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A Fast-response automated gas equilibrator (FaRAGE) for continuous *in situ* measurement of methane dissolved in water

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Abstract

Biogenic methane (CH_4) emissions from inland waters contribute substantially to global warming. In aquatic systems, CH_4 dissolved in freshwater lakes and reservoirs is highly heterogeneous both in space and time. To better understand the biological and physical processes that affect sources and sinks of CH_4 in lakes and reservoirs, dissolved CH_4 needs to be measured with a highest temporal resolution. To achieve this goal, we developed the **Fast-Response Automated Gas Equilibrator (FaRAGE)** for real-time *in situ* measurement of dissolved CH_4 concentration at the water surface and in the water column. FaRAGE can achieve an exceptionally short response time ($t_{95\%}$ = 12 s when including the response time of the gas analyzer) while retaining an equilibration ratio of 63% and a measurement accuracy of 0.5%. An equilibration ratio as high as 91.8% can be reached at the cost of a slightly increased response time (16 s). The FaRAGE is capable of continuously measuring dissolved CH_4 concentrations in the nM-to-mM (10^{-9} - 10^{-3} mol L^{-1}) range with a detection limit of sub-

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nM (10^{-10} mol L^{-1}), when coupled with a cavity ring-down greenhouse gas analyzer (Picarro GasScouter). It enables the possibility of mapping dissolved CH_4 concentration in a "quasi" three-dimensional manner in lakes. The FaRAGE is simple to operate, inexpensive, and suitable for continuous monitoring with a strong tolerance to suspended particles. The easy adaptability to other gas analyzers such as Ultra-portable Los Gatos and stable isotopic gas analyzer (Picarro G2132-i) also provides the potential for many further applications, e.g. measuring dissolved $^{13}\delta$C-CH_4 and CO_2.

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1 Introduction

Despite the well-established perception of inland waters as a substantial source of atmospheric methane (CH_4) (Bastviken et al., 2011; Cole et al., 2007; Tranvik et al., 2009), large uncertainties remain owing to poorly constrained sources and sinks (Saunois et al., 2019). Most freshwater lakes and reservoirs are often oversaturated with CH_4 (relative to atmosphere) and its distribution is characterized by high spatio-temporal heterogeneities (Hofmann, 2013). Point-based and short-term measurements can result in biases in estimating diffusive CH_4 flux (Paranaíba et al., 2018). Thus, resolving the spatio-temporal dynamics of dissolved CH_4 concentration in lake water is a prerequisite for better budgeting sources and sinks in freshwater lakes.

Methane within lakes is often characterized by pronounced vertical and horizontal concentration gradients, which can occur either below or above thermocline. In many deep stratified lakes, a sharp vertical gradient below the thermocline can develop in the anoxic hypolimnion (mM range) (Encinas Fernández et al., 2014; Liu et al., 1996). In contrast, in some stratified lakes with a fully oxygenated hypolimnion CH_4 can accumulate above the thermocline (~μM range) (Grossart et al., 2011; Donis et al., 2017; Günthel et al., 2019). The concentration of dissolved CH_4 is also regulated by loss due to oxidation and emission to the atmosphere (Bastviken et al., 2004; Juutinen et al., 2009). Both rates can be highly variable, particularly for the flux term which is strongly affected by wind and convective mixing (Read et al., 2012; Vachon and Prairie, 2013). In addition to the uneven vertical CH_4 distribution, apparent horizontal gradients have been observed in lakes where littoral sediments are identified as a CH_4 source (Murase et al., 2003). This horizontal CH_4 gradient can also contribute to the epilimnetic CH_4 peak in pelagic waters via lateral transport (Hofmann et al., 2010; Fernández et al., 2016; Murase et al., 2005; Peeters et al., 2019). Nevertheless, dissolved CH_4 in lake water is not only featured with variable spatial patterns, it also changes

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57 at different time scales as most processes that contribute to the spatial heterogeneity are not
58 always synchronized.

59 The rise and fall of lake CH_4 concentration often show strong seasonality that are
60 driven primarily by thermal stratification (Encinas Fernández et al., 2014) and phytoplankton
61 dynamics (Günthel et al., 2019). While the build-up of hypolimnetic CH_4 storage is a slow
62 process that is closely related to the development of lake hypoxia, the epilimnetic CH_4
63 maximum can be highly variable even at a daily basis as it is strongly affected by
64 phytoplankton dynamics (Günthel et al., 2019; Hartmann et al., 2020; Bižić et al., 2020). In
65 addition, storms can act as another driver for short-term CH_4 dynamics in the lake because it
66 often leads to higher evasion rates caused by strong vertical turbulent mixing (Zimmermann et
67 al., 2019) and enhanced horizontal transport (Fernández et al., 2016). While the seasonal
68 patterns of dissolved CH_4 concentration in lake water seem recurrent and can be simulated
69 (Bartosiewicz et al., 2019), the unpredictable effects of short-term phytoplankton dynamics
70 and storm events can present a challenge in modeling lake CH_4 dynamics.

71 While there is urgent need for resolving the spatio-temporal variabilities of CH_4 in
72 large water bodies (e.g. deep, stratified lakes), we recognize limitations in the available
73 methodology. Like most gases in dissolved phase, CH_4 cannot be measured directly in water.
74 Instead, a carrier gas (synthetic air or at air concentration) is added to achieve (full/partial)
75 gas-water equilibration. The headspace gas sample is then measured with a gas spectrometer
76 and the concentration of targeted gas can be calculated according to Henry's law (Magen et
77 al., 2014). To save sampling effort, continuous gas equilibration devices have been developed,
78 which generally can be classified to four categories: 1) Membrane type (Schlüter and Gentz,
79 2008; Boulart et al., 2010; Gonzalez-Valencia et al., 2014; Hartmann et al., 2018) - gases are
80 extracted from water by using a gas-permeable membrane; 2) Marble type (Frankignoulle et
81 al., 2001; Santos et al., 2012) - gas exchange is enhanced by pumping water through marbles

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that increases the gas-water contact area; 3) Bubble type (Schneider et al., 1992; Körtzinger et al., 1996; Gülzow et al., 2011) - dissolved gases are stripped out by bubbling the water sample; 4) Showerhead type (Weiss-type) (Johnson, 1999; Rhee et al., 2009; Li et al., 2015) - water is pumped from top and then mixed with a circulated headspace carrier gas. A full evaluation on the performance of these devices was provided in a recent review (Webb et al., 2016), where, the most important paprameter, response time, was found to vary between 2-34 min for dissolved CH_4. While it is already encouraging, improvements are expected to further shorten the response time.

Driven by the need to resolve temporal and spatial variabilities of dissolved CH_4 in lakes/reservoirs with sufficient precision, we developed a novel, low-cost equilibrator to achieve fast gas-water equilibration. The **Fast-Response Automated Gas Equilibrator (FaRAGE)** can be coupled with a portable gas analyzer, which makes it perfect for field use. Here, the performance of the FaRAGE is evaluated by investigating its response time, detection limit and equilibration ratio. Applications are provided exemplarily to demonstrate the potential of the FaRAGE for improving our understanding on the spatial distribution and temporal dynamics of dissolved CH_4 in inland waters.

2 Materials and Methods

2.1 Device description

The design of the FaRAGE is modified from two types of equilibrators: Bubble-type (Schneider et al., 1992) and Weiss-type (Johnson, 1999). In contrast to the traditional bubble-type and Weiss-type equilibrators that create a large-volume headspace and circulates air back to the headspace, the FaRAGE is a flow-through system that adds gas flow into a constant water flow to produce a minimal headspace for continuous concentration measurement of CH_4 dissolved in water.

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106 The operation principle of the FaRAGE is depicted in Fig. 1 and photos of the main
107 parts of the prototype are provided in Fig. S1. A list of information on suppliers and cost of
108 each part can be found in Table S1. A mass flow controller (SIERRA C50L, Netherlands) is
109 used to generate a constant carrier gas (normal air/synthetic air) flow (1 L min^{-1}) from a
110 compressed air tank coupled with a pressure regulator. Water samples are taken continuously
111 using a peristaltic pump (500 mL min^{-1}), and the flow is monitored using a flow meter
112 (Brooks Instrument, Germany). The two flows mix in a gas-water mixing unit that is
113 composed of a gas bubble generating unit and a coiled hose for further gas-water turbulent
114 mixing. In the bubble unit (modified from a 10 mL plastic syringe), a jet flow is created by
115 adapting narrowed tubing (2 mm inner diameter) to the water pumping hose (3.2 mm inner
116 diameter). Degassing occurs when the jet flow enters the chamber with a sudden enlarged
117 diameter (14 mm). Degassing is further enhanced by micro-bubbles that are generated by a
118 bubble diffusor attached to the carrier gas hose (inside the bubble unit). The gas-water
119 mixture flows through the 2-m long Tygon tube (3.2 mm inner diameter) where additional
120 equilibration occurs. The flow is finally introduced to a gas-water separation unit (a 30 mL
121 plastic syringe) where the headspace gas is separated from the water. In this chamber, water
122 falls down freely to the bottom while the headspace gas is taken directly to a greenhouse gas
123 analyzer (1 L min^{-1} gas pumping rate; GasScouter G4301, Picarro, USA). A 2-m long Tygon
124 tube (3.2 mm inner diameter) is attached to the top of the chamber for venting excess gas flow
125 while stabilizing gas pressure in the headspace. The bottom water is discharged back to the
126 lake using another peristaltic pump (500 mL min^{-1}). To protect the gas analyzer from
127 damaging high water vapor content, a Teflon membrane filter (pore size 0.2 μm) is placed
128 before the gas intake (resulting in a ~210 mL min^{-1} reduction in flow rate of gas sample,
129 which is vented from the bypass at the top of the gas separation unit). A desiccant (a 20 mL
130 plastic syringe filled with dried silicone beads) is used to reduce moisture concentration to <
131 0.1% when attaching to a Picarro G2132-i isotope analyzer (Picarro, USA), in which < 1%

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moisture level is required for $^{13}\delta$C-CH_4 measurement. The temperature of the water sample at the point of equilibration with the headspace gas is monitored using a fast thermometer (precision 0.001 °C, 1 Hz, TR-1050, RBR, Canada) attached to the end of water discharging hose.

As concerns might arise from the availability of gas analyzer coupled to the FaRAGE, in addition to Gas Scouter from Picarro, two additional widely used models of greenhouse gas analyzers were tested. They are the Ultraportable Los Gatos (Los Gatos Research, USA) and stable isotopic CH_4 analyzer (G2132-i, Picarro, USA). The main technical details of all three tested gas analyzers are listed in Table S2.

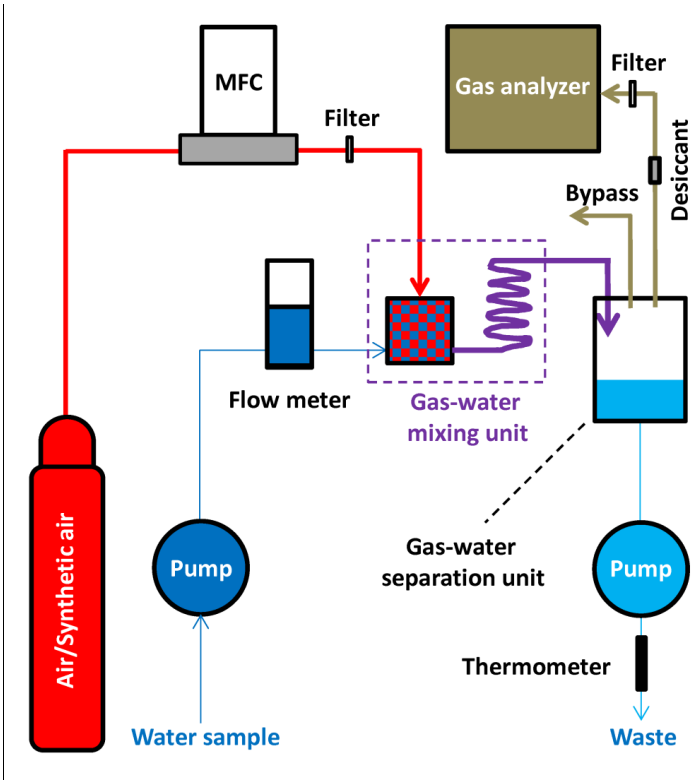

Fig. 1 Schematic design of the FaRAGE. The components include: Air tank containing compressed carrier gas (air or synthetic air) with a pressure regulator, a mass flow controller

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(MFC) for generating constant carrier gas flow, two peristaltic pumps for taking and discharging water, respectively, a flow meter for monitoring water sample flow, a gas-water mixing unit, a gas-water separation unit, a gas analyzer, and a thermometer for measuring water temperature at phase equilibration. A Teflon membrane filter is placed after the MFC and another is added before the gas analyzer to protect from being flooded. A desiccant is used to dry the gas flow to the gas analyzer (if Picarro isotopic analyzer is used). The red color marks the flow of carrier gas, dark blue line indicates the water sample, purple line shows the flow of gas-water mixture, the light brown line shows the flow of gas sample (after partial equilibration) and the light blue line depicts the water discharged back to lake. The thickness of the lines scales with the gas/water flow rates. The arrows show the flow directions.

2.2 Lab validation

The FaRAGE prototype was first tested intensively in the lab to determine both the equilibration ratio and response time. The equilibration ratio is defined as the percentage of the gaseous CH_4 concentrations at the outlet of the gas equilibrator in comparison to the equilibrium concentration (full gas-water equilibration). The equilibration ratio was established by measuring a range of CH_4 stock solutions (nano-to-micro molar dissolved gas concentrations). These standard solutions were prepared by adding different amounts of CH_4 into a 200 mL headspace of a 2 L Schott bottle filled with Milli-Q water. The exact dissolved CH_4 concentrations in these solutions were tested with the traditional manual headspace method: a 400 mL headspace was created in a 500 mL plastic syringe with nitrogen gas. The CH_4 concentration of the headspace gas was then measured using GasScouter G4301 (Picarro, USA). At the same time, CH_4 concentrations of these standard solutions were measured with the FaRAGE for at least 2 min and an average was calculated from more than 60 individual

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data points. For simplicity, we directly compared dissolved CH_4 concentrations measured using the two different methods, i.e., our equilibrator and manual headspace method.

The response time of the device was investigated by switching the water sample inlet between two water samples with different CH_4 concentrations. Triplicated measurements were performed. An exponential fit was applied to the concentration change curve and the response time was determined as time needed to reach 95% of the final concentration.

The effect of water-to-gas mixing ratio on equilibration ratio and response time of the device was investigated. By fixing the carrier gas flow rate to 1 L min^{-1}, the water-to-gas mixing ratio was varied from 0.04, 0.08, 0.12, 0.15, 0.24, 0.29, 0.36, 0.43 and 0.5 by adjusting the water sample flow rate. The effect of tube length on performance of the device was also examined by adapting 1, 2, 4.4 and 8.4 m Tygon tube onto the gas-water mixing unit. For all these tests, triplicated measurements of the equilibration ratio and response time were performed corresponding to different mixing ratios and the mean values were used for analysis.

Tests were performed to investigate the performance of the device when adapting to two other types of gas analyzers. As the equilibration ratio is unaffected by the model of gas analyzers, only response time was determined. This was done by fixing carrier gas and water sample flow rates to 1 and 0.5 L min^{-1}, respectively. The surplus gas was vented to the air as Ultraportable Los Gatos and Picarro G2132-i have a gas intake flow rate of only 500 and 25 mL min^{-1}, respectively. The effect of desiccant on response time of Picarro G2132-i was checked by measuring gas samples with and without a desiccant installed.

2.3 Field tests

Two lakes in Germany were chosen for field test. Lake Stechlin is a deep meso-oligotrophic lake with a maximum depth of 68 m and Lake Arend is a eutrophic lake with a

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maximum depth of 48 m. Pronounced CH_4 peaks in the epilimnion of Lake Stechlin have been previously reported that were measured with various methods (Grossart et al., 2011; Hartmann et al., 2018; Tang et al., 2014). This makes it ideal for our testing purpose. While CH_4 profiles at Lake Arend have never been reported, the metalimnetic oxygen minimum in the lake observed during summer (Kreling et al., 2017) renders it interesting for CH_4 profiling throughout the entire water column.

Due to the high potential of the FaRAGE for real-time *in situ* measurement of dissolved CH_4 concentrations, we explored potential field applications. These field tests included depth profiling of dissolved CH_4 concentrations in Lake Arend and Lake Stechlin and investigations of the horizontal distribution of surface dissolved CH_4 concentration across the entire Lake Stechlin. For the first application, a fast-response CTD (conductivity, temperature and depth) profiler (XR-620 CTD+, RBR, Canada) was mounted onto a winch with a 30 m long water hose (4 mm inner diameter) attached. The CTD profiler with hose was lowered down continuously at a constant speed (1 m min^{-1}). The exact depth and temperature of sampled water can be extracted from the CTD profiler by correcting for the travel time of water sample flow in hose. For the spatial mapping, a GPS antenna (Taoglas, AA.162, USA) was attached to the Picarro gas analyzer. The water intake was submerged 0.5 m below the water surface together with the CTD profiler and fixed to one side of the boat. The boat was driven at a constant speed of 5 km h^{-1}.

2.4 Theoretical background and data processing

The FaRAGE shares a similar working principle to the Weiss-type gas equilibrator described by Johnson (1999). The theoretical background and equations are provided in S3.

A simplified calculation is described by referring to the manual headspace method. In principle the gas-water mixture is analogous to the static headspace method with the final CH_4

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concentration in the gas phase assumed to reach a full equilibrium with that dissolved in the aqueous phase. Therefore, by specifying the mixing ratio of air and water, the total mass of CH_4 can be calculated by summing up the CH_4 in the headspace with the dissolved CH_4 (at equilibrium according to Henry's law, which is temperature and pressure dependent) in the aqueous phase and subtracting the mass of background CH_4 (from carrying gas with known concentration). The dissolved CH_4 concentration is then expressed as the volumetric concentration of total net mass of CH_4 in the dissolved phase in the given sample volume. A separated exemplary calculation sheet (excel file S5) is provided, which allows for correction for temperature and pressure change.

As the equilibration is only partially reached (< 92%), a correction coefficient is needed. This can be obtained by measuring the water samples with known concentrations across a large gradient. By referring to the results measured with the manual headspace method assuming full equilibration (Magen et al., 2014), an equation for precise correction of the measured CH_4 concentrations can be obtained.

3 Results and Discussion

3.1 Detection limit, equilibration ratio and response time

The FaRAGE is capable of achieving a high gas equilibration ratio. We observed a high correlation (R^2 = 0.999, p < 0.01) between the concentrations obtained using the traditional headspace method and those measured using the FaRAGE (Fig. 2a) across a wide range of dissolved CH_4 concentrations. The measurement accuracy is 0.5% (standard deviation in relation to final concentration) once a stable plateau was reached (Fig. 2b). The FaRAGE reaches a high equilibration ratio (63%) and ensures a rapid response. The determined response time $t_{95\%}$ is only 12 s when switching from low-to-high (nano-to-micro molar) dissolved CH_4 concentrations while the $t_{95\%}$ is a little longer (15 ± 2 s) when switching

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from high-to-low concentration (Fig. 2b). For the current design specifications that allow for a high equilibration ratio, the detection is theoretically limited by the sensitivity of the coupled gas analyzer. In the lab tests, a clear response was observed at least for CH_4 concentration at air saturation (16.9 nM inside the lab building). The measureable CH_4 concentrations should be at least sub-nM (10^{-10} mol L^{-1}) given the high performance of cavity-ring-down gas analyzers. This is more than sufficient for applications in inland waters where dissolved CH_4 concentrations are often above air saturation.

The response time for the FaRAGE results from two components: 1) the response of the gas analyzer to changes in gas concentration and 2) the physical gas-water exchange process. The response time for the gas analyzer is 5 s when the CH_4 concentration increases (Fig. S2). The FaRAGE itself needs < 10 s to reach 95% of the final steady-state concentration.

Equilibration ratio and response time of the FaRAGE is not sensitive to water-to-gas mixing ratio (Fig. 2c) but rather to the length of the tube in the gas-water mixing unit (Fig. 2d). Little effect was observed on the equilibration ratio in response to the increase of water-to-gas mixing ratio. Also, the increase of water-to-gas mixing ratio did not significantly change the response time of the device (on average 9 s for low-to-high and 13 s for high-to-low, respectively). This is in contrast to other types of equilibrators in which an increase of water-to-gas mixing ratio was found to result in a faster response (Webb et al., 2016). However, a sharp enhancement of equilibration ratio was observed due to the extended length of the tube for the gas-water mixing unit. A 91.8% equilibration ratio can be achieved by extending the tube length to 13 m while extended response times (low-to-high 17 s and high-to-low 47.5 s, respectively). Further enhancement of the equilibration ratio was not possible when a longer tube (e.g. 18 m) was used. The gas flow rate cannot be stabilized at 1 L min^{-1} due to the increased resistance in response to the further extension of tube length.

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As shown in Table S2 and Fig. S2, the fast response of the FaRAGE is partly due to the extremely fast response of the Picarro Gas Scouter. This makes it unfair to compare with other equilibrators in which different gas analyzers were used. Tests were performed by adapting the FaRAGE to two other greenhouse gas analyzers (Ultraportable Los Gatos and Picarro G2132-i) and the response times are listed in Table S3. Comparisons were made in Webb et al. (2016) and Hartmann et al. (2018) where both CH_4 and $^{13}\delta C\text{-}CH_4$ were measured using a Picarro G2201-i (Picarro, USA). Here we used a similar Picarro stable isotopic gas analyzer (Picarro G2132-i) and unified all previous reported response time τ to $t_{95\%}$ by applying the equation $t_{95\%} = 3\tau$. The comparison between up-to-date previous studies and this study (Table S4) demonstrated the extraordinary fast response relative to all existing gas equilibration devices. A 53 s response time was achieved when the FaRAGE was adapted to the Picarro G2132-i, which is significantly faster than others (171-6744 s).

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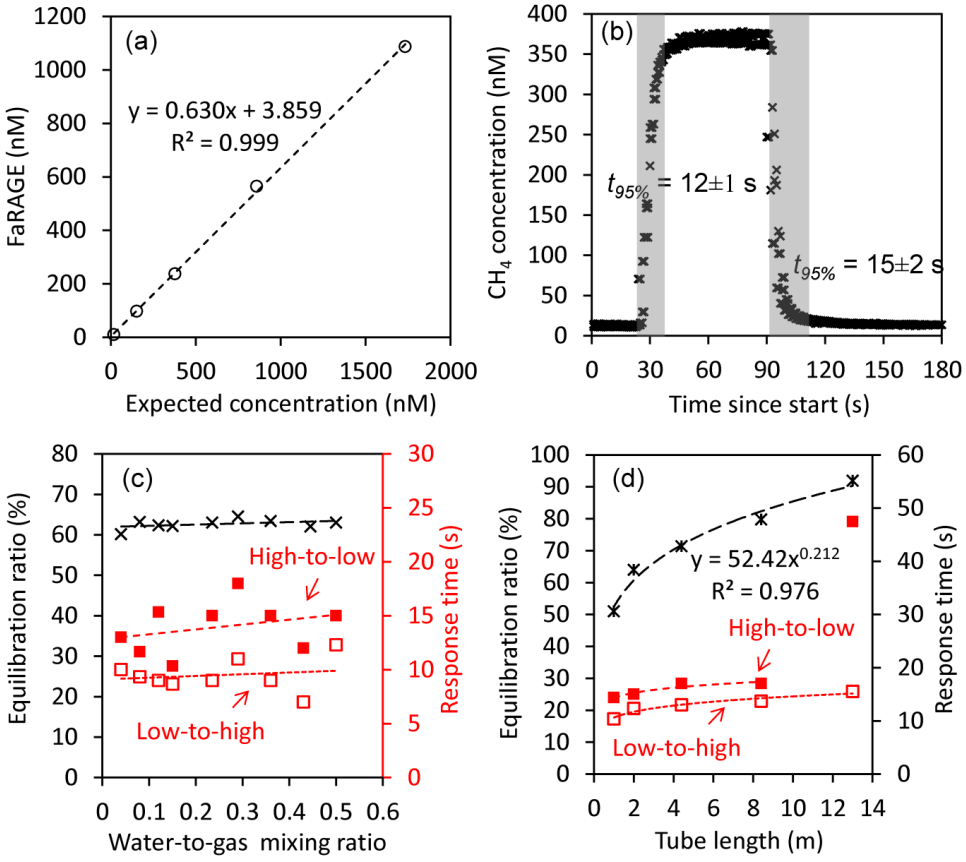

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279 **Fig. 2** Performance of the Fast-Response Automated Gas Equilibrator (FaRAGE). (a)
280 Exemplary correlation between measurements with the FaRAGE (with a 2-m tube in the gas-
281 water mixing unit) and expected concentrations measured using the manual headspace method.
282 (b) Exemplary response time of FaRAGE for low-to-high and high-to-low concentration
283 changes (with a 2-m tube in the gas-water mixing unit; water-to-gas mixing ratio 0.5).
284 Triplicated tests were performed and averaged response time was taken at the time point when
285 95% of the final concentration was reached. (c) Equilibration ratio and response time in
286 response to changing water/gas mixing ratio (with a 2-m tube in the gas-water mixing unit).
287 Black cross symbols are equilibration ratios, and low-to-high and high-to-low response times
288 are represented by red open and solid squares, respectively. (d) Equilibration ratio and

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response time in response to changing tube length of gas-water mixing unit (with a fixed water-to-gas mixing ratio of 0.5). Black cross symbols are equilibration ratios, and low-to-high and high-to-low response times are represented by red open and solid squares, respectively.

3.2 Depth profiles of dissolved CH_4 from multiple lakes

Good agreement was observed between depths profiles of dissolved CH_4 concentration measured using two different methods (Fig. 3). The observed occurrence of a maximum in the vertical profile of dissolved CH_4 concentration in the upper layer of Lake Stechlin (Fig. 3b) is consistent with previous observations (Grossart et al., 2011; Tang et al., 2014; Hartmann et al., 2018). In Lake Arend we also observed a CH_4 peak (Fig. 3a), although the overall concentration was lower. In contrast, with the headspace method the FaRAGE allowed for the localized CH_4 concentration maximum to be described at a high vertical resolution, similar to that obtained with more sophisticated membrane filter equilibrators (Hartmann et al., 2018; Gonzalez-Valencia et al., 2014). The FaRAGE was capable of resolving differences in dissolved CH_4 concentration in lake water at decimeter scales with ease. Whilst care should be taken to ensure the sampling hose moves smoothly and slowly through the water column, continuous profiling of a 20 m deep lake can be completed in 30 min. This is a big advantage since *in situ* CH_4 concentrations can vary at very short time scales (hours to days) subject to internal production, oxidation, weather conditions and etc. (cf. Hartmann et al. (2020)).

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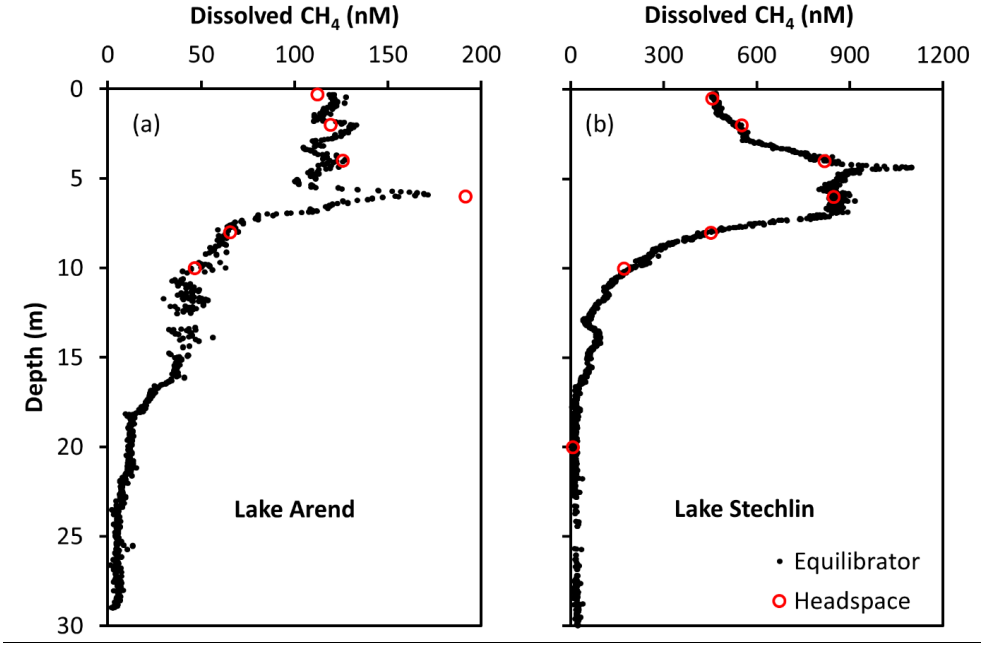

Fig. 3 Depth profiles of dissolved CH_4 concentration from two lakes in Germany: (a) eutrophic Lake Arend on June 17, 2019 and (b) meso-oligotrophic Lake Stechlin on July 23, 2019. Results from the headspace method are designated as red open circles and measurements using the FaRAGE are shown as solid black dots.

3.3 Resolving spatial variabilities of dissolved CH_4 concentrations

We confirmed the capability of the FaRAGE to operate continuously over a 7-h period without notable decreases in performance (Fig. 4a). Benefitting from its fast response rate, surface water CH_4 concentrations across the 4.52 km^2 Lake Stechlin was mapped with great detail within one day. During the cruise, 10 reference measurements were made at different times, which were consistent with nonstop online *in situ* measurements. The cruising survey demonstrated the capability of this device for resolving not just vertical dynamics of CH_4 in lake water, but also the potential for studying horizontal distributions of CH_4 across large distances, for instance large lakes and rivers. With a driving speed of 5 km h^{-1} and a response

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time of 12 s, a spatial resolution of 17 m can be achieved, which is sufficient for such a medium-sized lake. The relative higher dissolved CH_4 concentrations in the shallow littoral zone of Lake Stechlin (Fig. 4b) reflect higher CH_4 release from the local sediment.

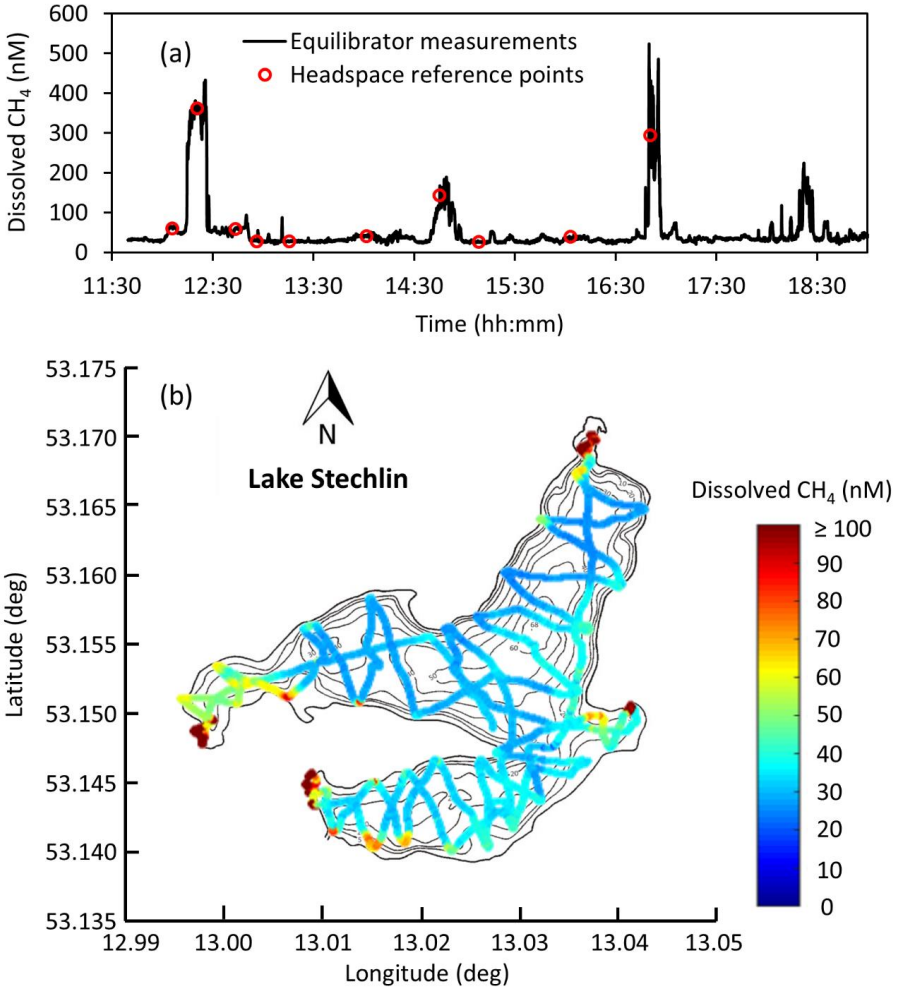

Fig. 4 Map of surface dissolved CH_4 concentration at Lake Stechlin. (a) Time series of 7-h continuous surface water CH_4 measurement on March 28, 2019. The reference headspace measurements are shown as red circles. (b) Spatial distribution of surface water CH_4 concentration is given on top of the lake's bathymetry. Colored symbols show CH_4

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concentration according to the color bar. Black lines show the outline of the lake with depth contours.

4 Comments and Recommendations

4.1 Adaptability to different gas analyzers

The reasons for the significantly shortened response time of the FaRAGE compared to other types of gas equilibrators are two-fold. While the working principle of the FaRAGE is based on the bubble-type (Schneider et al., 1992) and Weiss-type equilibrators (Johnson, 1999), a reduced headspace volume is adopted, which enhances the physical gas-water exchange. Another reason is the use of extremely fast-response gas analyzer (Picarro Gas Scouter 4301). It is a highly recommended combination for concentration measurement when the best time-wise performance is preferred due to its great mobility (Table S2). However, coupling to other Cavity-Ring-Down gas analyzers is also possible (Table S3). This feature enables a possibility to investigate stable isotopic nature of dissolved CH_4, which is important when sources of CH_4 need to be identified.

When a portable gas analyzer (Picarro Gas Scouter or Ultraportable Los Gatos) is used for measuring CH_4 concentration only, the gas equilibrator can be optimized for different application environments. The length of coiled tube for gas-water mixing can be adjusted to change the response time (Fig. 2d). For smaller lakes a higher spatial resolution can be obtained by shortening the equilibration tubing, which shortens the response time, and hence increases the spatial resolution, whilst maintaining an acceptable equilibration ratio (51% when tube length is 1 m). In environments with extremely low dissolved CH_4 concentrations, e.g. ocean waters, a longer gas-water mixing tube should be used to ensure a high gas equilibration ratio.

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To measure stable isotopic CH_4 in water, the sensitivity of the FaRAGE can be modified to better adapt to the choice of gas analyzer (e.g., when Picarro G2201-i or G2132-i is used). For example, high dissolved CH_4 concentrations (e.g. μM-to-mM range) can be measured with greater accuracy by increasing the flow rate of the carrier gas relative to the sample water flow, therefore diluting the CH_4 concentrations to the range of the gas analyzer. This can be particularly useful, for instance, when an instrument has an optimal precision at a low concentration range (1.8-12 ppm for Picarro isotopic gas analyzer) for $^{13}\delta$C-CH_4 measurements. By using pure N_2 gas or carrier gases (e.g. Helium and Argon) and corresponding gas analyzers, it would be possible to measure other dissolved gas concentrations, e.g. CO_2 can be measured simultaneously (CO_2 was tested in this study, but not shown for simplicity). In addition, benefited from the high equilibration ratio of this device (max. 91.8%), it would be possible to measure dissolved CH_4 (and other gases) close to equilibrium concentrations.

4.2 Uncertainties due to suspended solids, temperature and pressure change

The FaRAGE is proven to be resistant to suspended solids in freshwater lakes without having to use additional accessories. As shown in Fig. S3, apparent phytoplankton blooms were observed in the two studied lakes each with a high biomass (Chl-a > 30 μg L^{-1}) in the epilimnetic water. The measurements were unaffected, without any interruptions during measurements. As algal particles are a large component in freshwater systems, it is safe to claim the resistance of this device to suspended solids in such a system. However, care must be taken to avoid the water intake hose hitting the bottom sediment, which could cause blockage of the water hose.

The temperature and hydrostatic pressure could both change when water is pumped out through a water hose. To consider the temperature effect, a fast temperature logger is used

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(Fig. 1) which allows for corrections in calculation. Instead of using *in situ* lake temperature, the temperature measured at the gas equilibrator should be used where gas equilibration occurs. Our measurements found a minor effect when measuring surface waters but an apparent warming for hypolimnetic water in deep lakes. While a calibration can be done directly by taking water samples from multiple depths of the lake (e.g., Fig. 3) to consider this effect, one could make the calculation without taking many samples by applying temperature correction.

The temperature correction can be made by referring to the manual headspace method. The constant gas and water flow can be used as headspace and water volume, respectively. By considering the temperature and pressure effects on gas solubility, the dissolved CH_4 concentrations can be calculated (an example calculation sheet is provided in Table S5). The calibration curve can be established using the manual headspace measurements as standards. The final concentrations can be corrected for partial equilibration by applying the equation from the calibration curve (e.g., Fig. 2a). The response time should be deduced when calculating CH_4 depth profiles and spatial distributions, in addition to the time lag caused by pumping water samples by using an extended water hose.

4.3 Calibration, maintenance and mobility

The FaRAGE can be readily adopted for measuring other trace gases when coupled with other portable gas analyzers. Due to differences in gas solubility (Duan and Sun, 2003; Wiesenburg and Guinasso Jr, 1979), for each new gas, it would be necessary to establish the relative equilibration efficiency and response time, following the approach we outlined here for CH_4. Once set, a new calibration is only required when the tubing diameter or length is changed (when the old one is filthy due to biofilm growth). This can be done by referring to a number of known concentrations that covers a wide range (at least 5), e.g., taking water samples from different water depth of the lake or a gradient from littoral to pelagic zones.

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Once this full calibration is made, the calibration curve can be used for calculating the subsequent measurements. A one-point reference measurement should be performed between depth profiles or transects to check for apparent drifting. This can usually be done by taking one surface water sample from a lake for manual headspace measurement. Care should be taken when measuring in lakes with an anoxic hypolimnion where hydrogen sulfide is likely to accumulate. The performance of Cavity-Ring-Down gas analyzers can be potential affected by organics, ammonia, ethane, ethylene, or sulfur containing compounds (Kohl et al., 2019). At these sites, it is always recommended to take additional samples and measure them with traditional methods (e.g., with a Gas Chromatograph Analyzer).

The gas equilibrator should be carefully maintained. Replacement of parts is recommended at a monthly basis provided the device is heavily in use. They include bubble diffusor and the coiled gas-water mixing tube. In addition, to ensure the performance and prevent biofilm formation the gas-water mixing and separation units should be cleaned after use. Running with distilled or Milli-Q water would help to rinse the device and reduce the risk of biofilm development in the inner tubes. The performance of peristaltic pumps should be also regularly checked and the inner pump tubes need to be replaced to ensure a constant water flow.

The combination of FaRAGE with the Picarro Gas Scouter provides the most mobility. The system can be easily carried by one person and work in a small aluminum or inflatable boat with a maximum capacity of three people is possible. The device can also work in bad weather with additional measures based on protecting the gas analyzer from water damage by rain or flooding.

Code availability

Not applicable.

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Data Availability

An example calculation sheet (raw data of Fig. 2a) is provided as part of supporting information for device calibration and for temperature and pressure correction when calculating dissolved methane concentration. The full data sets associated with lab and field tests are available upon request.

Supplement link

From Copernicus.

Author contributions

SBX and WW proposed the idea and built the first prototype. LL improved the prototype and conducted lab and field tests. JW contributed to the field tests. AL contributed to the derivation of equations; HPG advised the development of the modified prototype. LL drafted the initial manuscript. All authors discussed the results and commented on the manuscript.

Competing interests

The authors declare that they have no conflict of interest.

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