmol m}^{-2} \text{ year}^{-1}$; Sanches et al., 2019). The diffusive methane emissions during autumn overturn in Illmensee (72 , 120 , and 267 mmol m^{-2} in 2013, 2017, and 2018, respectively) are rather in the lower range compared with other lakes such as lake Mindelsee (529 mmol m^{-2}), Rotsee (337 mmol m^{-2}), or Soppensee (77 and $1,016 \text{ mmol m}^{-2}$ in 2016 and 2017; Encinas Fernández et al., 2014; Schubert et al., 2012; Vachon et al., 2019). These results indicate how important multiple annual measurements are to estimate methane storage and emission from lakes.

5. Conclusion

Our study provides evidence that within a lake methane storage and emission during autumn overturn can be highly variable between the years. Degradation of sedimented autochthonous organic matter not only results in anoxic deep water but also enhances methane fluxes from the sediments within the same year. Production of biomass that settles to the sediment, therefore, affects methane storage in two ways: (a) it influences the duration and extent of anoxic conditions in the deep water and thus the duration of methane accumulation and the area of the sediment surface at which methane fluxes from sediments are not oxidized. (b) It leads to an increase in methane production and therefore in the source of methane in anoxic waters and thus in methane storage within the same year. Interannual variability in methane storage is therefore strongly linked to interannual variability in autochthonous primary production of biomass.

The release of the methane stored in anoxic waters during autumn overturn can constitute a major contribution in the annual methane release from lakes with anoxic deep waters (Encinas Fernández et al., 2014), whereby the fraction of stored methane released to the atmosphere depends on gas transfer velocity.

Because lake productivity affects hypolimnetic oxygen depletion and methanogenesis and both processes affect methane storage, eutrophication can be expected to substantially enhance methane storage by leading to an increase in the methane stored in lakes that already have anoxic deep water and by increasing the number of lakes that have anoxic waters in which methane is stored. Hence, eutrophication and climate warming are expected to enhance methane emissions from lakes and thus increase their contribution to global methane emissions.

Data Availability Statement

Wind, chemical, and phytoplankton data are available upon request from the Institute of Lake Research (ISF, Landesanstalt für Umwelt Baden-Württemberg LUBW). All other data for this research are available from the Zenodo repository as soon as the manuscript is accepted (<https://doi.org/10.5281/zenodo.4626810>).

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