2023-08

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Peacock, M

10.1029/2023jg007668
Journal of Geophysical Research: Biogeosciences
American Geophysical Union (AGU)

JGR Biogeosciences

DATA ARTICLE
10.1029/2023JG007668

Spatial and Seasonal Variations in Dissolved Methane Across a Large Lake

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Key Points:

- Lakes are globally important sources of atmospheric methane but there is a lack of data from large lakes >500 km^2
- We measured methane concentrations across a large (1,074 km^2) Swedish lake on five occasions over an annual period
- Methane varied seasonally and spatially, and higher concentrations were associated with nutrient inputs, lower dissolved oxygen, and shallower waters

Supporting Information:

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

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Citation:

Peacock, M., Davidson, S. J., Kothawala, D. N., Segersten, J., & Futter, M. N. (2023). Spatial and seasonal variations in dissolved methane across a large lake. *Journal of Geophysical Research: Biogeosciences*, *128*, e2023JG007668. https://doi.org/10.1029/2023JG007668

Received 29 JUN 2023
Accepted 4 AUG 2023

Abstract Lakes process large volumes of organic carbon (OC), are important sources of methane (CH_4), and contribute to climatic warming. However, there is a lack of data from large lakes >500 km^2, which creates uncertainty in global budgets. In this data article, we present dissolved CH_4, OC bioreactivity measurements, water chemistry, and algal biovolumes at 11 stations across Lake Mälaren, the third largest (1,074 km^2) Swedish lake. Total phosphorus concentrations show that during the study period the lake was classed as mesotrophic/eutrophic. Overall mean CH_4 concentration from all stations, sampled five times to cover seasonal variation, was 2.51 μg l^{-1} (0.98–5.39 μg l^{-1}). There was no significant seasonal variation although ranges were greatest during summer. Concentrations of CH_4 were greatest in shallow waters close to anthropogenic nutrient sources, whilst deeper, central basins had lower concentrations. Methane correlated positively with measures of lake productivity (chlorophyll *a*, total phosphorus), and negatively to water depth and oxygen concentration, with oxygen emerging as the sole significant driver in a linear mixed effects model. We collated data from other lakes >500 km^2 ($n = 21$) and found a significant negative relationship between surface area and average CH_4 concentration. Large lakes remain an understudied contributor to the global CH_4 cycle and future research efforts should aim to quantify the spatial and temporal variation in their diffusive and ebullitive emissions, and associated drivers.

Plain Language Summary Lakes contribute to climatic warming, because they emit large amounts of the powerful greenhouse gas methane into the atmosphere. This occurs because lake bottom sediments and lake waters are home to microbes that produce methane, which then travels diffusively in a dissolved form, or as bubbles, through the lake water and into the air. There is large uncertainty about how much methane is released by lakes on a global scale, and more measurements are required to reduce this uncertainty, particularly from very large lakes. In our study, we measured dissolved methane from 11 sampling locations across a very large Swedish lake, and repeated this five times over a year. Levels of methane within the lake were generally low, but they varied over space and time. Higher methane levels occurred in shallower waters near large towns and cities, and were associated with greater concentrations of nutrients such as phosphorus, which act as food for the methane-producing microbes.

1. Introduction

Lakes emit globally relevant volumes of the potent greenhouse gas (GHG) methane (CH_4) (Saunois et al., 2020) and therefore contribute to climatic warming. Total lake emissions have been estimated as ~100 Tg CH_4 yr^{-1} (Bastviken et al., 2011) although there is considerable uncertainty in this figure, with recent estimates ranging 40–150 Tg CH_4 yr^{-1} (Johnson et al., 2022; Lauerwald et al., 2023b; Rosentreter et al., 2021; Zheng et al., 2022). Synthesis studies show that small lakes have the largest emissions on an areal basis (i.e., per m^2 of lake surface), and the largest cumulative emissions (i.e., when all lakes are summed) (Holgerson & Raymond, 2016; Rosentreter et al., 2021). However, the majority of lake CH_4 research has focused on small lakes (<1 km^2) and emissions from lakes >100 km^2 remain understudied (Deemer & Holgerson, 2021; Lauerwald et al., 2023a).

Emissions of CH_4 from lakes are generally positively correlated with measures of lake productivity such as nutrient (often phosphorus—P) and chlorophyll *a* concentrations (Bastviken et al., 2004; DelSontro et al., 2018), and temperature (Yvon-Durocher et al., 2014), because these increase the activity of CH_4-producing methanogens (Segers, 1998). Thus, synergistic effects of climatic warming and eutrophication could further enhance lake CH_4

Table 1
Mean and Ranges in Surface CH_4 Concentrations for Other Large Lakes (>500 km^2), Ordered by Surface Area

Lake	Country	Lake area (km^2)	Average CH_4 ($\mu g\ l^{-1}$)	CH_4 range ($\mu g\ l^{-1}$)	Reference
Biwa	Japan	674	1.02	0.66–1.36	Miyajima et al. (1997)
Tumba	the DRC	694	1.06	*not given*	Borges et al. (2022)
St-Jean	Canada	1,065	0.14	0.08–0.19	DelSontro et al. (2018)
Mälaren	Sweden	1,074	2.51	0.98–5.39	This study
Champlain	Canada & US	1,269	1.42	1.01–2.34	DelSontro et al. (2018)
Vättern	Sweden	1,912	1.99	0.55–3.67	Pajala et al. unpublished
Mai Ndombe	the DRC	1,955	4.00	*not given*	Borges et al. (2022)
Edward	Uganda & the DRC	2,253	2.32	*not given*	Borges et al. (2022)
Taihu	China	2,338	2.47	0.22–7.68	Li et al. (2018)
Kivu	Rwanda & the DRC	2,371	0.99	*not given*	Borges et al. (2022)
Poyang	China	3,500	2.60	0.67–6.35	Wang et al. (2021)
Albert	Uganda & the DRC	5,402	1.17	*not given*	Borges et al. (2022)
Onega	Russia (European)	9,700	20.70	1.64–80.3	Gar'kusha and Fedorov (2015)
Ontario	Canada & US	19,009	0.51	0.22–0.69	DelSontro et al. (2018)
Winnipeg	Canada	23,750	0.67	0.08–11.7	Mandryk et al. (2021)
Erie	Canada & US	25,700	1.20	0.23–12.5	Fernandez et al. (2020)
Baikal	Russia (Asian)	31,722	0.08	0.01–66.4	Schmid et al. (2007)
Tanganyika	Tanzania, the DRC, Burundi, Zambia	32,821	0.30	*not given*	Borges et al. (2022)
Michigan	US	58,030	0.27	0.05–1.70	Joung et al. (2019)
Victoria	Kenya, Uganda, Tanzania	67,075	0.86	*not given*	Borges et al. (2022)
Superior	Canada & US	82,000	0.07	0.05–0.31	Joung et al. (2019)

Note. Average is mean, unless otherwise stated. Note that samples in Gar'kusha and Fedorov (2015) were collected from the shore only, most of which is under urban/industrial land cover. Overall mean = 2.2 $\mu g\ l^{-1}$, or 1.3 $\mu g\ l^{-1}$ if the unusually high values from Gar'kusha and Fedorov (2015) are excluded. Spearman correlation shows a significant negative relationship between lake area and CH_4 concentration (rho = −0.46, $p = 0.037$).

emissions (Davidson et al., 2018) and create positive feedbacks to climate (Meerhoff et al., 2022). However, rising nutrient concentrations are not a certainty; many lakes, including some very large lakes, show declining P levels (Fink et al., 2018; Tong et al., 2017). Thus, there is a need to assess CH_4 dynamics in large lakes in order to reduce the uncertainty in global CH_4 budgets and provide baseline data for evaluating and tracking future changes.

Studies of CH_4 in large lakes (defined as having a surface area >500 km^2, Herdendorf, 1982) have taken place in North America (Fernandez et al., 2020; Joung et al., 2019; Mandryk et al., 2021), Asia (L. Li et al., 2018; Liu et al., 2017; Miyajima et al., 1997; Schmid et al., 2007) and Africa (Borges et al., 2022; Roland et al., 2018) (Table 1). Studies in large European lakes are severely lacking and have often been process-focused; Sollberger et al. (2014) investigated benthic CH_4 dynamics in Lake Geneva whilst Hofmann et al. (2010) examined wave effects on littoral sediments and CH_4 release in Lake Constance. Gar'kusha and Fedorov (2015) measured shoreline CH_4 concentrations in one basin of Lake Onega in Russia (Gar'kusha & Fedorov, 2015) but shoreline measurements will likely overestimate CH_4 concentrations due to the proximity of anthropogenic nutrient point sources. Well-designed, temporally replicated, full lake surveys are needed to generate robust estimates of "what the atmosphere sees" (sensu Prairie et al., 2018).

Here, we measured dissolved CH_4 concentrations across 11 basins of a very large Swedish lake, with sampling repeated five times during different months to cover seasonal variation. Our study took place in conjunction with an established monitoring program, which provided a wealth of nutrient and algal data to place our measurements into context. We made additional laboratory measurements of dissolved organic carbon (OC) bioreactivity which, like CH_4, is an understudied component of large lakes (Minor & Oyler, 2021). Our data set is likely to be a valuable resource for those researching biogeochemistry and phytoplankton in large lakes, and should provide guidance for those designing and planning GHG measurement campaigns in such waterbodies.

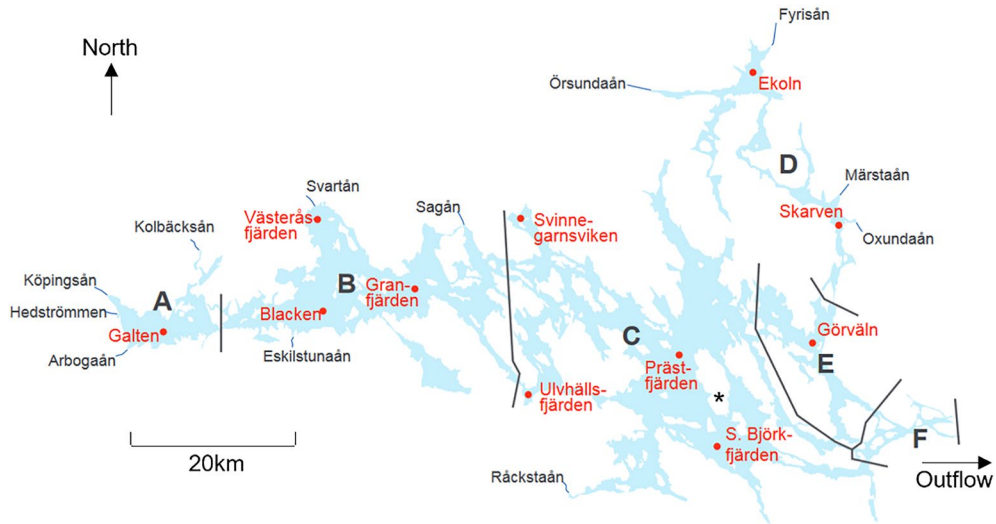

Figure 1. Map of Lake Mälaren, showing sampling points (red circles), lake basins (letters a–f, and demarcated by black lines), main rivers draining into Mälaren (blue lines, with river names in black), and location of the weather station (*). Map is adapted from Sonesten et al. (2013).

2. Materials and Methods

2.1. Study Site

We collected samples from 11 locations across Mälaren (Figure 1) (59°24′N 17°24′E), on five separate occasions to cover seasonal variation: May, July, August and September 2019, and February 2020. Mälaren is the third largest Swedish lake and has a surface area of 1,074 km^2, a volume of 14 km^3, retention time of 2.8 years and mean and maximum depths of 12.8 and 66 m (SMHI, 2022a). Mälaren is dimictic (Johansson et al., 2010) and has a unique hydrogeomorphology and includes several interconnected basins with their own water residence times (Table 2). The shallowest waters are in the western basins (A and B) where several medium/large watercourses enter the lake, and the outlet is in the south-east at the capital city of Stockholm. Mälaren is in the hemiboreal vegetation zone (Sjors, 1999), and has a catchment of 22,620 km^2 which is predominantly forest (58%) agricultural land (19%), and lakes and watercourses (11%) (SMHI, 2022b). Urban land in the catchment is 3% and there are numerous cities and towns on, or within several kilometers of the lake shore. The climate is humid continental with a mean annual temperature (1st March 2019–29th February 2020) of 8.7°C, and total precipitation of 499 mm, both higher than long-term (1996–2021) means of 7.3°C and 468 mm (SMHI, 2022c). Winter temperatures are typically sub-zero, and the lake is usually ice covered for 1–5 months (SMHI, 2022d). The winter period (1st December 2019–29th February 2020) during our study was mild; mean daily temperatures were sub-zero on only 14 days, with the result that no long-term ice formed.

Table 2
Areas, Volumes, Depths and Residence Times of the Individual Six Lake Basins

Basin	Area (km^2)	Volume (km^3)	Mean depth (m)	Max depth (m)	Residence time (years)
A	61	0.21	3.4	19	0.07
B	306	2.57	8.4	35	0.6
C	512	8.57	16.9	60	1.8
D	94	1.08	11.5	50	1.2
E	96	1.32	14	63	0.5
F	26	0.28	10.4	35	0.05

Note. Data from Sonesten et al. (2013). Note that no samples were collected from Basin F.

2.2. Sampling and Analysis

Samples for analysis of dissolved CH_4 concentration were made using the headspace technique, with one sample being collected at each location on each sampling occasion: 30 ml of surface water was taken in a 60 ml syringe directly from the lake, and then 30 ml of ambient air was also taken into the syringe. The syringe was then shaken for 1 min, which has been shown to be sufficient for efficient headspace CH_4 equilibrium (Roberts & Shiller, 2015). Whilst in the field, a sample of headspace gas was then injected into a pre-evacuated 12 ml glass Exetainer vial and returned to the lab, where CH_4 concentrations were measured using a Picarro GasScouter G4301 fitted with a sampling loop (Wilkinson et al., 2018). It has been suggested that some Exetainers may contain residual air that may introduce uncertainty into GHG

measurements (Sturm et al., 2015)—we made no adjustment for this possibility, but note that potential errors would be relatively low at the CH_4 concentrations in Lake Mälaren. Measurements of CH_4 in ppm were converted to dissolved concentrations using the solubility function of Wiesenburg and Guinasso (1979) and accounting for lake temperature and atmospheric pressure at the time of sampling, water:air volume in the syringe, and ambient air concentration (measured as 1.86 ppm by taking a sample of ambient air for analysis in an Exetainer). Atmospheric pressure data were taken from a weather station (SMHI, 2022c, see Figure 1). Flux measurements using floating chambers connected to the GasScouter may have been a preferable approach by allowing us to directly measure CH_4 emissions, but sampling logistics meant that we were limited to the quicker, simpler headspace sampling. Note that no analytical replicates of dissolved CH_4 concentration were taken; that is, only one Exetainer sample was taken for analysis at each sampling station on each occasion. Therefore, there is the possibility for some bias to enter our results due to sampling or analytical error.

Our CH_4 measurements took place within the framework of the research collaboration between the Swedish University of Agricultural Science (SLU) and Lake Mälaren's water conservation association (Mälarens vattenvårdsförbund) (Drakare et al., 2021). At each site, measurements of water temperature, Secchi depth and dissolved oxygen (O_2) were made in situ, and samples were taken for water chemistry analysis at SLU's SWEDAC-accredited Geochemical Laboratory for a wide variety of determinands: pH, alkalinity, electrical conductivity, turbidity, chlorophyll *a*, total organic carbon (TOC), total phosphorus (TP), total nitrogen, nitrite + nitrate, calcium, chloride, fluoride, potassium, magnesium, sodium, ammonium, silicon, sulfate, and filtered and unfiltered absorbance at 420 nm. All methods and any known issues are well-documented and are available online (SLU, 2022). During August and February additional sampling takes place at each station at depths throughout the water column to the lake bed; note that we refer to these measurements to put our results into context (see Drakare et al., 2021 for more detail). Within the same project framework, samples were collected for detailed measurements of phytoplankton at five stations (Ekoln, S. Björkfjärden, Granfjärden, Galten and Görväln) during May, July and September, and six stations during August (the aforementioned five stations, plus Blacken) (Drakare et al., 2021). We downloaded all water chemistry and phytoplankton data, which is freely available, for May, July, August and September 2019, and February 2020 (Miljödata-MVM, 2022a). For phytoplankton, we summed the biovolume of taxa within each of the following groups: Bacillariophyta, Charophyta, Chlorophyta, Choanoflagellidea, Chrysophyceae, Cryptophyta, Cyanobacteria, Dinophyceae, Euglenophyceae, Haptophyta, Raphidophyceae, Synurophyceae, and "other phytoplankton".

2.3. TOC Degradation Experiments

To investigate variations in TOC lability, we conducted laboratory incubation experiments. On each sampling occasion and at each station, a 500 ml sample of surface water was collected in a pre-rinsed 500 ml Nalgene bottle. Once returned to the lab, aliquots of each sample were measured for absorbance at 254 nm using a 1 cm path length cuvette and an Avantes AvaLight DH-S-BAL light source. Specific ultraviolet absorbance (SUVA), which provides information on the aromaticity of OC, was then calculated by normalizing absorbance at 254 nm by TOC concentration. Aliquots of all samples were then immediately transferred to 40 ml glass vials and placed in a WTW 1008-i thermostat cabinet at 20°C in the dark for 6 days. After this, samples were sent to the SLU Geochemical Laboratory for TOC analysis. Any changes in TOC concentration during incubations were therefore due to microbial activity (or physical processes such as flocculation) and represent short-term bioreactive OC (Soares et al., 2019).

2.4. Statistical Analysis

Trophic state was calculated for each station using mean annual TP concentrations: oligotrophic (TP < 12 μg l^{-1}), mesotrophic (TP 12–24 μg l^{-1}) and eutrophic (TP > 24 μg l^{-1}) (IPCC, 2019). We calculated molar stoichiometric ratios for macronutrients: TOC:TP, TOC:TN, and TN:TP. Statistical analyses were first conducted in SPSS Statistics 26. Shapiro-Wilk tests showed that the total data set ($n = 55$) of CH_4 measurements was non-normally distributed. Log10 transformations were used to normalize the data, before ANOVAs (with Tukey's HSD post-hoc tests) were used to test for differences in dissolved CH_4 concentration between sampling stations and sampling months. We used Spearman correlations, incorporating all data points, to test for relationships between dissolved CH_4, OC bioreactivity, all water chemistry determinands, and algal biovolume. We then used a linear mixed effects (LME) model (R version 3.6.1 (R Core Team, 2013) with the nlme package (Pinheiro et al., 2018)), including all varia-

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10.1029/2023JG007668

Table 3

Sampling Station Locations, Plus Means and SEMs for CH_4 Concentration and Selected Water Quality Determinands, for All Five Sampling Months

Station	Location (lat, long)	Water depth (m)	CH_4 (µg l^{-1})	Chlorophyll (µg l^{-1})	$NH_4 - N$ (µg l^{-1})	$NO_2 + NO_3 - N$ (µg l^{-1})	pH	PO4-P (µg l^{-1})	Secchi depth (m)	O_2 (mg l^{-1})	TOC (mg l^{-1})	Tot-N (µg l^{-1})	Tot-P (µg l^{-1})	Turbidity (FNU)	EC (µS cm^{-1})	SUVA (l mg C^{-1} m^{-1})	TOC loss (mg l^{-1})
Galten	59.446142, 16.187665	11	2.47 ± 0.59	16.4 ± 2.8	12.8 ± 4	148 ± 82	7.36 ± 0.07	6.8 ± 3.7	0.83 ± 0.12	11.18 ± 0.69	10.7 ± 1.1	644 ± 106	46.9 ± 7.4	20.2 ± 6.2	142 ± 3	3.06 ± 0.4	0.7 ± 0.4
Västeråsfjärden	59.592772, 16.552613	10	4.43 ± 0.32	13 ± 3.5	23.2 ± 5	379 ± 125	7.57 ± 0.1	7.2 ± 4.3	1.11 ± 0.18	11.52 ± 0.79	10 ± 1	865 ± 150	41.3 ± 7.5	12.9 ± 3.8	386 ± 5	2.92 ± 0.4	0.42 ± 0.3
Blacken	59.473605, 16.544335	30	2.45 ± 0.24	9 ± 1.8	13.8 ± 3.2	378 ± 67	7.52 ± 0.05	5.8 ± 3.1	1.41 ± 0.21	11.44 ± 0.85	9.5 ± 0.7	810 ± 80	31.4 ± 4.8	9.9 ± 3	109 ± 6	2.59 ± 0.6	0.36 ± 0.3
Granfjärden	59.494454, 16.810836	36	2.28 ± 0.38	7.2 ± 1.4	17.8 ± 6.3	286 ± 74	7.64 ± 0.09	6.4 ± 3.8	1.61 ± 0.21	11.47 ± 0.9	8.9 ± 0.6	701 ± 79	30.8 ± 6.1	8.8 ± 3.2	231 ± 4	2.88 ± 0.4	0.2 ± 0.3
Svinnegarnsviken	59.581140, 17.045103	10	3.33 ± 0.39	9.5 ± 2.4	15.4 ± 3.6	227 ± 131	7.74 ± 0.13	6.8 ± 5	1.31 ± 0.19	11.46 ± 0.42	8.4 ± 0.4	655 ± 127	29 ± 6.1	8.2 ± 3.1	152 ± 3	3.15 ± 0.6	0.34 ± 0.2
Ulvhällsfjärden	59.367831, 17.055091	9	3.05 ± 0.41	12.8 ± 3	34.6 ± 11.6	148 ± 85	7.64 ± 0.04	4.4 ± 3.5	1.51 ± 0.17	11.46 ± 0.76	8.7 ± 0.4	632 ± 77	32.4 ± 3.1	7.3 ± 1.8	174 ± 1	2.6 ± 0.2	0.48 ± 0.3
Prästfjärden	59.426957, 17.426581	50	1.29 ± 0.1	5.1 ± 1.1	8.2 ± 1.4	60 ± 37	8.02 ± 0.17	4.6 ± 3.5	3.36 ± 0.12	12.02 ± 0.86	7.4 ± 0.1	436 ± 25	16.8 ± 2.6	1.8 ± 0.5	396 ± 1	2.72 ± 0.5	0.26 ± 0.2
Södra Björkfjärden	59.290190, 17.519937	44	1.43 ± 0.13	4.2 ± 0.8	14.2 ± 4.4	49 ± 32	8.02 ± 0.14	4.2 ± 3.5	3.5 ± 0.24	12.03 ± 0.96	7.3 ± 0.1	424 ± 23	15.6 ± 2.6	1.6 ± 0.3	173 ± 1	2.94 ± 0.2	0.18 ± 0.2
Ekoln	59.751114, 17.608240	30	2.38 ± 0.36	13.2 ± 3.9	11.2 ± 3	1,116 ± 145	8.04 ± 0.08	8.4 ± 5.9	1.99 ± 0.37	11.52 ± 0.8	13.3 ± 0.8	1744 ± 165	33.9 ± 7.5	5.5 ± 2.8	178 ± 4	2.61 ± 0.1	0.68 ± 0.1
Skarven	59.553666, 17.807456	30	2.42 ± 0.31	10.3 ± 2.1	13.2 ± 2.9	551 ± 178	8.17 ± 0.11	6 ± 5.4	2.38 ± 0.35	11.7 ± 1.06	11.7 ± 0.4	1132 ± 153	27.3 ± 4.5	3.1 ± 1.2	158 ± 2	2.82 ± 0.3	0.4 ± 0.3
Görväln	59.419460, 17.739984	48	2.1 ± 0.16	7.8 ± 2.3	7.2 ± 0.9	59 ± 47	8.13 ± 0.13	3.2 ± 2.9	2.92 ± 0.18	12.17 ± 0.86	8.2 ± 0.1	493 ± 38	17.4 ± 2.4	1.6 ± 0.4	152 ± 3	3.0 ± 0.7	0.44 ± 0.4

Note. Stations are ordered approximately west to east across the lake (i.e., the direction of water flow).

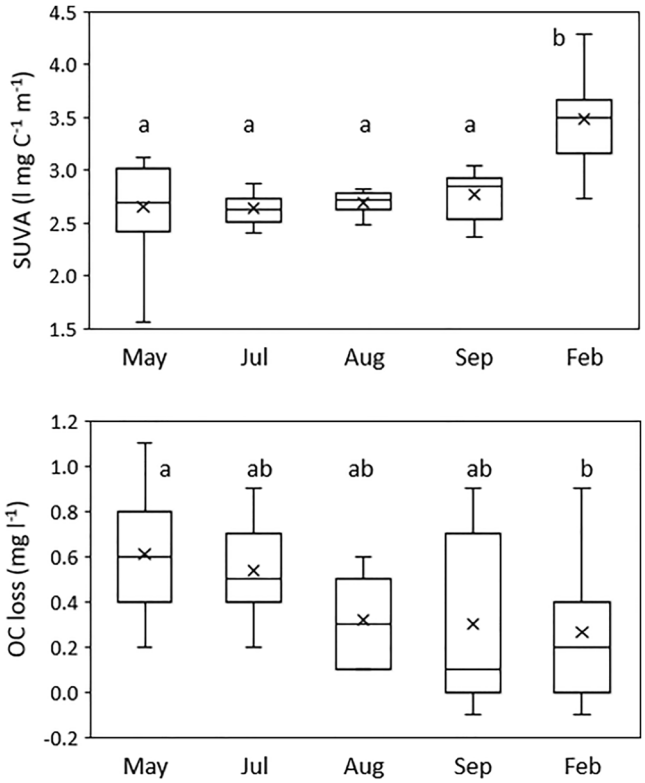

Figure 2. Box plots of Specific ultraviolet absorbance (SUVA) and short-term bioreactive organic carbon (OC) for all five sampling months for each sampling station. Boxes represent medians and interquartile range (IQR), whiskers mark minimum and maximum values. Also shown are mean concentrations (x). There are no outliers. ANOVA shows significant differences for SUVA ($F = 14.0$, $p < 0.001$) and bioreactive OC ($F = 3.75$, $p = 0.01$) between months; months with shared letters indicate no significant differences.

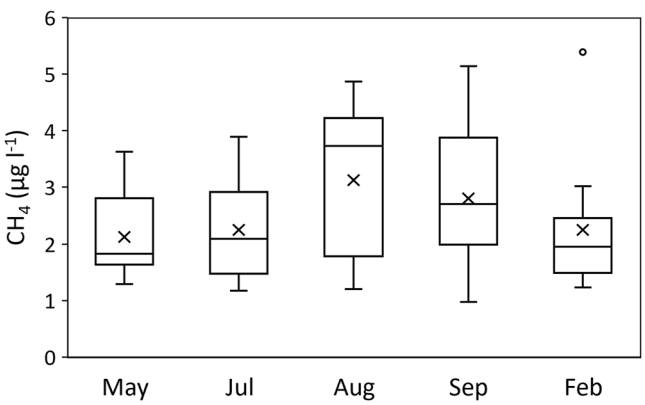

Figure 3. Box plot of CH_4 concentrations from all 11 sampling stations for each sampling month. Boxes represent medians and interquartile range (IQR), whiskers mark minimum and maximum values, excluding outliers (calculated as box limits $\pm 1.5 \times$ IQR). Also shown are means (x) and outliers (o). ANOVA shows no significant difference between months.

bles that were significantly correlated with CH_4 in the Spearman correlations (with the exception of water depth as this was considered unchanging at each station throughout the study, and phytoplankton which wasn't measured at all stations and dates). Site was included as a random effect. We calculated the amount of variance described by the model as $R2_{GLMM}$ (Nakagawa & Schielzeth, 2013), using the package MuMIn (Bartoń, 2019). Results for all tests were considered significant if $p < 0.05$, and nominal p values are presented throughout. Errors are given as standard error of the means.

3. Results and Discussion

3.1. Lake Biogeochemistry and OC Bioreactivity

Measured TP concentrations showed that the lake's trophic state was mesotrophic/eutrophic: the stations Görväln, Prästfjärden and S. Björkfjärden were mesotrophic, whilst all other stations were eutrophic (Table 3). For all 11 stations and months there was a clear seasonality to surface water temperature through May, July, August, September 2019, and February 2020, with respective means of 14.2, 17.7, 20.0, 14.8, and 2.3°C. For all stations and seasons, mean SUVA was 2.85 (range 1.56–4.28) l mg C^{-1} m^{-1}, suggesting a low/medium degree of OC aromaticity (Weishaar et al., 2003). SUVA values from the Laurentian Great Lakes are ~1.2 l mg C^{-1} m^{-1} (Zhou et al., 2016). These lakes are an order of magnitude larger than Mälaren, and thus the higher SUVA values we report likely indicate greater terrestrial OC inputs. Bioreactivity experiments showed that over 6 days the mean change in OC was 0.4 (range −0.1–1.1) mg l^{-1}. There is a lack of comparable data (Minor & Oyler, 2021), but others have found that OC in large lakes can be bioavailable over short time periods (Laird & Scavia, 1990). Our OC losses are greater than those reported for Swedish rivers by Soares et al. (2019) who also measured over 6 days, with a mean loss of 0.17 mg l^{-1}. The difference may be due to trophic state; their sites had lower TP concentrations and were predominantly mesotrophic, and they found that greater nutrient inputs stimulated primary production and therefore increased short-term OC losses. Our results agree with this interpretation; a significant correlation was found between OC bioreactivity and chlorophyll a (rho = 0.37, $p = 0.005$, Figure S1 in Supporting Information S1). For seasonal variation SUVA was significantly ($F = 14.0$, $p < 0.001$) higher during February (mean 3.48 l mg C^{-1} m^{-1}) than all other months (mean = 2.7 l mg C^{-1} m^{-1}) (Figure 2). The only significant difference for OC loss was between February and May (respective means of 0.26 and 0.6 mg l^{-1}, $p = 0.03$). ANOVAs showed no significant differences in SUVA ($F = 0.93$, $p = 0.5$) or OC loss ($F = 2.0$, $p = 0.06$) between sites (Figure 2).

3.2. Spatial and Seasonal Variations in CH_4

Overall mean dissolved CH_4 for the study was 2.51 ± 0.15 µg l^{-1}, range 0.98–5.39 µg l^{-1}, which is similar to mean concentrations in other large lakes (overall mean = 1.41 µg l^{-1}, Table 1), including unpublished measurements from Vättern, Sweden's second largest lake (1,900 km^2 surface area, mean depth of 41 m) where 4 years of summer/autumn headspace measurements gave a mean of 1.99 µg l^{-1}, range 0.55–3.67 µg l^{-1} (Pajala et al., unpublished). No significant differences were found between the five sampling campaigns ($F = 1.35$, $p = 0.26$), although there was a clear seasonal pattern whereby means and ranges of CH_4 concentrations were greatest during the end of summer (August and September) (Figure 3), with a mean of

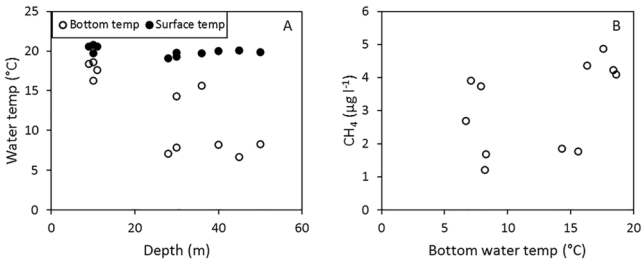

Figure 4. Panel (a) scatter plot showing water temperatures as a function of lake depth for the 11 sampling stations during August. Water temperatures are shown at the lake surface (filled circles) and in bottom waters (open circles). There is a significant correlation (rho = −0.7, $p = 0.016$) between depth and bottom water temperature. Panel (b) scatter plot of surface CH_4 concentration and bottom water temperature for the 11 sampling stations during August. The correlation is not significant (rho = 0.45, $p = 0.16$).

3.13 ± 0.38 µg l^{-1} for the whole lake in August when mean water temperature peaked. The lack of seasonality could be due to deep waters remaining thermally stratified, with the result that lake sediments are buffered from air temperature variations, and so deep-water sediments remain cold year-round, with no summer increase in methanogenesis rates. Monitoring data supports this (Figure 4a) and shows a clear disconnect between surface water and bottom water temperatures at the deep water stations; during our August sampling, surface water temperature at the station with deepest water (Prästfjärden) was 19.9°C, whilst at 50 m depth the temperature was 8.3°C. At the shallowest station (Ulvhällsfjärden) during August surface water was 20.6°C and the deepest waters (9 m) were 18.4°C. Thus, at the stations with shallow waters the sediments will be warmer during summer, favoring seasonal increases in CH_4 production and we note that others have shown that bottom water temperatures in very large lakes do relate to surface CH_4 emissions (Fernandez et al., 2020; Liu et al., 2017). However, although shallower, warmer stations tended toward higher summertime CH_4, there was not a significant correlation between bottom water temperature and CH_4 (Figure 4b) suggesting that other drivers are also involved.

Significant differences in CH_4 concentrations were found spatially between sampling stations (Figure 5, Table 3) with the highest mean concentrations in Västeråsfjärden (4.43 ± 0.32 µg l^{-1}), Svinnegarnsviken (3.33 ± 0.39 µg l^{-1}) and Ulvhällsfjärden (3.05 ± 0.41 µg l^{-1}). These three stations are all located in shallow bays or straits (depth ≤ 10 m) that are close to towns/cities with relatively large populations (respective populations of ~130,000, 30,000, and 15,000), and the waters are thus subject to anthropogenic nutrient inputs and particulate matter settling into the sediment. Although we did not track nutrient inputs into the lake, other research has shown high concentrations of organic micropollutants (including pharmaceuticals, industrial chemicals, pesticides, etc), particularly at sampling stations near to large towns and cities (Rehrl et al., 2020) demonstrating an anthropogenic influence on lake water quality. In contrast to this, lowest mean CH_4 concentrations were at stations in the center of the deep (44–50 m) basin C (Figure 5, Table 3, Prästfjärden, 1.29 ± 0.10 µg l^{-1}, and S. Björkfjärden, 1.43 ± 0.13 µg l^{-1}) where nutrient concentrations were also lower; total P and chlorophyll *a* concentrations were approximately half of their values at the three high-CH_4 stations (Table 3): overall means of 16.2 versus 34.2 µg l^{-1} total P, and 4.65 versus 11.8 µg l^{-1} for chlorophyll *a*.

Mean CH_4 was low during February 2020 (2.25 µg l^{-1} ± 0.34), and the variation in CH_4 across the whole lake was also smallest at this point. However, a clear outlier occurred at this time, with the shallow-water Västeråsfjärden

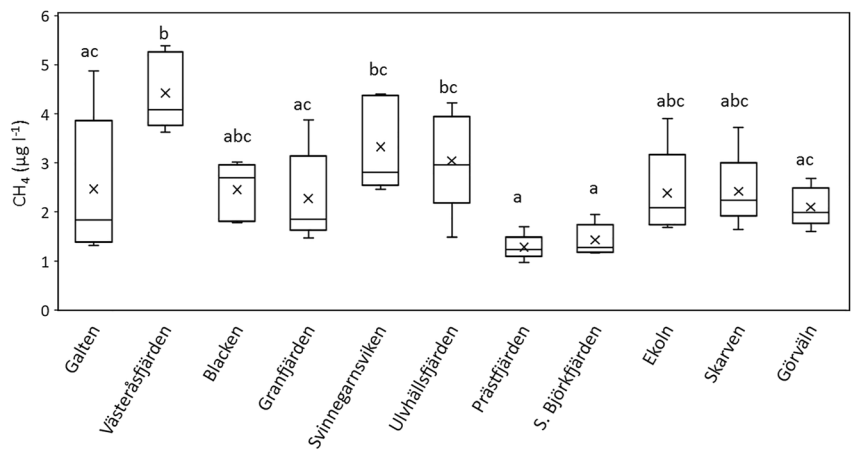

Figure 5. Box plot of CH_4 concentrations for all five sampling months for each sampling station. Stations are ordered approximately west to east across the lake (i.e., the direction of water flow). Boxes represent medians and interquartile range (IQR), whiskers mark minimum and maximum values. Also shown are mean concentrations (*x*). There are no outliers. ANOVA shows significant differences ($F = 6.07$, $p < 0.001$) between stations; stations with shared letters indicate no significant differences.

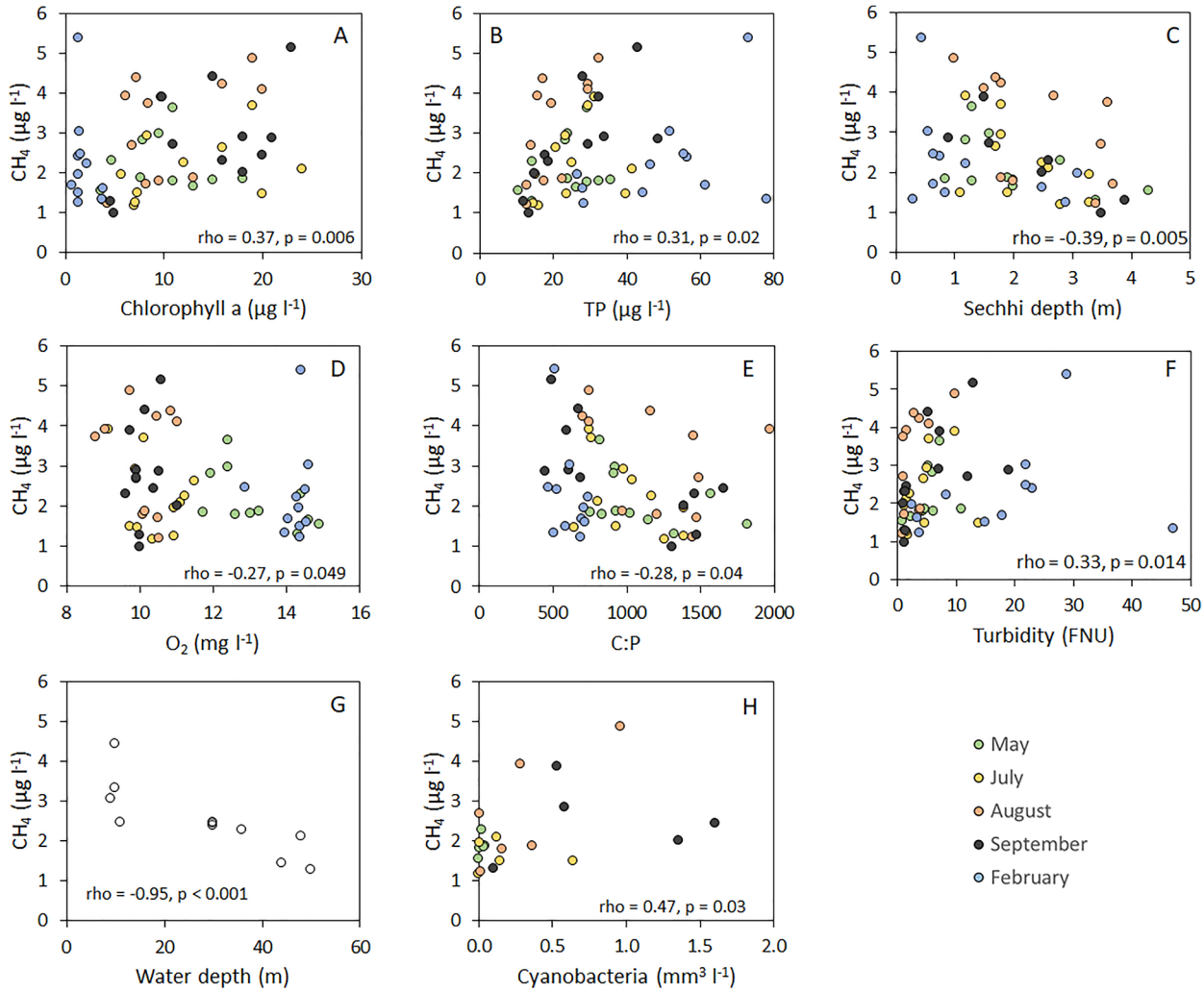

Figure 6. Scatter plots showing relationships between CH_4 concentrations and: chlorophyll *a* concentrations (a), total phosphorus concentration (b), Sechhi depth (c), oxygen concentration (d), the molar stoichiometric ratio of organic carbon to phosphorus (e), turbidity (f), water depth (g) and Cyanobacteria biovolume (h).

station having the highest CH_4 concentration measured during the entire study (5.39 µg l^{-1}) (Figure 3). This was despite cold temperatures (mean surface water 2.3°C) which would be expected to decrease CH_4 production rates (Fernandez et al., 2020; Liu et al., 2017). Without analytical replicates (see Section 2.2) we cannot fully eliminate the possibility that this value relates to analytical or sampling error. Assuming it is real, one possibility is that this anomaly could arise following several days of low wind speeds, whereby a decrease in piston velocity might lead to an increase in water column CH_4 concentrations—this hypothesis can be dismissed, because wind speeds during the study period were highest at the start of 2020, with monthly means of 4.2 m s^{-1} for January and February (SMHI, 2022c). Another, more plausible hypothesis involves rain: at the start of 2020, high volumes of precipitation fell on bare ground, which was free of snow and ice due to unusually mild winter temperatures. Within the Mälaren catchment, high flows are positively related to turbidity and TOC (Lannergård et al., 2021; LeDesma et al., 2012), and therefore this winter rain event led to elevated levels of both within some of the rivers entering the lake (Drakare et al., 2021). These increased terrestrial inputs are also evident in the significantly higher SUVA values during February (Figure 2). In turn, this led to unusually high increases in TP concentrations, because phosphorus transport within the catchment is largely driven by particle-associated P from agricultural clay soils (Lannergård et al., 2019), and the mobilization of these particles can be particularly high during winter when riparian vegetation is absent (Lannergård et al., 2021). Upon entering the lake, riverine particulates will settle out, thus delivering additional P to bottom sediments. TP and TOC were particularly high at Västeråsfjärden in February, reaching 73.1 µg l^{-1} and 14.6 mg l^{-1}, respectively 149% and 54% higher than overall means for those

measures. Assuming that these high water column P and C concentrations translate into elevated nutrient levels in sediments, then CH_4 production will be enhanced (Bastviken et al., 2004; Deemer & Holgerson, 2021) despite low temperatures (Juutinen et al., 2009), although additional samples or lab incubations would be necessary to confirm this suggestion. Intriguingly, another station (Galten) had even higher concentrations of TP and TOC during February (78 μg l^{-1} and 15.4 mg l^{-1}, respectively) but CH_4 remained low, at 1.32 μg l^{-1}. The difference between CH_4 responses to high nutrient loads at this time may be due to residence times; Västeråsfjärden's basin has a residence time of 0.6 years whilst Galten's is 0.07 years. Thus, the nutrient inputs to Galten could have been rapidly fluxed through the basin and on into deeper lake waters, with the result that no in situ sedimentary CH_4 hotspot developed.

3.3. Drivers of CH_4 Variation

There were no significant Spearman correlations between CH_4 and surface water temperature (rho = 0.2, $p = 0.15$) in line with statistical tests highlighting a lack of seasonality (Section 3.2). Observations that nutrient status and water depth were important drivers of CH_4 concentrations (Section 3.2) were supported by correlations which showed significant positive relationships between CH_4 and chlorophyll *a*, and CH_4 and TP, and negative relationships between CH_4 and station depth, O_2, turbidity, Secchi depth, and C:P (Figures 6a–6g). The LME model, developed using these significant Spearman correlations (with the exception of station depth which was assumed constant at each station), detected a significant relationship between O_2 and CH_4 ($F_{1,34} = 5.4$, $p = 0.026$) but no significant relationships between CH_4 and Chlorophyll *a* ($F_{1,34} = 1.5$, $p = 0.25$), Secchi depth ($F_{1,34} = 1.9$, $p = 0.18$), TP ($F_{1,34} = 0.03$, $p = 0.87$), turbidity ($F_{1,34} = 7.9$, $p = 0.38$) or C:P ($F_{1,34} = 0.98$, $p = 0.32$). The model explained 38% of the variance. The difference in significant variables between the Spearman correlations and LME model is likely due to confounded variables. Thus, some correlations should not be used to infer mechanistic relationships with CH_4; for example, there were strong relationships between Secchi depth and turbidity (rho = −0.95, $p < 0.001$), and between TP and turbidity (rho = 0.89, $p < 0.001$) (Figure S2 in Supporting Information S1). Thus, we assume that TP controls CH_4 dynamics (Bastviken et al., 2004; DelSontro et al., 2016) and, because much of this TP is associated with particles (Lannergård et al., 2019), Secchi depth and turbidity are also correlated. Greater TP concentrations will result in high-chlorophyll *a*, low-O_2, eutrophic conditions (DelSontro et al., 2018), with higher rates of methanogenesis in sediments (West et al., 2016). The negative correlation between CH_4 and C:P (Figure 6e) shows that more C relative to P leads to lower CH_4, and has been reported in reservoirs (Z. Li et al., 2020). This finding agrees with a growing body of work arguing that nutrient stoichiometry, and not just absolute concentration, is important in controlling aquatic biogeochemistry (Graeber et al., 2021; Peacock et al., 2022; Stutter et al., 2018; Taylor & Townsend, 2010), including GHG emissions (Peacock et al., 2017; Webb et al., 2021). Finally, a negative relationship between surface water CH_4 concentration and water depth (Figure 6g) is frequently reported (Deemer & Holgerson, 2021; Juutinen et al., 2009; Natchimuthu et al., 2016) and is likely due to a greater opportunity for methanotrophy within the water column of deeper lakes (M. Li et al., 2020), as well as colder sediments having lower rates of methane production (Schulz et al., 1997). However, we emphasize again that many of these correlations could be confounded, making interpretations difficult. For instance, mean annual TP and station depth were also strongly negatively correlated (rho = −0.71, $p = 0.014$, Figure S3 in Supporting Information S1). In part this is likely due to the fact that fluvial nutrient loads discharge into shallow basins (Section 3.2), but sediment P resuspension will also be greater in shallow waters (Reddy et al., 1996). Thus, it becomes somewhat unclear whether TP controls CH_4, or whether TP and CH_4 are both controlled by depth; the lack of a direct correlation between sediment temperature and CH_4 (Section 3.2) points perhaps to a combined role of depth (via methanotrophy in the water column) and TP. Our theorizing of how depth affects surface CH_4 concentrations rests on the assumption that CH_4 production is primarily occurring in sediments. However, there is the possibility that CH_4 production is also taking place within the oxygenated water column (Bogard et al., 2014; Grossart et al., 2011). Our data offer an intriguing hint that this may be occurring. For the subset of sites and months where algal data were available (for 13 algal groups), the only significant algal relationship with CH_4 was a positive correlation with Cyanobacteria biovolume (Figure 6h). Unlike CH_4 concentration, cyanobacteria biovolume showed a clear seasonal trend, increasing steadily during the 2019 growing season, and peaking at 0.84 ± 0.25 $mm^3\ l^{-1}$ in September, despite water temperatures being higher in August (Figure S4 in Supporting Information S1). Freshwater cyanobacteria can produce CH_4 (Bižić et al., 2020), and high abundances of cyanobacteria have been linked to elevated lake CH_4 concentrations previously (Fazi et al., 2021), so this is a viable mechanism to explain growing season variations in surface water

CH_4. However, Cyanobacteria biovolume also significantly correlated with chlorophyll *a* and TP (Figure S5 in Supporting Information S1), and it thus becomes difficult to decipher which variables are directly controlling CH_4 production, and which are correlated but not mechanistically related. If CH_4 is produced in surface waters (the importance of which is highly debated; Günthel et al., 2019; Peeters & Hofmann, 2021), rather than in sediments, then the apparent relationship with water depth (Figure 6g) could simply be due to shallow waters being closer to anthropogenic nutrient inputs (see Section 3.2).

3.4. Implications

Our measured CH_4 concentrations are in keeping with measurements from other large lakes, and we found a significant negative relationship between surface area of large lakes and average surface water CH_4 concentration (rho = −0.46, $p = 0.037$) (Table 1). This is in agreement with other studies that find inverse relationships between lake area and CH_4 emission (Holgerson & Raymond, 2016; Rosentreter et al., 2021). To generalize, these relationships might suggest that Lake Mälaren would be a minor source of diffusive CH_4 fluxes on a per area basis. However, it is important to consider that ebullition can be the dominant pathway for CH_4 release in some lakes (Bastviken et al., 2011; Sepulveda-Jauregui et al., 2015). In temperate lakes ebullition has mostly been observed to occur at depths <3–6 m (DelSontro et al., 2016; West et al., 2016). The far eastern basin in Mälaren has a mean depth of 3.4 m, and also has a relatively high nutrient concentration, and so ebullition may be large there. However, there is a lack of CH_4 ebullition measurements from very large lakes (Deemer & Holgerson, 2021) and so future studies of large lakes should prioritize this. Additionally, the spatiotemporal sampling design we used (11 stations sampled five times) could potentially underestimate CH_4 concentrations; recommendations based on data from three very small subarctic lakes are that diffusive emissions should be measured on at least 11 occasions, at three stations to minimize bias (Wik et al., 2016), although it is currently unknown how these findings might apply to large lakes such as Mälaren.

There is the chance that the synergistic effects of climate change and eutrophication could enhance GHG emissions from lakes (Meerhoff et al., 2022), and Mälaren is already showing signs of warming, with ice cover becoming less predictable in recent years (Knoll et al., 2019); indeed, our study year is unusual in being entirely ice-free. Ice-out CH_4 emissions can represent a sizable fraction of the annual budget (Jammet et al., 2015), but a shorter ice cover period can also lead to greater cumulative CH_4 emissions (Wik et al., 2014), and so the complete effect of rising temperatures on CH_4 dynamics in northern lakes is difficult to predict. As far as we are aware, our data represent the first published detailed surface water CH_4 measurements from any large lake within the European Union and thereby offer a snapshot through which to gauge future anthropogenic-induced changes in how large European lakes contribute to climatic warming.

Acknowledgments
We thank Stina Drakare for her help in arranging the sampling, and for answering our many questions about Mälaren. We thank Gustav Pajala and David Bastviken for kindly allowing us to include their unpublished Vättern data in Table 1, and Joachim Audet, Yves Prairie, Antti J. Rissanen, and Bridget Deemer for pointing us to some studies for inclusion in Table 1 that we otherwise would have missed. We thank Mona Abbasi and Jeff Hawkes for interesting discussions about dissolved organic matter within Mälaren during the course of the project. We thank two anonymous reviewers and Bridget Deemer for their constructive review comments that helped to improve the manuscript, as well as the Associate Editor and Marguerite Xenopoulos (Editor in Chief) for their useful comments. Finally, we gratefully acknowledge the hard work and dedication of all those who collected and analyzed samples, and implemented and maintained the Mälaren monitoring program. No specific funding supported this work.

Data Availability Statement

Methane data, and associated water chemistry and algal data, are available online as Peacock (2022), https://doi.org/10.6084/m9.figshare.20026397.v4. Additionally, all water chemistry and algae data are available online from the Swedish national monitoring program (Miljödata-MVM, 2022a) here: https://miljodata.slu.se/MVM/Search. Data from the 11 Mälaren sampling stations only can also be downloaded here (Miljödata-MVM, 2022b): https://www.slu.se/en/departments/aquatic-sciences-assessment/research/forskningsprojekt/malaren-in-focus/environmental-assessment/.

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