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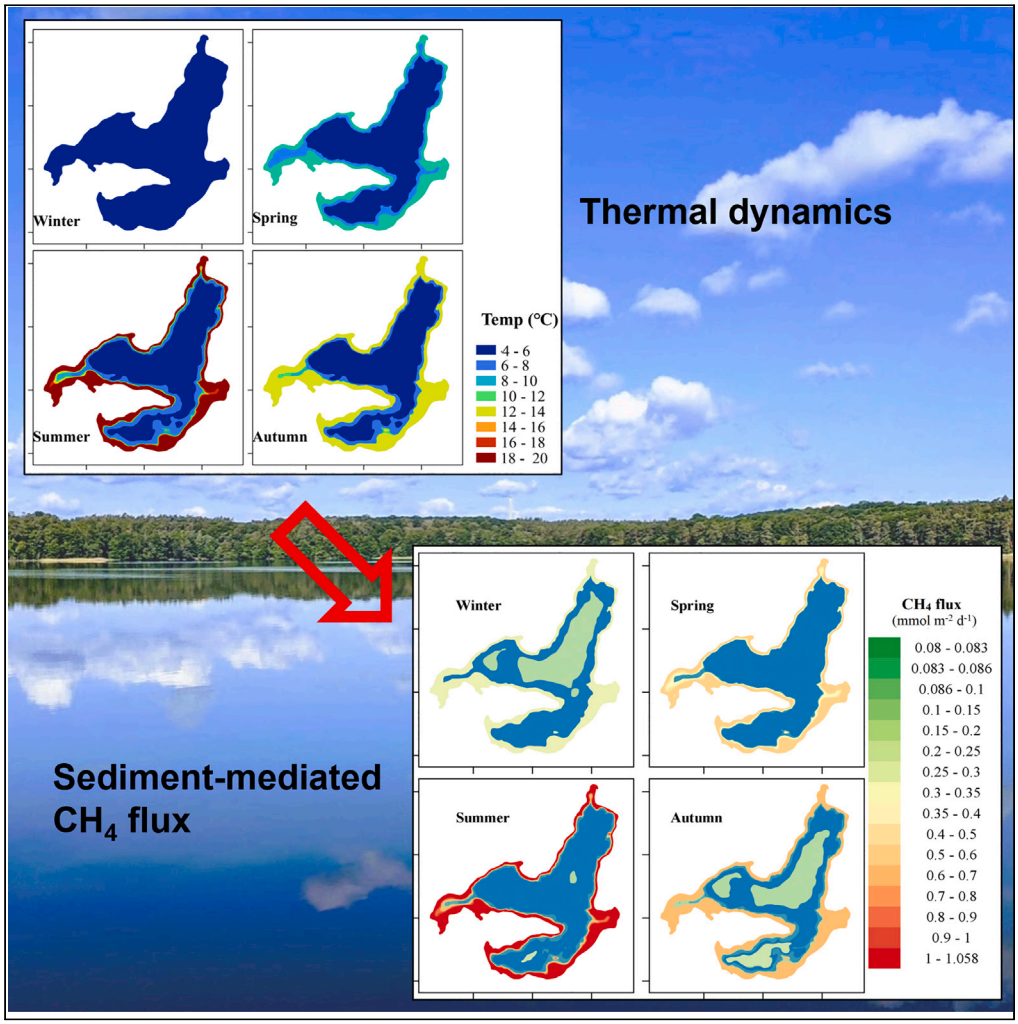

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Highlights

Disproportionally large contribution of CH_4 fluxes from lake littoral sediments

Thermal dynamics and OC quality drive the large spatial difference in CH_4 production

Sediment CH_4 production is more sensitive to warming than oxidation

Enhanced CH_4 emissions are projected due to warm climate and concomitant hypoxia

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Spatio-temporal variations of methane fluxes in sediments of a deep stratified temperate lake

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SUMMARY

Spatio-temporal variability of sediment-mediated methane (CH_4) production in freshwater lakes causes large uncertainties in predicting global lake CH_4 emissions under different climate change and eutrophication scenarios. We conducted extensive sediment incubation experiments to investigate CH_4 fluxes in Lake Stechlin, a deep, stratified temperate lake. Our results show contrasting spatial patterns in CH_4 fluxes between littoral and profundal sites. The littoral sediments, ~33% of the total sediment surface area, contributed ~86.9% of the annual CH_4 flux at the sediment-water interface. Together with sediment organic carbon quality, seasonal stratification is responsible for the striking spatial difference in sediment CH_4 production between littoral and profundal zones owing to more sensitive CH_4 production than oxidation to warming. While profundal sediments produce a relatively small amount of CH_4, its production increases markedly as anoxia spreads in late summer. Our measurements indicate that future lake CH_4 emissions will increase due to climate warming and concomitant hypoxia/anoxia.

INTRODUCTION

Freshwater lakes are significant emitters of methane (CH_4), a potent greenhouse gas.[1,2] CH_4 is primarily produced in anaerobic sediments, though CH_4 production has also been recently observed in oxic waters.[3,4] Driven by production, consumption, and transport processes, both the measured CH_4 in lake water and flux to the air can be highly variable across time and space.[5–7] Without careful consideration of spatio-temporal variability, short-term and point-based measurements result in large uncertainties.[8,9] This uncertainty hinders our ability to predict future lake CH_4 emissions in response to global climate warming, combined with increased eutrophication. How the sediment CH_4 flux varies with season and location and what drives its spatio-temporal variability must be well understood to develop a reliable CH_4 budget for a given lake.

Multiple drivers for in-lake variability of sediment-mediated CH_4 production have been identified. Among these, temperature and organic matter, both quantity and quality, are important controlling factors.[10,11] In seasonally stratified lakes, the warmer epilimnion floats above the cold hypolimnion in the warm season, separated by the metalimnion. Global lake surface temperatures have increased at a rate of 0.34°C per decade,[12] while bottom temperatures in many stratified lakes have not increased significantly[13,14] but are projected to increase worldwide 0.86°C–2.60°C by the end of the 21st century under representative concentration pathways (RCPs) 2.6–8.5.[15] Methanogenesis involves a series of microbial processes[15] and elevated temperatures in the littoral sediment and prolonged periods of anoxia in the profundal of stratified lakes dramatically promote the potential for CH_4 production.[14,16] Lake eutrophication magnifies the temperature sensitivity of methanogenesis more than of methanotrophy.[17] Compared to the permanently oxygenated littoral zone, the profundal zone of temperate lakes experiences seasonal anoxia due to thermal stratification, associated with global warming[17,18] and strong internal eutrophication,[17] and therefore, enhanced CH_4 emission.[19] In addition, organic carbon (OC) quality appears more important than quantity in governing spatial differences in methanogenesis rates,[20] while littoral sediments usually receive more fresh terrestrial OC[21,22] while profundal sediments tend to be enriched in autochthonous OC[23] that favors methanogenesis.[24] Inputs of organic matter to different zones of the lake sediment are often episodic, typically associated with storm events in the littoral zone and phytoplankton blooms in the profundal zone. How these climate-driven changes affect the temporal and spatial variability of CH_4 fluxes in lake sediments, and therefore, in-lake CH_4 budgets remain unclear.

Therefore, a systematic investigation of how lake CH_4 production and consumption respond to climate change is urgently needed to allow the development of more reliable predictions of climate-driven changes in atmospheric CH_4 release from lakes. In this study, we hypothesized

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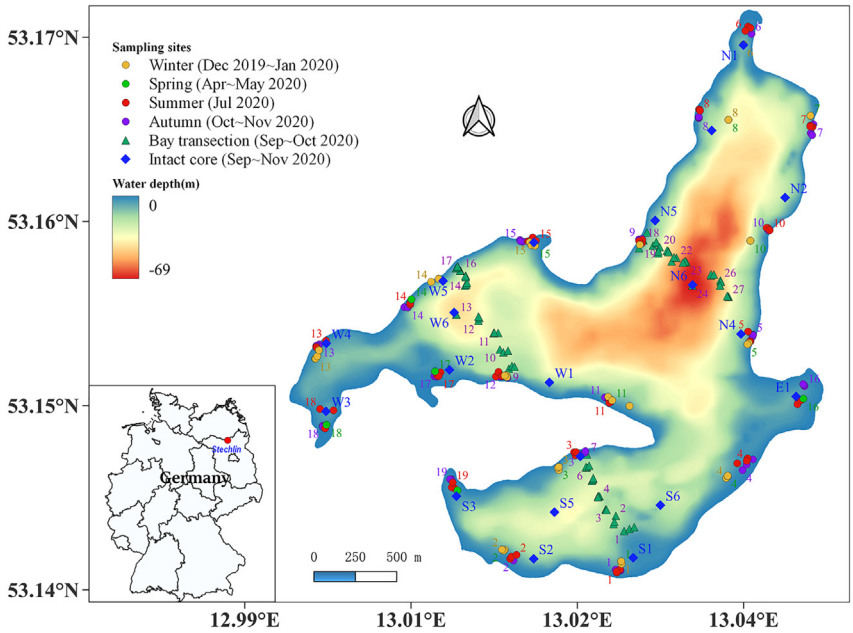

Figure 1. Map of sampling sites for Lake Stechlin sediment cores

The small map in the left-bottom corner indicates the geographical location of Lake Stechlin in Northeastern Germany; the colored contour map shows the bathymetry of the lake. Three sampling strategies were adopted: (1) intact short cores (20 cm) from the littoral site in the four seasons from December 2019 to November 2020 (winter—solid yellow circles, spring—solid green circles, summer—solid red circles, autumn—solid purple circles); (2) intact short cores (20 cm) along three cross-sections in autumn—solid green triangles; (3) intact long cores (~50 cm) from both littoral and pelagic zones—solid blue diamonds, site N6, W6, and S5 among them were also the profiling locations of water temperature and dissolved oxygen in the main, west, and south bight, respectively.

that spatially CH_4 flux at the sediment-water interface could be mainly contributed from littoral sediments rather than profundal zone, while seasonal stratification is responsible for its temporal variation. Sediment-mediated CH_4 production and consumption rates in a temperate lake (Lake Stechlin) were, hence, investigated to resolve spatial and seasonal variability (Figure 1). Drivers for spatio-temporal variations in CH_4 fluxes at the sediment-water interface (SWI) were examined. Climate effects, i.e., warming and deoxygenation, on sediment CH_4 production were studied by reconstructing sediment CH_4 production maps of the lake as a time series over the past two decades.

RESULTS

Water temperature (Temp) and dissolved oxygen (DO)

Temp in the epilimnion and metalimnion varies greatly when the lake is stratified and this was observed in most months of 2020, except for the well-mixed period from January to March (Figure 2). An average of 28.5% (15.2–56.8%) of the sediment surface belonged to the epilimnion with a higher and variable temperature ranging from 4.7°C to 21.6°C, and the metalimnion temperature varied from 4.7°C to 13.2°C. An average of 56.6% (0.5–69.0%) of the sediment surface belonged to the hypolimnion with relatively constant temperatures, ranging from 4.7°C to 5.8°C (Figure S1B). As a result of thermal stratification, anoxic hypolimnion (DO < 0.5 mg L^{-1}) occurred from July until mid-February of the following year. The proportion of the anoxic sediment surface ranged from a minimum of 0.5% in July to a maximum of 30.5% in December (Figure S1A).

Sediment OC content and grain size distribution (GSD)

Sediment properties (e.g., OC, grain size distribution [GSD]) are crucial in determining sediment CH_4 production. In this study, sediment OC in the upper 20 cm sediment layer was characterized by significant differences ($p < 0.001$) between littoral and profundal sites (Figure S2A). Sediment OC at littoral sites varied from 0.2 to 35.7% dry weight (DW) (mean = 6.7% DW) and a similar range (0.3–34.6% DW) was observed in the profundal zone but with a much higher mean value (20.9% DW). We found that between a water depth of 10–20 m, sediment OC content strongly increases with water depth and stabilizes from 20 m downwards (Figure S2A). At littoral sites, GSD varied little with water depth and sand (>63 μm) is the dominant particle size in littoral sediments (average of 87.0%), followed by silt (20–63 μm; an average of 11.2%), and clay (<20 μm; average of 1.8%). With increasing water depth, medium sand (200–500 μm) content drops from 40.3% in the littoral to 27.8% in the profundal zone, while silt and clay (<63 μm) content increases from 13.0 to 41.7% (Figure S2B). The lake sediment texture is mainly sandy, and OC linearly increases with the content of medium-sized sediment (with silt [$R^2 = 0.43$, $p < 0.01$] and clay [$R^2 = 0.16$, $p < 0.05$] content), but decreases with sediment sand content ($R^2 = 0.43$, $p < 0.001$; Figure S2C).

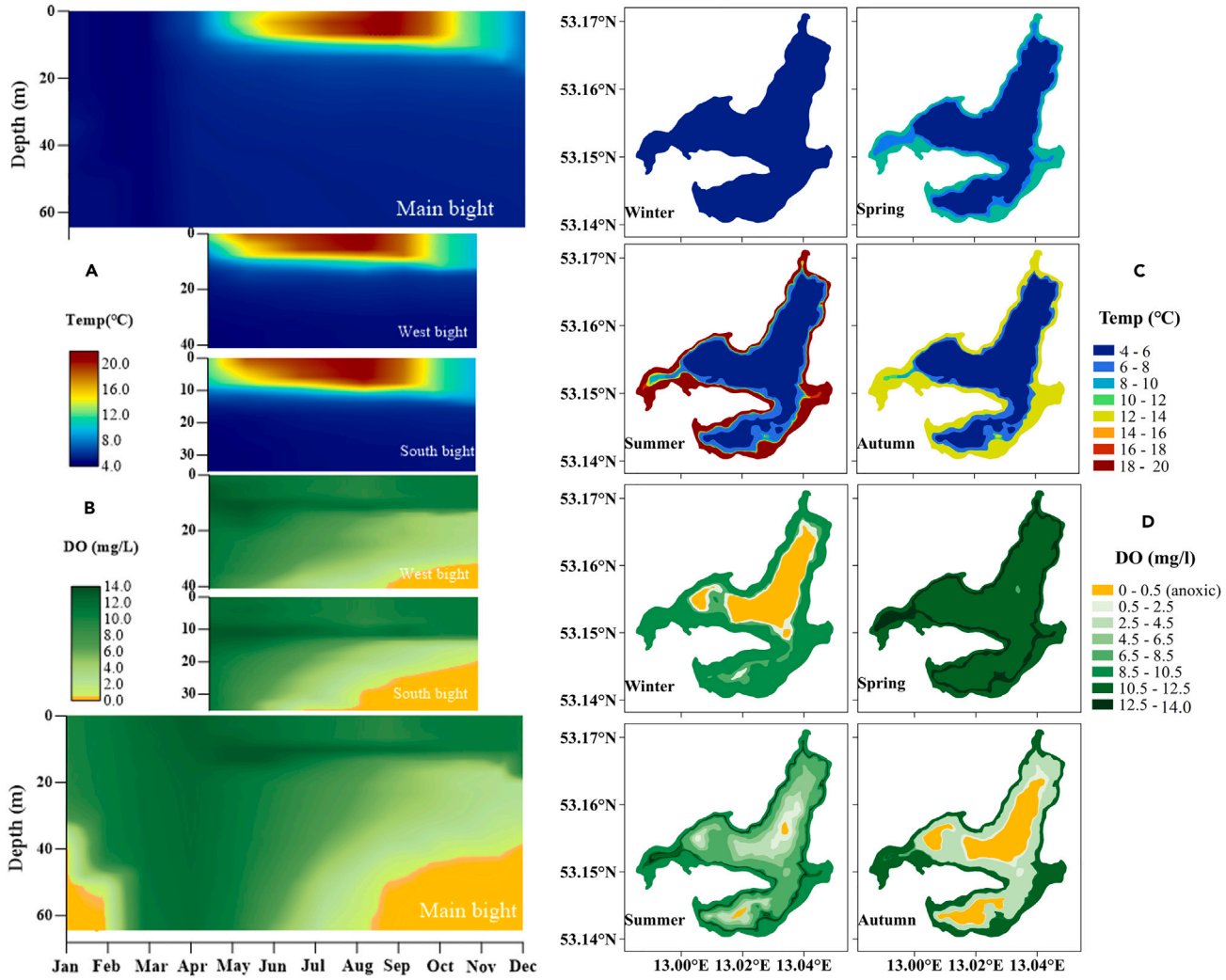

Figure 2. Spatial-temporal variations of water temperature and dissolved oxygen in Lake Stechlin in 2020

Depth profiles of (A) water temperature (Temp, °C) and (B) dissolved oxygen (DO, mg L^{-1}) with available Temp and DO in the western and southern bight from May to November displaying in the small frames; Spatial distributions of (C) Temp and (D) DO at the in-lake sediment surface in the four investigated seasons, anoxic zones (DO < 0.5 mg L^{-1}) are marked with orange in (D), all monthly Temp and DO data in 2020 can be found in Figure S6.

Depth profile of CH_4 production rate (t'_{CH_4}) in intact sediment cores (50 cm) at 20°C

The t'_{CH_4} was highest at the sediment surface (0–2 cm) in the northeastern and western bights (E1, N2, N3, N4, N5, N6, S4, W2, W4, W5, and W7). At these sites, the variation of t'_{CH_4} with sediment depth was well-fitted to a power-law (R^2 = 0.78–0.99, Figure S4), except at a few sites (e.g., W3, S2, and S3) where slightly elevated rates were found at greater depths. At other sites (S1, S5, and S6), a sub-surface maximum of t'_{CH_4} occurred at 3–5 cm or 6–8 cm depth. On average, the accumulated CH_4 production rate (Tot_{CH4}) from the upper 20 cm sediment layer accounted for 88.8% (±13.7%) of the total CH_4 production from the 50 cm sediment core. Further, depth-integrated Tot_{CH4} rates (0.201 ± 0.103 mmol L^{-1} d^{-1}) from littoral sediment cores are substantially higher than the rates (0.053 ± 0.074 mmol L^{-1} d^{-1}) from profundal sediment cores (Table S1).

Effects of temperature on CH_4 production (*MP*), oxidation (MO_x) rates, and CH_4 fluxes at the SWI

Both *MP* and MO_x rates increase exponentially with temperature from 5 to 20°C (Figures S5A and S5B) and a positive linear response of MO_x to increasing *MP* was observed (Figure 3A). The proportion of CH_4 loss due to aerobic oxidation decreases linearly with rising temperature (R^2 = 0.94, p < 0.01, Figure 3B), suggesting that CH_4 fluxes across the SWI can be expected to increase in response to warming. A 10°C increase in sediment temperature resulted in a 20.9% decrease in the fraction of CH_4 consumed. At low temperatures (<7°C), methanogenesis could be largely canceled out due to higher methanotrophic activity. Regardless of the level of oxygen deficiency, CH_4 fluxes across the SWI

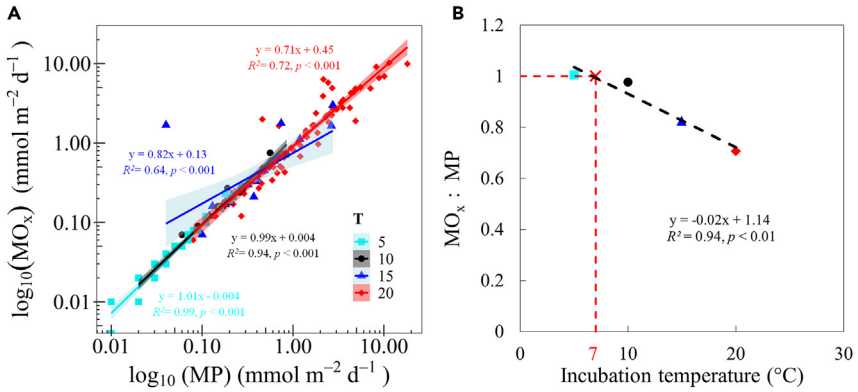

Figure 3. Thermal effects on potential sediment CH_4 production and oxidation

(A) Sediment *MP* vs. MO_x rates at four different incubation temperatures. Linear regressions between *MP* and MO_x are displayed at 5°C, 10°C, 15°C, and 20°C with equations and confidence intervals are shown as colored shadows.

(B) The ratio of MO_x to *MP* at the four incubation temperatures with colored shapes corresponding to those in (A). Based on the linear regression, CH_4 production and consumption are equal at 7°C, corresponding to MO_x: *MP* = 1. A p value of 0.01 or lower represents the statistical significance.

increased exponentially with temperature in both littoral and profundal sediments (Figures S5C–S5E). However, fitted curves indicated that anoxia at profundal sites stimulated an increase of CH_4 production by ~15.4 (Figures S5D and S5E), a striking contrast with the fact that *MP* under aerobic conditions can increase almost by two orders of magnitude when the thermal response of sediment methanogenesis at littoral sites is compared to profundal sites (Figures S5C and S5E).

Seasonal changes in spatial patterns of CH_4 flux at the SWI in 2020

Methane fluxes across the SWI increased from 0.18 ± 0.20 mmol m^{-2} d^{-1} in winter to 0.31 ± 0.42 mmol m^{-2} d^{-1} in spring, peaked at 1.69 ± 2.37 mmol m^{-2} d^{-1} in summer, and fell to 0.62 ± 0.79 mmol m^{-2} d^{-1} in autumn; the hotspots clearly occurred in the littoral zone, compared to the much lower fluxes observed in the profundal zone (Figure 4). The highest flux (5.35 mmol m^{-2} d^{-1}) was observed during summer and the lowest (0.005 mmol m^{-2} d^{-1}) in winter, consistent with the changes in water temperature (Figure 2C). Considering the area of the hypoxic sediment surface resulting from thermal stratification (Figures 2B–2D), small patches of elevated CH_4 flux occurred at the SWI in the profundal zone during summer, followed by a dramatic expansion of profundal high flux areas in autumn. These active profundal areas decreased in winter and were absent during spring. The estimated total CH_4 emission at the SWI in Lake Stechlin ranged from 1.03 × 10^4 g d^{-1} in winter to 9.33 × 10^4 g d^{-1} in summer. Over the four seasons, CH_4 fluxes across the SWI from the areas in direct contact with the epilimnion, metalimnion, and hypolimnion (Figure 5A) accounted for 86.8% (79.5–95.4%), 10.1% (0.2–19.1%), and 3.0% (0.4–6.0%), respectively, while the anoxic sediment contribution to the total flux was 11.8% in winter, 0.0% in spring, 0.1% in summer, and 4.0% in autumn (Figure 5B). In comparison to the long-term (2003–2018) oxic bottom, the conversion of sediment surface to recent seasonal anoxic hypolimnion (DO < 0.5 mg L^{-1}) in 2020 resulted in a 12.9-fold increase of CH_4 emission from summer to winter during 2019–2020 (Figure 5C).

Hindcasting CH_4 fluxes across the SWI over the last two decades

Associated with the seasonal development of thermal stratification and anoxia in 2020 (Figures S6 and S7), the total lake-wide CH_4 flux across the SWI peaked during the warm season (Figure S8). Consistent with the seasonal changes of measured CH_4 fluxes across the SWI in 2020, calculated fluxes were high from April to November from 2003 to 2020 (Figure S9). The sediment surface in contact with the epilimnion, metalimnion, or hypolimnion contributed 84.8% (78.8–90.1%), 13.6% (8.0–18.9%), and 0.38% (0.21–1.44%), respectively, to the total annual CH_4 fluxes across the SWI over 2003–2020 (Figure S8B). It is worth noting that the hypoxic sediment area started developing since 2010, and the extension of the anoxic sediment area has shown a substantial increase since 2018. However, both the annual CH_4 flux and the contribution from these anoxic sediment surface areas remained small in 2020 (449.1 g d^{-1}, or 0.8%, Figure 6).

DISCUSSION

Disproportional contribution of CH_4 fluxes from littoral sediment

Our data represent the first systematic and comprehensive evaluation of seasonal and spatial variability of sediment CH_4 fluxes from a deep stratified temperate lake. During our incubation experiments, higher spatial heterogeneities of *MP* were observed from littoral than from profundal cores, and at all sites. Profundal sediments are collectively less active than littoral ones in terms of *MP* (Figures S5C–S5E) when incubating at the same environmental temperature (i.e., 20°C). Seasonal CH_4 fluxes at the SWI ranged from 0.005 to 5.35 mmol m^{-2} d^{-1} in Lake Stechlin, which is in a similar range as various other temperate and boreal lakes, e.g., 0.54–6.54 mmol m^{-2} d^{-1} in the profundal zone of boreal lakes[25]; 0.8–11.9 mmol m^{-2} d^{-1} in eutrophic Lake Müggel[26]; 2.06–6.94 mmol m^{-2} d^{-1} in eutrophic Lake Pluβ[27]; and 0.19–7.44 mmol m^{-2} d^{-1} in

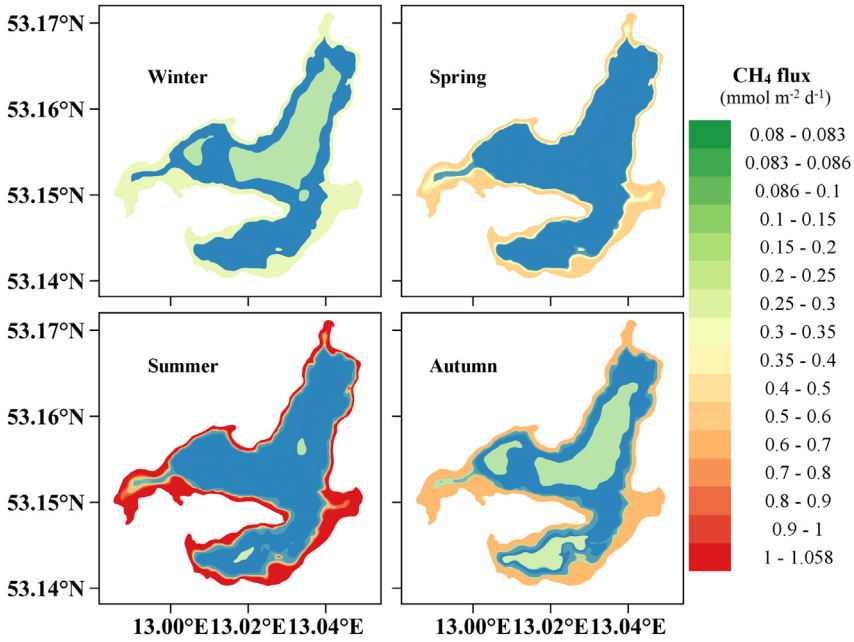

Figure 4. Spatial distribution of CH_4 fluxes at the SWI in Lake Stechlin over the four investigated seasons

Lake Orta.[28] In this study, hypolimnetic sediment CH_4 fluxes in the presence of seasonally hypoxic water (0.5–2.0 mg O_2 L^{-1}) overlying the sediments were estimated as under oxic conditions. This might lead to an underestimation of the contribution of profundal sediments to the lake-wide sediment CH_4 fluxes as waters with >0.5 mg O_2 L^{-1} were considered as fully aerated in our calculations.[29,30] However, we concluded that this underestimation could be minor, because even under strictly oxygen-free conditions the contribution of profundal sediment to the CH_4 fluxes across the SWI remained low. In contrast, while the surface area of the littoral sediment accounts for only 33% (22.3–56.8%) of the total sediment area in Lake Stechlin, the CH_4 fluxes from the littoral sediment contribute disproportionally 86.9% (79.4–95.4%) of the total sediment-derived CH_4 flux across the SWI (Figure S7C). Similar conclusions were drawn for a small northern lake in which ~75% of CH_4 emission took place in the rather shallow littoral areas.[31]

Sediment methane production outcompetes aerobic oxidation in response to warming

Global lake surface temperatures have increased at a rate of 0.34°C per decade,[12] and lake bottom temperatures are projected to increase worldwide by 0.86°C–2.60 °C at the end of the 21st century under RCPs 2.6–8.5.[15] Warming stimulates both methanogenesis (*MP*) and aerobic oxidation (MO_x), yet in some cases, MO_x was mainly dependent on *MP* rather than sediment properties and temperature.[10] Previous studies show that *MP* in sediment often exceeds MO_x in many lakes and reservoirs.[32] Similarly, a previous large-scale survey[17] including Lake Stechlin revealed that sediment *MP* is more sensitive to warming than water column MO_x. Here, we demonstrated that potential MO_x at the lake-wide SWI could annually remove >71% of the sediment-produced CH_4 (Figure 3A). Further, we show that *MP* increases faster than MO_x at temperatures >7°C in response to rising temperature, leading to a net increase in CH_4 fluxes at higher temperatures. At lower temperatures (<7°C), however, the rate of MO_x can equal or exceed sediment *MP* (Figure 3B) and thus efficiently removes sediment CH_4 at low water temperatures. Our results contradict previous findings by Fuchs et al. (2016)[33] that the effects of future warming on methanogenesis could be balanced by increasing MO_x rates. Our finding of a higher temperature-dependency of *MP* rates in littoral than profundal sediments (Figures S5C–S5E) is consistent with the results from a deep mesotrophic lake in Japan, where the *MP* rates in littoral sediments are also more sensitive to warming than in profundal sediments.[23] Consequently, the projected warming of global lake surface water[12] is expected to stimulate CH_4 emissions from the littoral sediments of temperate lakes like Lake Stechlin.

Drivers of spatio-temporal variability of in-lake CH_4 fluxes across the SWI

We examined the potential drivers of the temporal and in-lake spatial distribution of sediment CH_4 fluxes across the SWI. It has been reported that seasonal dynamics of sediment CH_4 fluxes (i.e., *MP*-MO_x) in lakes are mainly driven by temperature[34] and OC.[34,35] However, both structure and abundance of methanogens and methanotrophs in lake sediments varied with seasonal DO dynamics.[36] In Lake Stechlin, seasonal trends in sediment CH_4 fluxes were mainly regulated by temperature as shown in Figures 2C, 2D, and 4. Consequently, long-term trends in CH_4 fluxes would be related to changes in the climate warming-related thermal structure of the lake, the ongoing eutrophication and the resulting hypoxia/anoxia in the water column[37,38] (Figures 5 and 6). Profundal sediments differ spatially from littoral sediments in terms of light exposure,[39] quality and quantity of available OC, frequency of sediment resuspension, etc., which thus influence methanogenic and

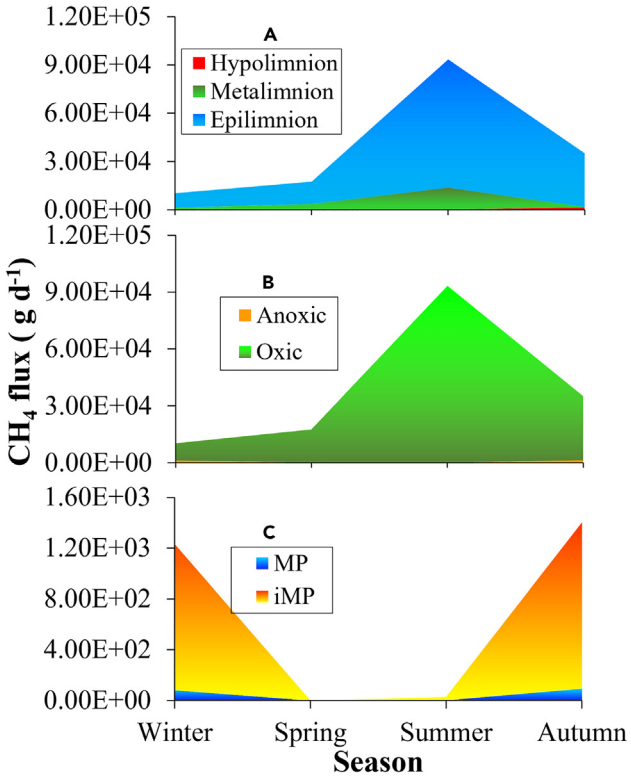

Figure 5. Seasonal variations in CH_4 fluxes at the SWI

(A) In the epilimnion, metalimnion, and hypolimnion.

(B) under oxic and anoxic conditions; and (C) seasonal variations in the increased CH_4 fluxes (iMP) at the SWI due to the conversion from a long-term oxic (2003–2018) to recent anoxic hypolimnion in 2020 in Lake Stechlin. The increased CH_4 flux contribution was estimated by comparison between the anoxic sediment surface in 2020 and the oxic sediment surface as in 2003–2018 under the bottom temperature in 2020.

methanotrophic community structure and their activities depending on the lake thermal stratification dynamics.[40–42] Firstly, in addition to the much warmer epilimnion than hypolimnion during thermal stratification (Figures 2A–2C), a more sensitive thermal response of *MP* in littoral sediments (Figures S5C–S5E) was observed in Lake Stechlin; similar findings were also reported by Lofton et al.[43] in Arctic lakes. This is likely due to more abundant methanogens in the littoral sediments[44] and the insignificant temperature-dependency in community sizes of both methanogens and methanotrophs in the profundal sediments.[33] This explains the striking difference in Tot_{CH4} (Figure S3) and CH_4 flux at the SWI (Figure S7C) of littoral vs. profundal sediments. Secondly, methanogenesis in the littoral and profundal zones could be driven by distinct differences in substrate availability that were regulated by quantity and source of sediment OC.[42] This in-lake spatial variability could be caused by distinct distribution patterns of degradable sediment OC.[11] For example, in Lake Stechlin, littoral sediments receive abundant fresh and labile substances, i.e., via fallen leaves[22] and submerged macrophytes,[21] and have a C:N value of 10.6–26, especially in the deep epilimnion.[45] In contrast, profundal sediments appear to have higher OC content (Figure S2), however, with a large fraction of refractory OC.[46] Consequently, profundal sediments have a lower C:N value (10)[45] than littoral sediments. This could be explained by: (1) sediment focusing[47]; (2) reduced OC mineralization rates under low hypolimnetic temperature[48]; (3) higher OC burial under reduced oxygen exposure[49]; and (4) accumulation of more recalcitrant OC produced from hypolimnetic mineralization of degradable (also autochthonous) OC.[50] As a result, the enrichment of sediment OC counterintuitively did not fuel intense sediment *MP* of the profundal zone (Figures S5D, S5E, and Table S1). This is different from the littoral zone (Figure S5C) and from different other ecosystems where high *MP* rates have been measured in the hypolimnion.[24,51,52] Whereas sediment and water column CH_4 production in the surface layers are usually suppressed by oxygen, high concentrations of sulfate and other electron acceptors can suppress *MP* in the profundal sediments as well. This notion is supported by the fact that in the deeper sediment layer of Lake Stechlin, potential *MP* seems to be controlled by methanogenic bacteria rather than Archaea.[53] Thirdly, as evidenced by the absence of any apparent Tot_{CH4} production peak in sediment depth profiles of several profundal sites (Figure S3) and the abundance of methanogens throughout the sediment depth profiles,[44] anaerobic methane oxidation (AMO) might also play an important role in regulating CH_4 fluxes at the SWI in the profundal zone, where electron acceptors, such as Fe(III) and Mn(IV), are enriched due to sediment focusing and recent eutrophication.[38] Theoretically, nitrate/nitrite dependent AMO is more likely to occur,[54] and also sulfate-AMO can be important.[55,56] In Lake Stechlin, however, nitrate/nitrite concentrations are very low and sulfate concentrations are slightly higher, but with the presence of Fe(III) and Mn(IV), the enrichment of these electron acceptors allows for a substantial CH_4 sink by AMO in sediments of Lake

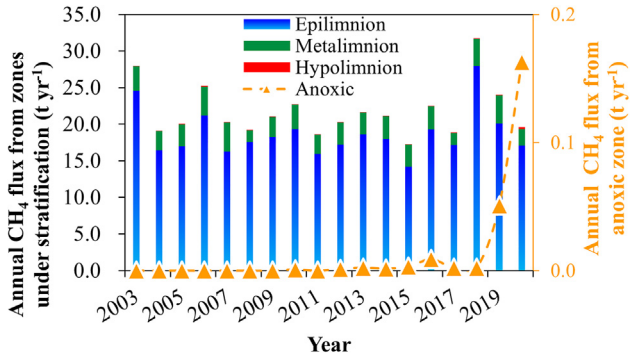

Figure 6. Temporal variations of annual CH_4 flux from 2003 to 2020 at the SWI of the epilimnion, metalimnion, hypolimnion, and anoxic water column

Stechlin.[57] Taken together, our results highlight that sediment *MP* in the hypolimnion of Lake Stechlin is rather limited by OC quality than quantity[20] and the availability of electron acceptors.[57]

Implications for the whole-lake CH_4 budget

While our estimated CH_4 fluxes across the SWI from both littoral and profundal zones cannot be directly translated to atmospheric CH_4 fluxes (as a maximal flux entering the water column), several implications can be tentatively drawn. The relatively well-oxygenated hypolimnion of Lake Stechlin throughout the entire year before the year 2007 represents the state of most oligo- to mesotrophic stratified lakes, suggesting a negligible contribution of profundal sediment-derived CH_4 emissions to lake-wide sediment-derived CH_4 emissions. Associated with the development of anoxia, increased CH_4 fluxes across the SWI can be expected, causing an accelerated CH_4 enrichment in the anoxic hypolimnion. However, most of the CH_4 stored in the hypolimnion can be oxidized during the lake's overturn.[58–60] Comparison with published CH_4 emission rates at the air-water interface in Lake Stechlin by Günthel et al.[61] enabled us to estimate that, on average, 32.9% of the CH_4 crossing the SWI was oxidized in the water column during lake stratification, in stark contrast to the more than doubled percentage of oxidized CH_4 (~72.8%) during lake mixing, which approximates among the reported 51–80% of total CH_4 being oxidized. So far, however, seasonal variations of CH_4 oxidation and *in situ* biological production of CH_4 in the oxic epilimnion[62–65] were not considered. Until today, climate warming and concomitant anoxia have played a minor role in modeling the full-scale lake CH_4 budget, but CH_4 emissions from profundal sediments are likely to increase (Figure 6). This notion is in good agreement with several recent studies,[17,66,67] that predicted increased CH_4 emissions from various lakes in response to global warming. Warming rates of lakes subjected to increased global temperatures, however, vary regionally and are highly related to individual lake characteristics, e.g., size, depth, bathymetry, etc..[12] For small, shallow lakes, both surface and bottom water experience direct heating or cooling dictated by climatic forcing, lake morphometry, and optical properties.[68] Consequently, warming climate may result in changes in the lake's thermal structure (e.g., increased daytime stratification[68]) and thereby increase eutrophication and subsequent decline in hypolimnetic DO in small temperate shallow lakes.[69,70] Together, this will lead to increased CH_4 emission rates.[17,19] Meanwhile, a much larger fraction of *MP* is expected to be released via ebullition or plant-mediated gas transport in more productive smaller lakes, which avoid the oxidation at the SWI and in the overlying water. This is different in deep lakes, as CH_4 from the profundal zone will dissolve in the water column during its upward transport.[71] For medium to deep temperate, stratified lakes, the temperature of surface vs. bottom waters diverges due to the development of a density gradient,[13,66] thereby the warming rates are unevenly distributed over the seasons and across the water column of different lakes.[72] Climatic warming further induced lake eutrophication via prolonging the stratification period, which resulted in increasing hypoxia/anoxia of bottom waters.[37,38] As a result, it can be expected that in eutrophic temperate lakes the contribution of profundal sediment-derived CH_4 increases substantially with increasing anoxia.[18] Yet, in Lake Stechlin, this contribution remains small in comparison to the littoral sediments (e.g., Figure S7). Moreover, projected surface temperatures in winter and spring increase strongly, but rarely in summer and autumn.[73] In combination with a higher temperature-dependency of sediment *MP* rates and the presence of abundant fresh labile substances in the littoral zone, this may lead to pronounced spatio-temporal heterogeneities in CH_4 fluxes at the SWI in deep temperate lakes. The large CH_4 fluxes from littoral sediments call for more attention, as most of the produced CH_4 can escape oxidation and may directly emit into the atmosphere.[74] Previous studies on CH_4 emission rates from lakes[46] were often based on limited data points with a generally poor spatio-temporal resolution. Our spatially and temporally well-resolved study reveals significant climate warming-induced changes in littoral sediment *MP* depending on location and season (Figure S3), but also a recently increased CH_4 flux contribution of the profundal zone due to its late summer anoxia (Figures 5C and 6). This eventually results in large variations in CH_4 fluxes to the atmosphere that should be considered for reliable lake-wide flux calculations and models predicting warming-induced consequences for lake-wide CH_4 emissions into the atmosphere.

In conclusion, this study resolved both CH_4 production and consumption rates in littoral vs. profundal sediments of Lake Stechlin, and examined the magnitude and drivers of lake-wide CH_4 fluxes at the SWI by taking its high spatial and seasonal variability into account. Our results highlight the high spatio-temporal variability in CH_4 fluxes at the SWI in littoral vs. profundal zones, indicating that temperature is a major driver for CH_4 fluxes across the SWI of stratified lakes. While, in Lake Stechlin, the littoral zone accounts for only ~33% of the total sediment surface area, on average, it contributes 86.9% to the total CH_4 release at the SWI. This fraction is expected to increase as lake surface water temperatures

globally increase. By reconstructing the time course of CH_4 fluxes at the SWI over the past two decades in Lake Stechlin, we show that the contribution of CH_4 from the profundal zone is currently small, but increases substantially with the recent and consistent development of an hypolimnic anoxia in late summer, fall and winter. Therefore, CH_4 fluxes across the SWI in the profundal zone can be expected to further increase due to substantial deoxygenation associated with lake eutrophication under climate warming. Our data inform lake managers to better counteract undesired site effects of global climate change on deep stratified lakes and their potentially positive climate feedbacks.

Limitations of the study

In the present study, the spatio-temporal variations of CH_4 fluxes at the SWI were examined in a temperate stratified lake as an example. More lakes from different climatic zones should be included in the future to investigate the effects of climate change on CH_4 emissions from global lakes. In addition, lake biogeochemical cycles and food web interactions as consequences of CH_4 flux variations at the SWI under climate change are needed.

STAR★METHODS

Detailed methods are provided in the online version of this paper and include the following:

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SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.isci.2024.109520.

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AUTHOR CONTRIBUTIONS

L.L. and H.-P.G. contributed to the design of the study. M.K. and L.L. collected the data; M.K. and L.L. analyzed the data with input from H.-P.G. M.K., L.L., and H.-P.G. wrote the paper with input from all coauthors.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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STAR★METHODS

KEY RESOURCES TABLE

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Deposited data		
Water temperature and dissolved oxygen (2003–2020)	FRED database of the Leibniz-Institute of Freshwater Ecology and Inland Fisheries (IGB)	https://doi.org/10.18728/igb-fred-823.1
Software and algorithms		
R-software (v3.6.3)	The R Foundation	https://www.r-project.org/
Rstudio (v1.3.1073)	RStudio Team	https://posit.co/products/enterprise/team/
QGIS (v3.22.3)	QGIS-A Free and Open Source Geographic Information System	https://www.qgis.org/en/site/index.html
General linear models (GLMs)	R Package: Stats	https://stat.ethz.ch/R-manual/R-devel/library/stats/html/glm.html
Nonlinear Least Squares (nLs)	R Package: Stats	https://stat.ethz.ch/R-manual/R-devel/library/stats/html/nls.html
Non-parametric Trend Tests	R Package: trend	https://cran.r-project.org/web/packages/trend/index.html

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Dr. Liu Liu (liu.liu@ynnu.edu.cn).

Materials availability

This study did not generate any new materials.

Data and code availability

- Data: All data reported in this study will be shared by the lead contact upon reasonable request.
- Code: This paper does not report original code.
- All other requests: Any additional information required to reanalyze the data reported in this paper will be shared by the lead contact upon request.

METHOD DETAILS

Study site

Lake Stechlin is a dimictic temperate glacial lake in northeastern Germany with a total area of 4.52 km^2. Its maximum and mean water depth are 69.5 and 22.8 m, respectively. The lake is characterized by three elongated-narrow bays: the northeast bay is where the deepest point is located with steep in-lake slopes; the west and south bights are shallower with less steep in-lake slopes. Iron and manganese enrichment in profundal sediment have been observed to be associated with sediment focusing[75] due to the steep slopes in the northeastern bight recent eutrophication and the subsequent areal spreading of anoxic conditions.[38] Lake Stechlin has been changing from an oligotrophic to eutrophic status since the early 2000s.[38,76] Development of deoxygenation in the hypolimnion during late summer has been reported over the last two decades.[18]

Water temperature and dissolved oxygen

Monthly depth profiles of water temperature (Temp) and DO were taken routinely using a multi-parameter probe (EXO, YSI, USA) at the deepest point of the northern bight (also main bight), the western and southern bights of the lake (i.e., site N6, W6, S5 in Figure 1). The water column with DO < 0.5 mg L^{-1} was defined as anoxic water; and the depth of the epilimnion, metalimnion, and hypolimnion were calculated using the water temperature profile data[77]; the profundal and littoral zone were defined as the deep water sediment exposed to the metalimnion and hypolimnion and the shallow water area in the epilimnion, separately. Combining the lake's bathymetric map and depth profiles of monthly temperature (Temp) and DO measurements from 2003 to 2020 (Figure S6), we hypothesized that each vertical water layer was horizontal homogeneous, and then the sediment surface was divided into patches that were: 1) covered by the epilimnion, metalimnion and hypolimnion

(or mixing), 2) overlaid by oxic and anoxic waters and 3) from the littoral and profundal zones, separately. Areas of these patches were also estimated for the calculation of CH_4 fluxes at the SWI of the entire lake.

Sediment sampling

CH_4 production is often active in sediment layers that contain fresh organic materials and underneath OC is considered effectively buried.[78] This indicates that the most active sediment layer for CH_4 production in Lake Stechlin is limited to the upper 1.2–2.4 cm sediment layer based on the ~2 mm/yr of the $^{137}C_s$-determined sedimentation rate[79]; In Lake Stechlin apparent higher potential CH_4 production rates have been confirmed in the surface 0–5 cm layer than in the deeper 20–25 cm layer.[53] In this study, the upper 20 cm sediment was incubated to investigate the temporal and spatial distribution of CH_4 production in Lake Stechlin. To justify the use of 20 cm sediment cores, numerous ~50 cm long intact sediment cores were also sampled to determine the active zone of sediment CH_4 production at different places in the lake. Sediment cores were seasonally taken at the same site from Dec. 2019 - Nov. 2020 using a gravity corer (Uwitec, Austria) (Figure 1).

Intact short sediment cores (~20 cm long)

Three replicates of intact short cores from both littoral (<8 m depth, 15 sites in winter and 19 sites in other seasons) and profundal zones (>8 m depth, 27 bight transection sites in autumn) were seasonally collected at each site (Figure 1). The upper 20 cm sediment layer was captured and immediately transferred into a short bottom-sealed acrylic tube (length 25 cm; i.d. 5.94 cm) with a 5 cm layer of overlying water. This was done with great care to avoid destroying the natural sediment structure. The sediment cores were then transported to the laboratory (ca. 50 m from the lake) and stored in the dark at 5°C for 24 h with the top end open to the air. This ensured the complete release of excessive dissolved gases in sediment porewater at atmospheric pressure. The next day a 4.5 cm-high air-filled headspace was created with a thin layer of overlying water (0.5 cm) left after carefully removing the water using a syringe.

Intact long sediment cores (~50 cm long)

Intact long cores from littoral and profundal zones were collected in autumn from 20 sites distributed across three bights (indicated as N1-N6, S1- S6, W1-W7, E1 in Figure 1) by following the above-mentioned methods. These cores were stored in the dark at 5°C for one-week until further processing for anaerobic incubation of sliced subsamples.

CH_4 production rates in sediment incubations

Intact short cores (20 cm long)

Aerobic/anaerobic incubation of the 20 cm upper sediment was performed at different temperatures to quantify potential CH_4 production (*MP*) rates under aerobic/anaerobic conditions and the potential rates of aerobic CH_4 oxidation (MO_x). The preprocessed sediment cores (20 cm long with 4.5 cm headspace) were stored in a climate chamber for 12 h to allow for the acclimation to the designated incubation temperature. The top end was then closed using an air-tight butyl rubber cap equipped with a port for gas sampling. The headspace was flushed for 10 min with pure N_2 gas to generate an anoxic environment for subsequent anaerobic incubation. The cores were then incubated in a temperature-controlled climate chamber for a week. 0.25 mL gas was sampled each time from the headspace each day using an air-tight syringe. CH_4 concentrations in gas samples were measured using the closed-loop (76.65 mL in volume) method[80] with a greenhouse gas analyzer (Picarro, GasScouter G4301, USA) and using outdoor air as the carrier gas. After one-week of anaerobic incubation, the headspace was flushed with air for a following one-week aerobic incubation at the same temperature. The oxic/anoxic conditions in the corer headspace were verified after finishing incubation with an Oxygen sensor (Micro TX3, Germany). All short sediment cores were incubated under four representative temperatures (20, 15, 10, and 5°C) in summer, autumn, spring, and winter, separately.

Intact long cores (~50 cm long)

Sediment subsamples were incubated anaerobically to acquire the depth profile of sediment CH_4 production rate (Tot_{CH4}). For each long sediment core, 6 mL sediment was subsampled from 7 to 9 depths (Table S1) with a 3 mL cut-syringe and immediately transferred into a 65 mL serum vial. The vial was capped with a butyl rubber stopper and flushed with N_2 gas for at least 5 min until headspace oxygen concentration dropped to 0 mg L^{-1} (tested using an oxygen microsensor (Firesting, Germany)). The vials were then closed with an aluminum cap using a crimper and stored in darkness at 20°C. Headspace CH_4 concentration was measured by taking a 0.25 mL gas sample with a syringe at a 3-day interval for 15 days.

Calculation of CH_4 production, oxidation rates and fluxes at the SWI

CH_4 fluxes under anaerobic and aerobic conditions

Based on the incubation of intact short cores, CH_4 fluxes across the SWI under anaerobic (F_{N2}) and aerobic (F_{air}) conditions were estimated according to Equation 1:

$$F_{N_2 \text{ or air}} = \frac{k \times V_{hs}}{M_{CH4} \times S_{sed} \times 1000} \quad \text{(Equation 1)}$$

Where F is CH_4 flux at the SWI ($mmol\ m^{-2}\ d^{-1}$), k ($ppmv\ d^{-1}$) is the slope of change in headspace CH_4 concentration, V_{hs} is the headspace volume (L), M_{CH4} is the molar volume of CH_4 (22.4 $L\ mol^{-1}$) at standard atmospheric pressure and S_{sed} is sediment surface area (m^2).

MP rate (MP) and oxidation rate (MO_x): F_{N2} is taken as the MP and MO_x (mmol m^{-2} d^{-1}) was calculated by comparing F_{N2} and F_{air}[81]:

$$MO_x = F_{N_2} - F_{air} \quad \text{(Equation 2)}$$

Depth profile of the CH_4 production rate (Tot_{CH4})

Tot_{CH4} ($mmol\ L^{-1} Sed\ d^{-1}$) was calculated based on the individual incubations of the sliced sediment samples at 7–9 depths of the intact long sediment core at 20°C under anoxic conditions, it was estimated by the following equation:

$$Tot_{CH4} = \sum t'_{CH_4} = \frac{k \times V_{hs}}{M_{CH4} \times V_{sed} \times 1000} \quad \text{(Equation 3)}$$

Where t'_{CH_4} is the CH_4 production rate ($mmol\ L^{-1} Sed\ d^{-1}$) of the sliced sediment sample, k ($ppmv\ d^{-1}$) is the slope of change in headspace CH_4 concentration, V_{hs} is the headspace volume (L), M_{CH4} is the molar volume of CH_4 (22.4 $L\ mol^{-1}$) at standard atmospheric pressure and V_{sed} is the sediment volume (0.006 L).

MP, MO_x rates and CH_4 fluxes at the SWI of classified sediment patches:

Thermal responses of MP, MO_x rates and CH_4 fluxes at the SWI shown as fitted formulas (Figures S5A–S5E) were obtained from *the incubation of intact short sediment cores.*

Spatio-temporal variation. Monthly CH_4 fluxes at the SWI from each sediment patch were calculated in 2020 according to Temp, DO and surface area of each patch. Depending on the Temp and DO conditions of the representative month for each season, CH_4 fluxes at the SWI in January, April, July and October in Lake Stechlin were taken as seasonal CH_4 fluxes in winter, spring, summer and autumn, respectively.

Proportions of CH_4 fluxes at the SWI covered by the epilimnion, metalimnion and hypolimnion, by the oxic or anoxic water, and from the littoral or profundal zones were monthly summarized, respectively. Meanwhile, contributions of CH_4 fluxes caused by the conversion from a long-term (2003–2018) oxic bottom to recent seasonal anoxic hypolimnion (DO < 0.5 mg L^{-1}) in 2020 were estimated and compared by assuming that the already anoxic bottom area still kept the long-term oxic status.

Long-term variation. Long-term variations of CH_4 flux at the SWI of Lake Stechlin from 2003 to 2019 were investigated by estimating the monthly CH_4 fluxes at the SWI by following the same procedures as for 2020.

Sediment grain size distribution and organic carbon content

The GSD of the top 20 cm layer sediment was determined by wet sequential sieving with *seven* classes (>500, 200–500, 100–200, 63–100, 40–63, 20–40 and <20 μm). The sediment was evenly mixed after removing large stones, and plant residues such as leaves and twigs, ~100 mL of each sediment sample was used for wet-sieving. Sediment OM was estimated based on loss on ignition (4 h at 550°C), sediment OC (% DW) content was then determined using a conversion factor of 1.724 between OM and OC based on the assumption that OM contains averagely 58% carbon.[82]

QUANTIFICATION AND STATISTICAL ANALYSIS

R-software (R v3.6.3, RStudio v1.3.1073) was used to test for linear relationships between parameters using General linear models, non-linear regressions between variables using Nonlinear Least Squares, and Mann-Kendall Trend analysis of water temperature using Non-parametric Trend Tests. The correlations between paired sediment MP and MO_x rates at varied Temp from different sites were tested. Statistics of spatial patterns of Temp and DO at the SWI, sediment area affected by thermal stratifications and development of anoxic hypolimnion, and corresponding CH_4 fluxes were processed in an open-source software QGIS (v3.22.3).