Response to Anonymous Referee #1

Major comment: Given that gas analyzers were used that simultaneously measure both CH4 and CO2, I really think that the authors should show the system's performance for CO2 as well. In L363, the authors write that have CO2 data but focus on CH4 for simplicity, but this choice makes life much less simple for all the researchers that want to measure both CH4 and CO2, and therefore need to do all the CO2 testing themselves. Showing the CO2 results would make this study much more useful and applicable for a much wider community, and certainly render more citations to this paper. At the very minimum, include the CO2 performance tests in the supplementary information, but I'd rather see that the CO2 data is fully integrated in the paper, including the title.

Response: We totally agree with the reviewer that CO2 should be included in the manuscript. We integrated CO2 results in the manuscript and mention CO2 in the title as well. Please see the manuscript.

Minor comments:

Title: Include "carbon dioxide".

Response: We included CO2 in the revised manuscript.

L13. Freshwater lakes and reservoirs are aquatic systems, so that's a repetitive formulation. Simplify.

Response: We deleted "in freshwater lakes and reservoirs" in Line 13. Please see line 14-15 in the revision.

L48-49. This sentence omits that dissolved CH4 concentration is very strongly a function of methanogenesis, this should be added.

Response: We added "In addition to formation processes that lead to CH4 accumulation" in the revised manuscript. Please see line 61-62 in the revision.

L69. Not only phytoplankton, but also other microbial life forms. I suggest to reword to "biological".

Response: We agree that many microorganisms might be involved and thus the word "biological" is more appropriate. We made this change in the revised manuscript (Line 91 in the marked revision).

Figure 1. The heart of the equilibrator is the gas-water mixing unit, and the gas-water separation unit. These should be illustrated much more clearly, as a technical drawing, such that people can build them themselves. The pictures in the SI don't really help very much.

Response: We have replaced Figure S1 with a technical drawing in which the gas-water mixing unit and the gas-water separation unit were both described in detail.

L150-154. This text could go to the figure caption.

Response: This text has been removed from the main text and now is part of the figure caption. Please see line 172-176 in the revision.

L155. Use full word "Laboratory"

Response: We changed "Lab" to "Laboratory". Please see line 177.

L178. The 13 m tubing length is not mentioned in this list, but it's shown in the figures.

Response: Thanks for pointing this out. We added 13 m to the text. Please see line 204.

L193. Mention which these various methods were.

Response: We described explicitly what the methods are in the text. Please see line 218-219.

L204. From what I read, the depth from which peristaltic pumps can pump up water is physically limited to about 14 m. So how come you could pump water from 30 m depth?

Response: Pump head that the pump needs to overcome is related to vertical distance of the pump to water surface only and unrelated to the vertical position of water intake below the water surface. Thus, often there is only < 0.5 m pump head when the FaRAGE is placed in a small boat.

L210. Was the effect of boat speed on equilibration tested? Depending on the type and placement of water intake, bubbles might start to form when driving too fast.

Response: We did not try higher boat speed than 10 km h-1. The driving speed should be chosen according to the spatial resolution that the users would like to have. In our case, 17 m spatial resolution (spatially averaged) was achieved at 5 km h-1 driving speed corresponding to 12 s response time (see line 377-378). Bubbles were not observed at 10 km h-1 speed when the water intake is mounted on the side wall of the boat, 0.5 m below the water surface. Driving too fast is not recommended as it may harm the CTD probe as well.

L229. Please give this correction equation.

Response: The correction equations for CH4 and CO2 are shown in Fig. 2a and b, respectively.

L255. No details on statistical methods or tests are given, yet it says "significantly" here. Which test were performed, and what test statistics did they return?

Response: Thanks. Indeed, statistical tests were not performed. We changed this word to "substantially" and gave mean ± standard deviation. Please see line 289-290.

L260. Please rephrase, "while extended response times" is unclear. Fig.2, panel d. Change the right y-axis colour to red (such as in panel c). Also, why is the red point for 13 m tubing length not connected to the other red points, and how come that its response time is so much longer for high-to-low than for low-to-high, and also so much longer than for the 8 m tubing?

Response: Thanks. This is an incomplete sentence. We rephrased the sentence to "A 91.8% equilibration ratio can be achieved by extending the tube length to 13 m while extended response times are expected."

We have changed the right-handed y-axis color to red in panel d. Please see the new Fig. 3c-d. The red point for the 13 m tube length severely deviated from the well-fitted power function. The sharp increase in response time of high-to-low is a result of increased resistance of the gas-water mixture flow. The instability (abnormal sharp increase in response time) started from 13 m tube length and became unacceptable when the tube length is 18 m. Please see our explanations in line 294-302.

L373. I would be more careful with this statement. You can state that the equilibrator was not negatively affected by high phytoplankton density, but you haven't tested suspended sediment, so it's not sure it would work in e.g. in a turbid river. You can't exclude that for sustained operation in a turbid system, a filter in the water intake might be required.

Response: Thanks. Indeed, so far the device has never been tested particularly in turbid rivers with suspended sediment particles. We confined this statement to lakes without high sediment loads and also pointed out explicitly that a filtration unit for the water intake might be needed in turbid rivers. Please see line 427-433.

L383. Unclear what this sentence means, please rephrase.

Response: Thanks. They are indeed misleading and unnecessary, therefore, we have removed them from the manuscript.

L408. "potentially be" instead of "be potential".

Response: We corrected this in the text. Please see line 466.

Supporting information:

L32. Coupling instead of couple.

Response: We corrected this in the text (line 33).

Fig.S1. The pictures of the syringes don't show much, and don't help those who want to build their own. Use better pictures and include a technical drawing.

Response: We improved these by replacing them with technical drawings.

L120. This is not a complete sentence.

Response: Thanks. We rephrased this sentence. Please see line 127-128.

Fig.S3. Please also show the corresponding depth profiles of CH4 and CO2 at this sampling occasion, such that the reader can judge in how far phytoplankton density might have affected measurements.

Response: We added depth profiles of CH4 and CO2 to Fig. S3.

Response to Anonymous Referee #2

I have two remarks to be considered and few suggestions

1) I was very interested in the CH4 profiles and - while impressed by the high vertical resolution they achieve – I understood the authors tested their system in different lakes, covering some "typical" methane concentration range. Indeed they show two profiles: one from mesooligotrophic Lake Stechlin and one from eutrophic Lake Arend – I supposed they choose trophic state as a proxy for GHG content (Beaulieu et al., 2019). Thus I was confused seeing that Lake Arend, that they present as eutrophic, shows especially low methane, even lower than what they show for the meso-oligotrophic (Lake Stechlin). So what is the criterion behind this choice? Why picking an eutrophic lake that has even less methane than the meso-oligotrophic? Why not a typical eutrophic lake with methane building up below the oxycline during summer stratification? (They show a large literature on this issue in the Intro). For calibration the authors limited the upper range of methane to <2 micromoles L-1. While for high concentrations (microM to mM range) the authors suggest dilutions (line 357) but they don't deal with the problem in this paper. I think the range they show is fair enough, but they should clarify this "lower range test", directly relatable to surface waters but not to littoral methane rich or eutrophic lake bottom waters, AND change the sentence in the abstract "The FaRAGE is capable of continuously measuring dissolved CH4 concentrations in the nM-to-mM range" as it may be capable of that, but is not shown here.

Response:

Thanks for the reviewer's very detailed comments. We have such CH4 profiles with a typical anoxic hypolimnion in summer where CH4 was enriched to sub milli-molar high concentration. We have added these data into the revised manuscript. Please see Fig. 4c-d.

We further added additional laboratory tests for high CH4 concentration (e.g., 33 μM). The measured concentration is about 245 ppm with the FaRAGE. For the Gas Scouter 4301 we use, linearity can only be guaranteed up to 500 ppm. Adjustment of water-gas mixing ratio is needed for CH4 concentrations in the mM range. Therefore, we agree with the reviewer's suggestion. We rephrased the measurement range-related statement accordingly.

2) One big step forward the authors claim is the “extraordinary fast response relative to all existing gas equilibration devices“ (line 274). However, when their system is used with PICARRO G2132-1 + a desiccant to measure stable isotopes of gas species, it does not get that much faster than Hartmann 2018 “High Spatio-Temporal Dynamics of Methane Production and Emission in Oxic Surface Water” (line 107 of supplementary material). If I understand correctly then, what showed in table S4 is not entirely correct since their system response time when using PICARRO G2132-1 is obtained without any dryer. As far as I know, for using a PICARRO G2132-1 with a moisty flow a dryer is absolutely necessary. How humid is the water entering the analyzer? In case the authors think that a dryer is needed, they should change the table S4 and the statement in line 274 “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).”

Response:

Thanks for suggesting this. We did not have appropriate dryers for testing when the tests were performed. Therefore a dryer made from silicone beads was tested and a 150 s extension in response time was observed. But we are aware that this has been well tested in Webb et al (2016), in which they tested both Drierite and magnesium perchlorate ($Mg(ClO4)2$) as dryers. We reproduced their results below. They show both types of dryer have no effect on CH4 and CO2, except for a 1.5 min time delay on CO2 was caused by using Drierite.

Yes, the water vapor content of the gas sample flow is above 1% and should be dried before entering the PICARRO G2132-i. We are currently using the drying materials as suggested by Webb et al (2016) and they work quite well.

So the numbers in table S4 and the statement in line 274 are all valid. We understand it is not well clarified. We clarified this in the revised version of the manuscript. Please see the revision in line 113-117 in the supporting information.

Reference

Webb, J. R., Maher, D. T., and Santos, I. R.: Automated, in situ measurements of dissolved CO_2, CH_4, and δ^{13}C values using cavity enhanced laser absorption spectrometry: Comparing response times of air-water equilibrators, Limnol. Oceanogr.: Methods, 14, 323-337, https://doi.org/10.1002/lom3.10092, 2016.

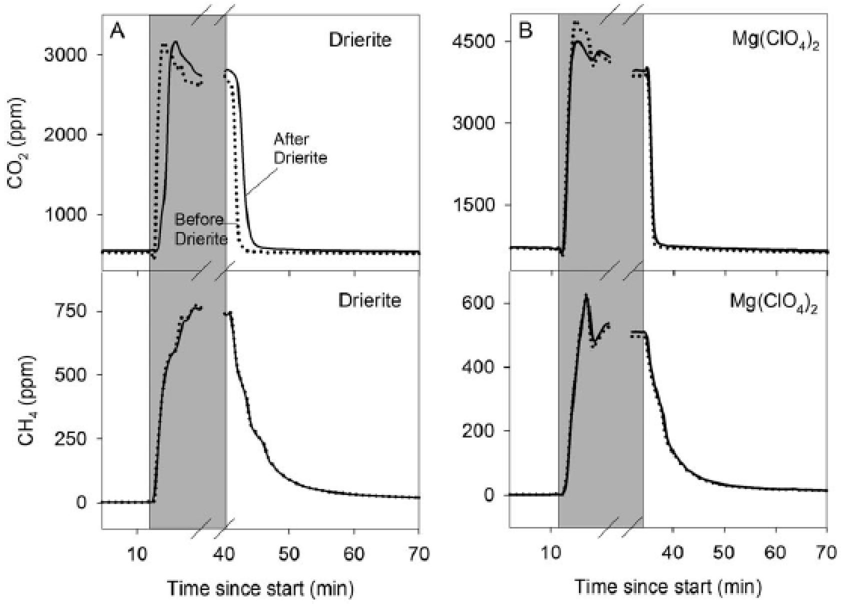

Fig. 2. Step experiments carried out to determine the effect of two desiccants, Drierite (**A**) and magnesium perchlorate ($Mg(ClO_4)_2$) (**B**), on the response times of CO_2 and CH_4 through a showerhead equilibrator. A time delay of 1.5 min was observed for CO_2 concentrations when Drierite was used as a desiccant. $Mg(ClO_4)_2$ had no effect on concentration response times and CH_4 remained unaffected by both desiccants.

Suggestions

When describing the set up the authors often refer to a “bubble unit”, which I suppose in the scheme (Fig.1) is called “gas-water mixing unit”. Consider harmonize.

Response:

Thanks for pointing this out. We checked this carefully and now the terms are used consistently throughout the manuscript.

Line 363- I think it would be better to rephrase the reason why CO2 is not shown. “for simplicity” for them or for the reader? Maybe they can mention which non-simple problems we meet when applying the system to CO2.

Response:

We have added CO2 as well and incorporated it throughout the full manuscript.

As to line 366 it is possible for the authors to use their system at sea enhancing the liquid to HS ratio to achieve low concentrations.

Response:

Thanks for suggesting this. We replaced one calibration point in Fig. 2, in which 5.5 nM dissolved CH4 concentration can be well characterized (with the 500 mL min-1 to 1000 mL min-1 water-gas mixing ratio). Indeed, lower concentrations in the ocean system can be also well measured by increasing water-gas mixing ratio.

I would recommend to make sure that the scientific community that works on GHG air-water exchange in oceans gets interested too (add to abstract and line 97?). For different reasons from the ones highlighted here for inland waters (to name one the massive lack of ground data to calibrate satellite infers) this system could be applied to voluntary observing ship programs to map CO2 and CH4 surface concentrations. In case the authors find a major obstacle to this it would be good to mention – making a suggestion for adapting their system for oceanographic applications.

Response:

Thanks for suggesting these. We agree that the FaRAGE can be a good method for studying GHGs from oceans. We added a sentence in abstract (line 35-36) and also in text (line 117-118).

Line 382- they mention how temperature should be corrected for the change along the hose- can give an example on how off can it get and does that mean to always measure temperature in situ at depth along with the profile?

Response:

We included an example in SI (Fig. S4) to show how much the water temperature (water flow inside the gas-water separation unit) can differ from the in situ water temperature. It's more important to monitor temperature of water flow inside the gas-water separation unit of the device. We recommend to installing a temperature logger in the device if someone would like to rebuild the device, but can only afford one thermometer.

Line 400 replace "filthy"

Response:

Thanks. We rephrased this sentence (see line 458).

Line 410- wouldn't a scrubber serve for that? Would that slow down the system RT?

Response:

Thanks. Yes, a copper scrubber can help to remove H2S from the gas samples (Malowany et al. 2015). According to Malowany et al. (2015), no time delay was observed when a copper scrubber was used. We also reproduced the figure they included in the publication. We added this reference to the revised manuscript (line 469-471).

Reference

Malowany, K., Stix, J., Van Pelt, A., and Lucic, G.: H2S interference on CO2 isotopic measurements using a Picarro G1101-i cavity ring-down spectrometer, Atmos. Meas. Tech., 8, 4075– 4082, https://doi.org/10.5194/amt-8-4075-2015, 2015.

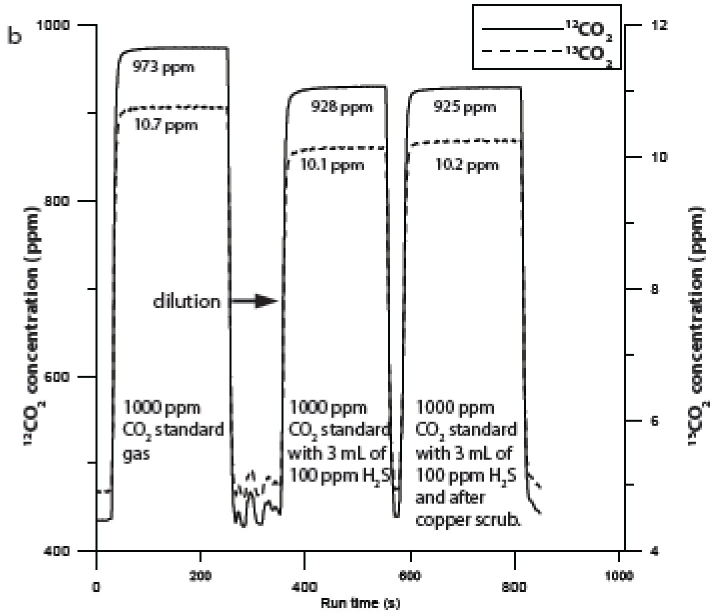

Figure 3. Change in the $^{12}CO_2$ and $^{13}CO_2$ concentrations with addition of H_2S to the standard gas. **(a)** Plot showing the percentage change in CO_2 concentration between gas with H_2S and gas scrubbed of H_2S. There is a visible increase in the $^{12}CO_2$ concentration and a decrease in the $^{13}CO_2$ concentration with addition of H_2S. The percentage decrease for $^{13}CO_2$ is significantly greater than the percentage increase for $^{12}CO_2$. **(b)** Plot showing the 1000 ppm standard CO_2 gas with the addition of 3 mL of 100 ppm H_2S and the subsequent response after the H_2S was removed with the copper scrub. There is a small, yet visible, increase in the $^{13}CO_2$ concentration and decrease in the $^{12}CO_2$ concentration when H_2S is removed.

References

Beaulieu, J.J., DelSontro, T. & Downing, J.A. Eutrophication will increase methane emissions from lakes and impoundments during the 21st century. Nat Commun 10, 1375 (2019). https://doi.org/10.1038/s41467-019-09100-5

A Fast-response automated gas equilibrator (FaRAGE) for continuous *in situ* measurement of ~~methane~~ CH_4 and CO_2 dissolved in water

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Abstract

Biogenic greenhouse gas ~~methane (CH_4)~~ emissions, e.g. of methane (CH_4) and carbon dioxide (CO_2) from inland waters contribute substantially to global warming. In aquatic systems, dissolved ~~CH_4- in freshwater lakes and reservoirs is~~ greenhouse gases are highly heterogeneous both in space and time. To better understand the biological and physical processes that affect sources and sinks of both CH_4 and CO_2 ~~in lakes and reservoirs~~, ~~its~~their dissolved ~~CH_4~~ concentrations need~~s~~ to be measured with ~~a~~ high~~est~~ spatial and 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 and CO_2 concentrations 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~~62.6% and a measurement accuracy of 0.5% for CH_4. A similar performance was observed for

dissolved CO_2 ($t_{95\%}$ = 10 s, equilibration ration 67.1%). 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 CO_2 and CH_4 concentrations in the nM-to-sub mM (10^{-9} - 10^{-3} mol L^{-1}) range with a detection limit of sub-nM (10^{-10} mol L^{-1}), when coupl~~ed~~ing 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. Additional tests demonstrated a sSimilarly good performance of FaRAGEthe equilibrator could be demonstrated for measuring dissolved CO_2.~~ FaRAGE ~~enables~~allows for the possibility of mapping dissolved concentration in a “quasi” three-dimensional manner in lakes and ~~The FaRAGE~~ provides an inexpensive alternative ~~for~~to other commercial gas equilibrators. It is simple to operate and suitable for continuous monitoring with a strong tolerance to suspended particles. While the FaRAGE is developed for inland waters, it can be also applied to ocean waters by ~~slightly~~ tuning the gas-water mixing ratio. The FaRAGE is ~~e easy adaptability~~ easily adapted to suit ~~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~~expanding the range of potential applications, including nitrous oxide and isotopic composition of the gases.~~e.g. measuring dissolved $^{13}\delta C$-CH_4 and $^{13}\delta C$-CO_2 and CO_2.~~

1 Introduction

Despite the well-established perception of inland waters as a substantial source of atmospheric methane (CH_4) and carbon dioxide (CO_2) (Bastviken et al., 2011; Cole et al., 2007; Tranvik et al., 2009), the magnitude of these greenhouse gases remains ~~large uncertainties~~ uncertain owing to the fact that ~~poorly constrained~~some key processes affecting CH_4 (e.g. bubbling) and CO_2 budget are still poorly constrained ~~sources and sinks~~ (Saunois et al., 2019). Most freshwater lakes and reservoirs are often oversaturated with CH_4 and CO_2 (relative to atmosphere) and their distribution are characterized by high spatio-temporal heterogeneity (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 both dissolved CH_4 and CO_2 ~~concentration in lake water~~ is a prerequisite for a better ~~budgeting~~ understanding of ~~sources and sinks~~production and loss processes of these gases in freshwater lakes.

The distribution of CH_4 and CO_2 in lakes is often characterized by pronounced vertical and horizontal concentration gradients, which ~~can occur either below or above~~often coincides with the position of the thermocline. In many deep stratified lakes, a sharp vertical gradient of CH_4, for instance, 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). In addition to formation processes that lead to CH_4 accumulation, the concentration of dissolved CH_4 is also regulated by losses due to oxidation and emission to the atmosphere (Bastviken et al., 2004; Juutinen et al., 2009). ~~Both rates can be~~~~Particularly the e~~Emission rates, in particular, are highly variable~~, particularly for the flux term~~ ~~as which is strongly affected~~~~it depends~~dependent ~~by~~ on turbulence ~~generated~~induced by wind ~~and~~ or convective mixing (Read et al., 2012; Vachon and Prairie, 2013). ~~In addition to the uneven v~~Vertical ~~CH_4~~ distributions of CH_4 and CO_2~~,~~ can be further confounded the contribution of littoral sediments which can result in distinct horizontal gradients of CO_2 and CH_4 ~~apparent horizontal gradients have been observed in lakes where littoral sediments are identified as a CH_4 source~~ (Murase et al., 2003). ~~This~~ Accounting for horizontal ~~CH_4~~ gradients ~~can also~~is therefore critical as lateral transport may account for ~~contribute to the~~ a proportion of the epilimnetic CH_4 peak observed in pelagic waters via ~~lateral transport~~ (Hofmann et al., 2010; Fernández et al., 2016; Murase et al., 2005; Peeters et al., 2019).

~~These spatial~~Spatial ~~pattern~~distributions of CH_4 and CO_2 in aquatic systems~~, however, are subject to temporal variation in response to~~ vary over time, particularly as factors which control their production, consumption and loss to the atmosphere fluctuate. ~~variable drivers as well as water motion. Nevertheless, dissolved CH_4 in lake water is not only featured with variable spatial patterns, it also changes at different time scales as most processes that contribute to the spatial heterogeneity are not always synchronized.The rise and fall of l~~L~~ake CH_4 concentration~~ Concentrations of CH_4 and CO_2 in lakes demonstrate ~~often show strong~~profound seasonality, ~~that are is~~ driven primarily by thermal stratification (Encinas Fernández et al., 2014) and phytoplankton dynamics (Günthel et al., 2019). While the build-up of hypolimnetic CH_4 storage is a slow process that is closely related to the development of lake hypoxia, ~~the~~ epilimnetic CH_4 and CO_2 ~~maximum~~ can be highly variable even at a daily basis as ~~it is~~they are strongly affected by phytoplankton dynamics (Günthel et al., 2019; Hartmann et al., 2020; Bižić et al., 2020). In addition, storms can act as another driver for short-term ~~CH_4~~ dissolved gas dynamics in the lake because ~~it~~ they often ~~leads~~ contribute to higher evasion rates caused by strong vertical turbulent mixing (Zimmermann et al., 2019) and enhanced horizontal transport (Fernández et al., 2016). While the seasonal patterns of dissolved CH_4 and CO_2 concentration in lake water seem recurrent and can be simulated (Stepanenko et al., 2016), the unpredictable effects of short-term ~~phytoplankton~~ biological dynamics and storm events can present a challenge in modeling ~~lake CH_4~~ the dynamics of greenhouse gases in lakes.

While there is an urgent need for resolving the spatio-temporal ~~variabilities~~variability of CH_4 in large water bodies (e.g. ~~deep, stratified~~ lakes), we recognize limitations in the available methodology. Like most gases in dissolved phase, CH_4 and CO_2 cannot be measured directly in water. Instead, a carrier gas (synthetic air or at air concentration) is added to achieve (full/partial) gas-water equilibration. The headspace gas sample is then measured with a gas spectrometer and the concentration of targeted gas can be calculated according to Henry's law (Magen et al., 2014). To save sampling effort, continuous gas equilibration devices have been developed, which generally can be classified ~~to~~ in four categories: 1) Membrane type (Schlüter and Gentz, 2008; Boulart et al., 2010; Gonzalez-Valencia et al., 2014; Hartmann et al., 2018) - gases are extracted from water ~~by~~ using a gas-permeable membrane; 2) Marble type (Frankignoulle et al., 2001; Santos et al., 2012) - gas exchange is enhanced by pumping water through marbles 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~~variability of dissolved CH_4 and CO_2 in inland waters~~lakes or~~ /~~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. Although FaRAGE is developed for inland waters, it can be also adapted for oceanographic applications. 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 and CO_2 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 CO_2 and CH_4 dissolved in water.

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

~~As concerns might arise from the availability of gas analyzer coupled to the FaRAGE, i~~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.

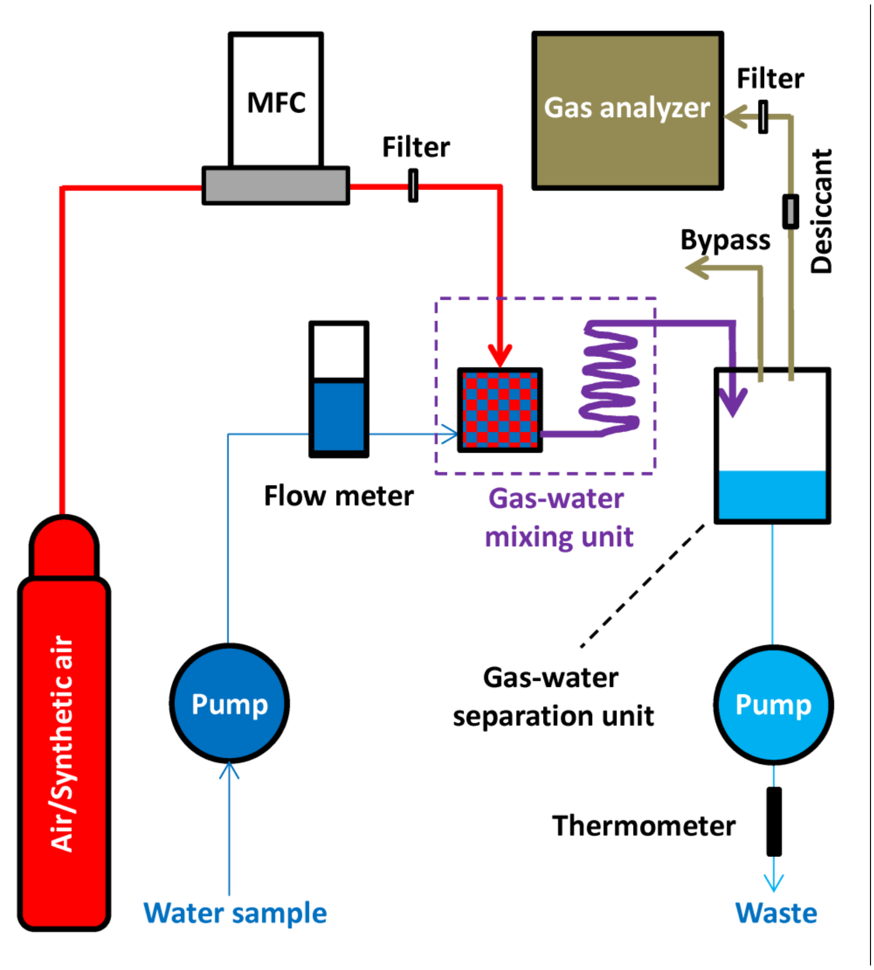

Fig. 1 Schematic design of the FaRAGE. The components include: Air tank containing compressed carrier gas (air or synthetic air) with a pressure regulator, a mass flow controller (MFC) for generating constant carrier gas flow, two peristaltic pumps for taking and discharging water, respectively, a flow 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 flowing 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 Laboratory validation

The FaRAGE prototype was first tested intensively in the laboratory to determine both the equilibration ratio and response time. The tests were performed for both CH_4 and CO_2 ~~as~~with a GasScouter G4301 (Picarro, USA), which measures both gases simultaneously. ~~For simplicity, only the results for one gas (CH_4) areis explained in the following text.~~ The equilibration ratio is defined as the ~~percentage~~ concentration of the ~~gaseous CH_4~~gas ~~concentrations~~ at the outlet of the gas equilibrator in comparison to the equilibrium concentration (full gas-water equilibration). The equilibration ratio was established ~~by~~ across ~~measuring~~ a range of ~~CH_4~~ stock solutions (nano-to-milli molar dissolved gas concentrations). These standard solutions were prepared by adding different amounts of either CH_4 or CO_2 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~~ gas concentration of the headspace gas was then measured using GasScouter G4301 ~~(Picarro, USA)~~. At the same time, ~~CH_4~~ dissolved CH_4 and CO_2 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 data points. We directly compared dissolved ~~CH_4~~ gas 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 of either CH_4 or CO_2. 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 and 13 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~~ Four lakes in Germany were chosen for field tests. Lake Stechlin is a deep meso-oligotrophic lake with a maximum depth of 68 m and Lake Arend is a eutrophic lake with a maximum depth of 48 m. Pronounced CH_4 peaks in the epilimnion of Lake Stechlin have been previously reported that were measured with ~~various~~ two different methods (manual headspace method in Grossart et al. (2011) and Tang et al. (2014); membrane-based gas equilibrator in Hartmann et al. (2018)). 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. ~~Another two~~ Additionally, we selected both eutrophic lakes with an anoxic hypolimnion ~~lakes~~ (Lake Großer Pälitz and Lake Zotzen), where CH_4 and CO_2 can accumulate ~~are both eutrophic with an anoxic hypolimnion~~ during the period of thermal stratification.

Measurements were conducted in these two lakes to test the capability of FaRAGE to measure ~~anoxic hypolimnetic~~ water with high dissolved CH_4 and CO_2 ~~accumulated~~concentrations.

Due to the high potential of the FaRAGE for real-time *in situ* measurement of dissolved CH_4 and CO_2 concentrations, we explored potential field applications. These field tests included depth profiling of dissolved CH_4 concentrations in ~~Lake Arend and Lake Stechlin~~ the four lakes and investigations of the horizontal distribution of surface dissolved CH_4 and CO_2 concentrations 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~~ gas 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, for instance, 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 the carrying gas with known concentration). The dissolved ~~CH_4~~ gas concentration is then expressed as the volumetric concentration of the total net mass of either CH_4 or CO_2 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 (Goldenfum, 2010).

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~~ dissolved gas ~~(alsoand CO_2)~~ 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~~1.000, $p < 0.01$) 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 and CO_2 concentrations. The measurement accuracy is 0.5% (standard deviation in relation to final concentration) once a stable plateau was reached (Fig. ~~2b~~2c). For CH_4, the FaRAGE reaches a high equilibration ratio (~~63~~62.6%) and ensures a rapid response. The determined response time $t_{95\%}$ is only 12 ± 1 s when switching from low-to-high (nano-to-sub micro molar) dissolved CH_4 concentrations while the $t_{95\%}$ is a little longer (15 ± 2 s) when switching from high-to-low concentration (Fig. ~~2b~~2c). 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~~5.5 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. Despite CO_2 (Weiss, R. F., 1974) is an order of magnitude more soluble in water than CH_4 (Wiesenburg and Guinasso, 1979), similar performances of the FaRAGE were observed when measuring dissolved CO_2. An equilibration ratio of 67.1% (Fig. 2b) was achieved with a fast response (Fig. 2d; $t_{95\%}$ = 10 ± 2 and 15 ± 2 for low-to-high and high-to-low, respectively) when a 2 m mixing tube was used.

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 the water-to-gas mixing ratio (Fig. ~~2c~~3a) but rather to the length of the tube ~~in installed~~attached after the gas-water mixing unit (Fig. ~~2d~~3c). ~~Little~~ A small effect, of the increased water-to-gas mixing ratio was also observed on the equilibration ratio~~ in response to the increase of water-to-gas mixing ratio~~. ~~Also, t~~The increase~~ of~~d water-to-gas mixing ratio did not ~~significantly~~ substantially change the response time of the device (~~on average~~ 9.5 ± 1.5 s for low-to-high and 13.9 ± 2.4 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 are expected (low-to-high 17 s and high-to-low 47.5 s, respectively). ~~The instability~~Increases in response time were notable when the tube-length exceeded 13 m and were considered excessive at a tube length of 18 m (Fig 3c-d).~~ (abnormal sharp increase in response time) started from athe 13 m tube length (Fig.~~

~~3c-d) and became unacceptable when tube length isreached 18 m.~~ Further enhancement of the equilibration ratio was thus 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. Equilibration ratio and response time were affected by the length of the tube after the gas-water mixing in a similar way as it was for CH_4 (Fig. 3b, d) with only one exception in the response time when the dissolved CO_2 concentration changed from high to low. The response time increased linearly ($R^2 = 0.910$, $p < 0.01$) from 11 s to 18 s in response to the increase of water-to-gas ratio from 0.04 to 0.5.

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-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 times 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~~ substantially faster than ~~others~~ previously reported (171-6744 s).

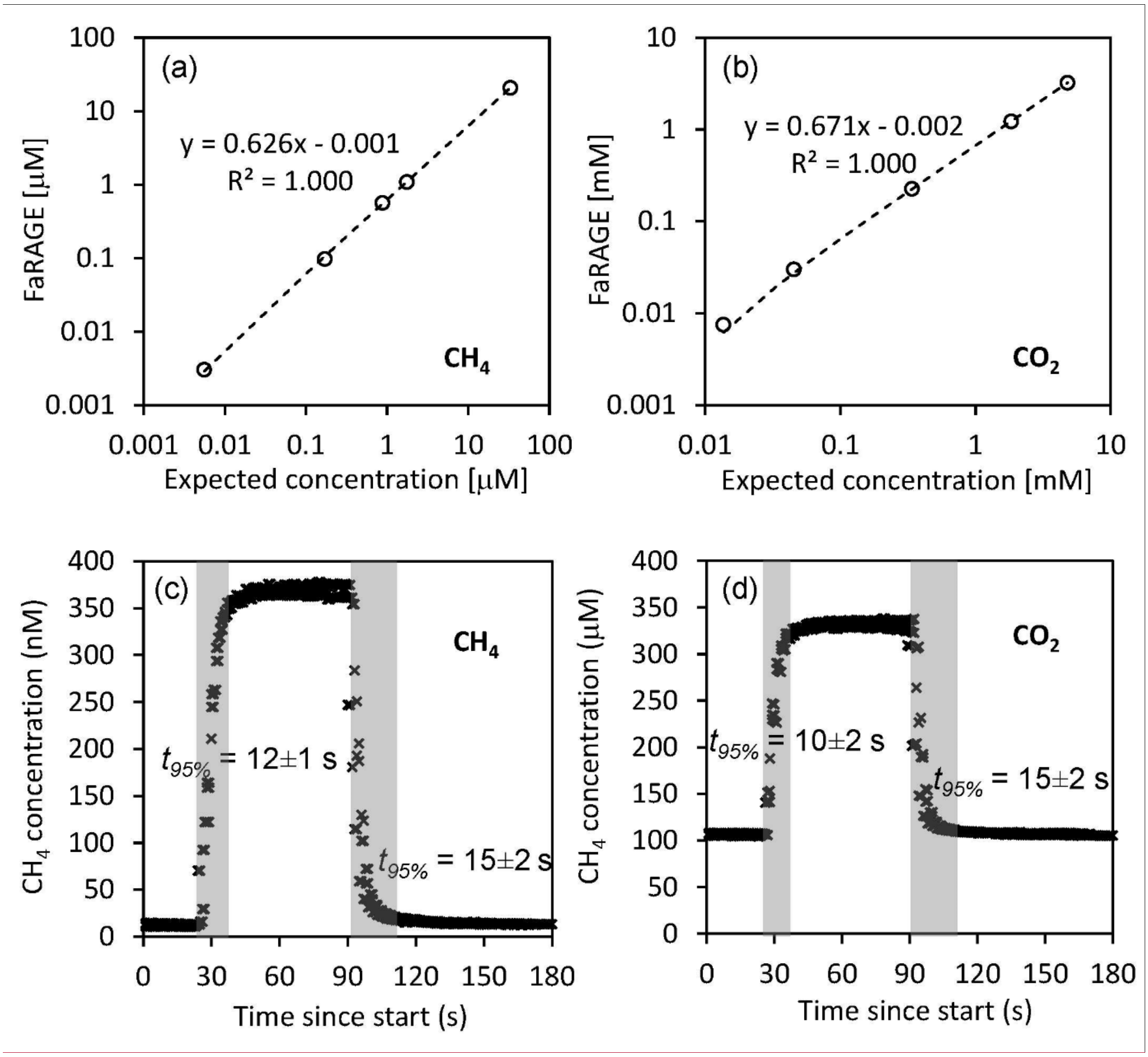

Fig. 2 Performance of the Fast-Response Automated Gas Equilibrator (FaRAGE with a 2-m tube in the gas-water mixing unit) for both dissolved CH_4 and CO_2. (a)-(b) Correction equations for dissolved CH_4 and CO_2, respectively by referring FaRAGE measurements to expected concentrations measured using the manual headspace method. The dashed lines show a linear fit and the equations are shown next to the lines. Note that in the two graphs both axes are log transformed. (c)-(d) Exemplary response time of FaRAGE for low-to-high and high-to-low concentration changes (water-to-gas mixing ratio 0.5). Triplicated tests were performed and the average response time was taken at the time point when 95% of the final concentration was reached.

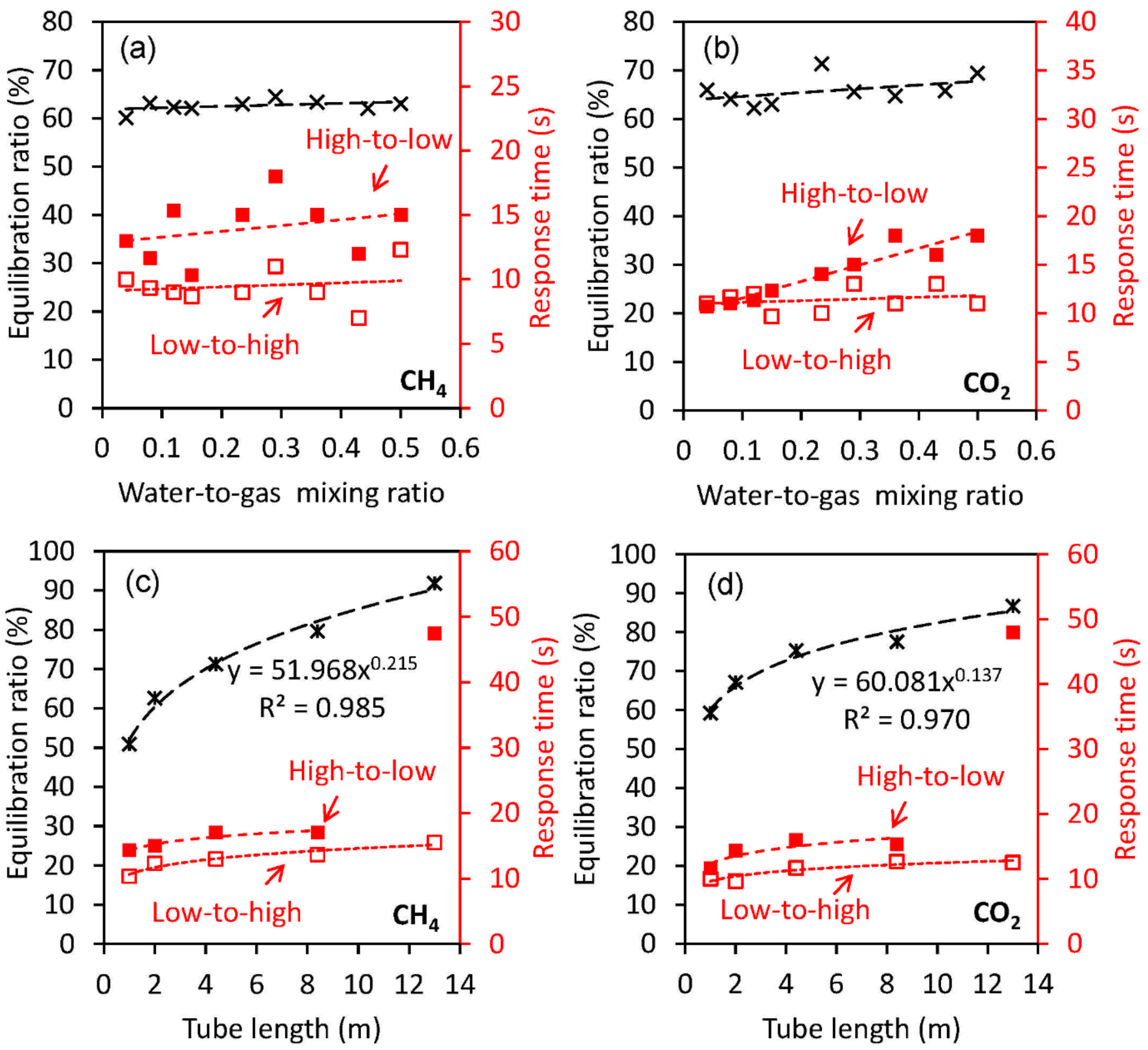

Fig. 3 Factors affecting performance of the gas equilibrator for both dissolved CH_4 and CO_2. (a)-(b) Equilibration ratio and response time in response to changing water/gas mixing ratio (with a 2-m tube in the gas-water mixing unit). Black cross symbols are equilibration ratios, and low-to-high and high-to-low response times are represented by red open and solid squares, respectively. (c)-(d) Equilibration ratio and 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 and CO_2 from multiple lakes

Good agreement was observed between depths profiles of dissolved CH_4 and CO_2 concentration measured using ~~two different methods~~the FaRAGE and the manual headspace method (Fig. ~~3~~4). ~~The observed~~ The ~~oO~~occurrence of a maximum in the vertical profile of dissolved CH_4 concentration in the upper layer of Lake Stechlin (Fig. ~~3b~~4a) 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~~4a) although the overall concentration was lower. The opposite was observed at Lake Großer Pälitz and Lake Zotzen (Fig. 4c) with an anoxic hypolimnion, where the dissolved CH_4 concentration was three orders of magnitude higher than ~~at~~in the epilimnion. Higher dissolved CO_2 (10^2 - 10^3 µM) was also observed in the hypolimnion of these two lakes (Fig. 4d) in comparison to ~~the~~ Lake Stechlin and Lake Arend (< 10^2 µM in Fig. 4b).

In contrast~~, with~~ to the headspace method, the FaRAGE allowed for ~~the localized~~profiles of CH_4 and CO_2 ~~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 and CO_2 concentrations in lake water at decimeter ~~scales~~ resolution 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)).

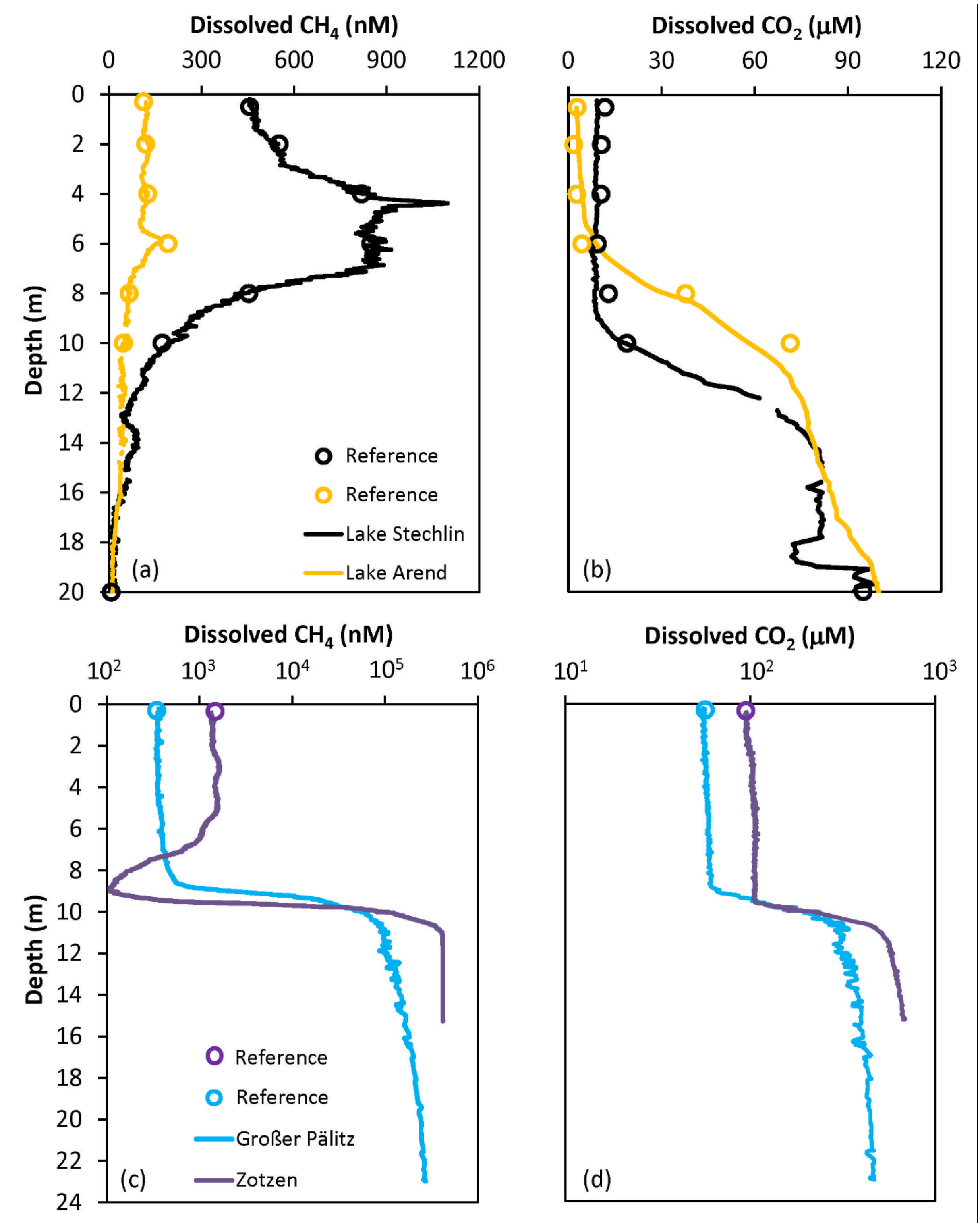

Fig. 4 Depth profiles of dissolved CH_4 and CO_2 concentration from a set of lakes in Germany: (a)-(b) Lake Stechlin and Lake Arend with an oxygenated hypolimnion in summer; (c)-(d) Lake Großer Pälitz and Lake Zotzen, both with an anoxic hypolimnion in October. Note the log transformed x-axis is used in (c)-(d). References using the headspace method are designated as red open circles and measurements using the FaRAGE are shown as solid lines.

3.3 Resolving spatial ~~variabilities~~variability of dissolved CH_4 and CO_2 concentrations

We confirmed the capability of the FaRAGE to operate continuously over a 7-h period without notable decreases in performance (Fig. ~~4a~~5a-b). Benefitting from its fast response rate, surface water dissolved CH_4 and CO_2 concentrations across the 4.52 km^2 Lake Stechlin ~~was~~ were mapped with great detail within one day (Fig. 5c-d). During the cruise, 10 reference measurements were made at different sites and 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 and CO_2 in lake water, but also the potential for studying horizontal gas 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 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.~~

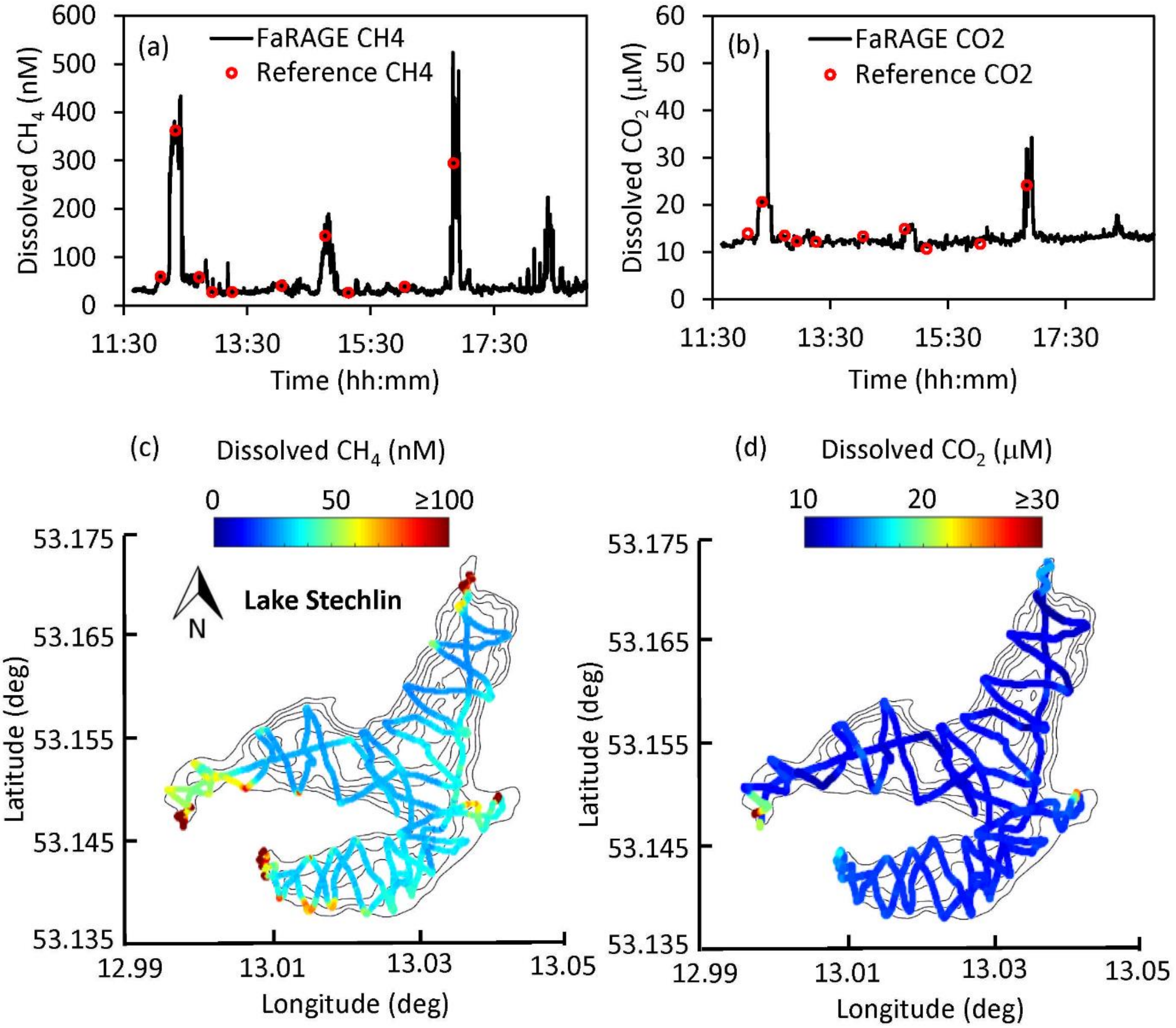

Fig. 5 Map of surface dissolved CH_4 concentration at Lake Stechlin. (a)-(b) Time series of 7-h continuous surface water CH_4 and CO_2 measurement on March 28, 2019. The reference headspace measurements are shown as red circles. (c)-(d) Spatial distribution of surface water CH_4 and CO_2 concentration is given on top of the lake's bathymetry. Colored symbols show CH_4 and CO_2 concentrations according to the color bars. 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~~ substantially 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 an extremely fast-response gas analyzer (Picarro Gas Scouter 4301). It is a highly recommended combination for ~~concentration~~ measurement of dissolved gasses 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 and CO_2, which is important when sources of CH_4 and CO_2 need to be identified.

When a portable gas analyzer (Picarro Gas Scouter or Ultraportable Los Gatos) is used for measuring CH_4 and CO_2 concentrations 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~~3c-d). 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.

To measure stable isotopic CH_4 and CO_2 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~~ e.g., Picarro G2201-i or G2132-i analyzers~~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 trace gas concentrations, e.g. ~~CO$_2$ can be measured simultaneously (CO$_2$ was tested in this study, but not shown for simplicity)~~N$_2$O. ~~In addition, benefited due tofrom 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 of suspended particle concentration in ~~freshwater clearwater~~ lakes without ~~a~~ high suspended sediment ~~load~~concentration~~systems~~, it is safe to claim the resistance of this device to suspended solids in such ~~a~~ systems. However, care must be taken to avoid the water intake hose hitting the bottom sediment, which could cause blockage of the water hose. An additional filtration unit for the water intake might be needed when the device is to be applied to turbid rivers.

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 (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, should be used. Our measurements found a minor effect when measuring surface waters but an apparent warming for hypolimnetic water in deep lakes (Fig. S4). ~~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 and CO_2 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-b). The response time should be deduced when calculating CH_4 and CO_2 depth profiles and spatial distributions, in addition to the time lag caused by pumping water samples by using an extended water intake 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 and CO_2. Once set, a new calibration is only required when the tubing diameter or length is changed (when the old one is ~~filthy~~ no longer usable 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. 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 potentially affected by ~~organics, ammonia, ethane, ethylene, or sulfur containing compounds~~H_2S ~~gas~~ (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).~~it is recommended to use a copper scrubber to remove H_2S from the gas samples (Malowany et al. 2015) and no time delay will be induced.

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~~ where 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.

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 led the project and 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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Supporting Information for

A Fast-response automated gas equilibrator (FaRAGE) for continuous *in situ* measurement of ~~methane~~CH_4 and CO_2 dissolved in water

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S1. Details of parts, gas analyzers and costs

To make the FaRAGE field deployable, parts were tightly packed into an aluminum box with a built-in power supply. The electric parts were separated from other parts containing water in the box by using a plastic board. Ports were well labelled on the right-handed side so that even somebody new to the system can work with it. To help interested readers rebuild the device, the two key components (gas-water mixing unit and gas-water separation unit) were shown in the detailed technical drawings (Fig. S1). The suppliers and costs for these parts were listed in Table S1. A total of 3,560 € was calculated for building the complete device excluding the costs for the power supply. As the expensive RBR temperature logger is not a necessity since we happen to have it in storage, a cheaper temperature logger can always be used. For example, a fast HOBO temperature logger (HOBO U12 with a Temperature probe TMC1-HD) is available for < 200 €. The total cost can be cut down significantly to < 3,000 €.

The FaRAGE is capable of couplinge with different greenhouse gas analyzers, depending on the research question and instrument availability. Three most widely used field-deployable gas analyzers were compared in Table S2 to provide a reference for readers when choosing a gas analyzer. They are GasScouter G4301 (Picarro, USA), Ultraportable Greenhouse Gas Analyzer (Model 915-0011, LosGatos Research, USA) and Picarro G2132-i isotope analyzer (Picarro, USA). We noticed Picarro 2201-i has been more often used, but our Picarro G2132-i is an equivalent instrument except that the module for isotopic CO_2 is not installed. The former two instruments measure CH_4, CO_2 and H_2O and the last one additionally measures stable isotopic CH_4. As shown in Table 2, clearly GasScouter G4301 is most suitable for field measurement of dissolved CH_4 concentrations due to its extremely high mobility. The built-in battery pack can support 8 h continuous measurements and the ability to amount GPS antenna offers the advantage in doing spatially-resolved measurements. The Picarro G2132-i isotope analyzer is most immobile because of it is heavy and relative high power consumption in addition to its particularly long time to warm up (30 min). However, Picarro G2132-i measures stable isotopic CH_4, while the other two instruments cannot. Care must be taken and a proper boat with stable power supply is needed in order to use Picarro G2132-i as a coupling unit for the FaRAGE.

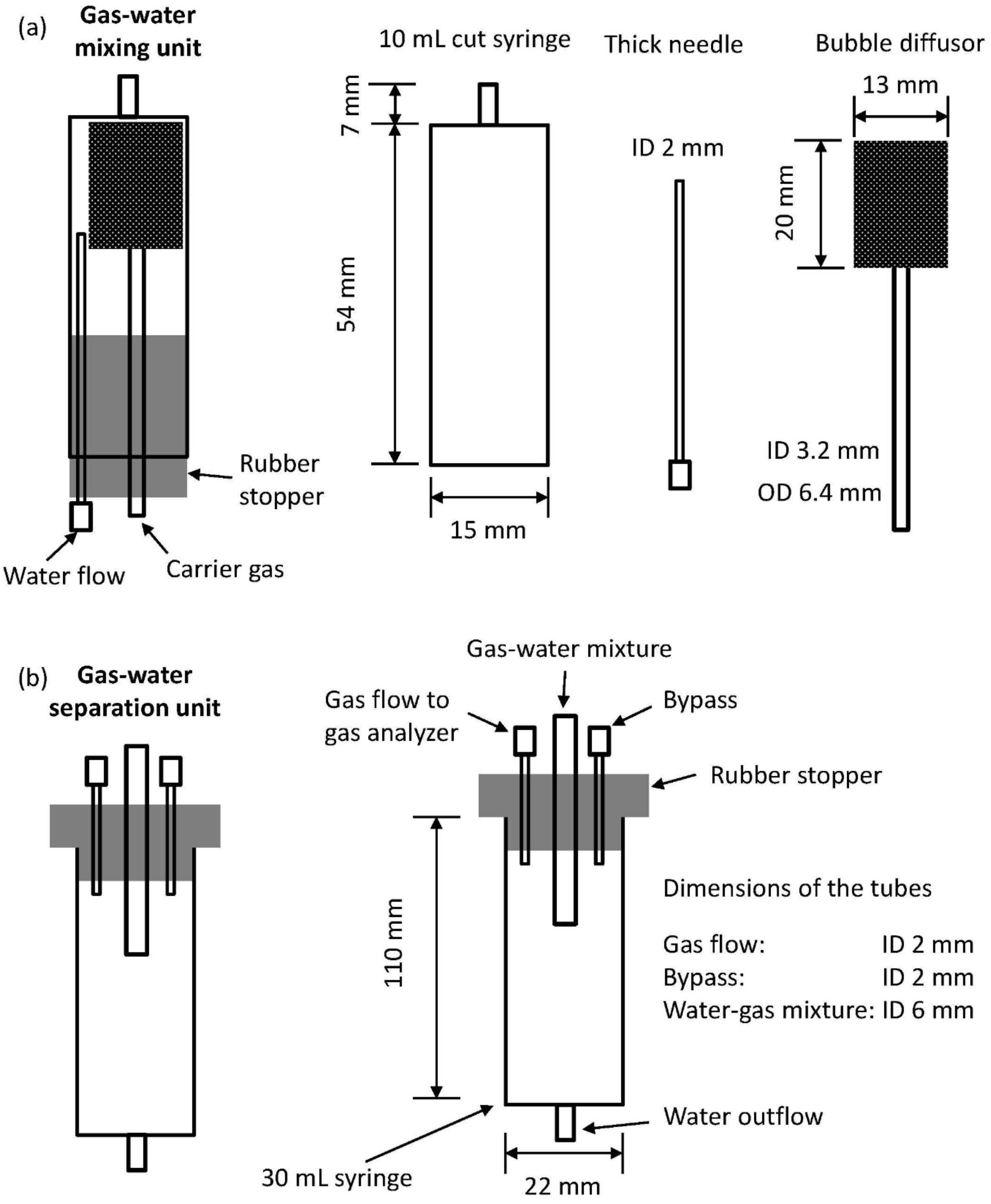

Fig. S1 ~~Assembled~~ Technical drawings of FaRAGE key components. ~~in an aluminum box with built-in power supply. Main parts and ports are marked on the figure. The power supply is made from a 100 Ah (12 V) Li-ion battery coupled with a power transformer that converts 12 V DC power to 230 V AC power.~~(a) Gas-water mixing unit and (b) gas-water separation unit. Note: ID and OD are the abbreviations of inner diameter and outside diameter, respectively.

Table S1. List of materials for parts of the FaRAGE prototype. Details on dimensions, model, producer/supplier and cost are provided.

Items	Dimensions	Model specifications	Producer/Supplier	Quantity	Cost
Diving tank	10 L	Pressure up to 230 bar	Atlantis Berlin	1	199 €
Pressure regulator		200 bar / 0 - 10 bar, HERCULES CK1401	Gase Dopp	1	59.98 €
Mass flow controller (for air)		SIERRA Model C50L SMART-TRAK	SCHWING Verfahrenstechnik GmbH	1	995 €
Flow meter (for water)		0.082-0.82 L min-1, 1355GAF3CBXN1AAA	Brooks Instrument GmbH	1	943.91 €
Peristaltic pump	9 x 11 x 16 cm	0-500 mL min-1, 24V/1A DC power	Purchased from Taobao, China	2	200 €
Temperature logger		Precision 0.001 °C, maximum 6 Hz measurement frequency, TR-1050	RBR, Canada	1	1,000 €
Tygon tube	3.2/6.4 mm in./out. Ø	Saint-Gobain Schlauch Tygon S3 E-3603 2.5bar	RS Components GmbH	15 m	68.78 €
Plastic syringe for mixing unit	5 mL	Cut to 3 mL, sealed with a rubber stopper	BD plastipak	1	1 €
Plastic syringe separation unit	30 mL	Sealed with a rubber stopper	BD plastipak	1	1 €
Plastic syringe for desiccant	50 mL	Filled with silicone beads, sealed with a rubber stopper	BD plastipak	1	1 €
Rain pipe			Toom	1	10 €
Bubble diffusor	12 mm Ø, 16 mm length	Pawfly 0.6 Inch Air Stone, UL266	Ebay	1	1 €
Teflon membrane filter	25 mm Ø	PTFE 0.2 µm	Lab Logistics Group GmbH	2	2 €
Tube connector	for 3.2-4.2 mm	LL male, barbed hose connection: PP, 10 pcs/pack | 2-1882	neoLab Migge GmbH	10	12 €
Aluminium box	38.3 x 57 x 37.5 cm	65 L, Stier aluminium box	Amazon	1	64.95 €
Total					3,560 €

Table S2. Summary of technical details for the three greenhouse gas analyzers tested in this study.

Analyzer	Gases	Gas flow rate	Cavity pressure	Measurement frequency	Concentration range	Precision	Response time	Dimensions	Weight	Power consumption	GPS Kit	Mobility
GasScouter G4301	CH_4 CO_2 H_2O	1 L min^{-1}	> 700 Torr	1 Hz	CH_4: 0-800 ppm CO_2: 0-3% H_2O: < 3%	CH_4: 3 ppb CO_2: 0.4 ppm	5 s	35.6 × 17.7 × 46.4 cm	10.4 kg	25 W, built-in Li-ion battery	Yes	Very high
Ultraportable Greenhouse Gas Analyzer 915–0011	CH_4 CO_2 H_2O	0.5 L min^{-1}	140 Torr	1 Hz	CH_4: 0.01-100 ppm CO_2: 1-2% H_2O: < 7%	CH_4: 2 ppb CO_2: 0.6 ppm	~10 s	17.8 x 47 × 35.6 cm	17 kg	70 W, on battery/AC power	No	High
Picarro G2132-i	CH_4 δ^{13}C-CH_4 CO_2 H_2O	25 mL min^{-1}	148 Torr	0.5 Hz	CH_4: 1.8-10 ppm high-performance mode; 10-1000 high-range mode CO_2: 200 - 2000 ppm guaranteed range H_2O: <2.4 % guaranteed range	CH_4: 5 ppb + 0.05 % of reading (12C); 1 ppb + 0.05 % of reading (13C) CO_2: 1 ppm + 0.25 % of reading (12C)	~30 s	43.2 x 17.8 x 44.6 cm	27.4 kg	205 W, AC power	No	Fair

Note: 1) GasScouter G4301 does not use a vacuum pump to maintain a stable cavity pressure and the gas flow rate should be stable but slightly above/below the recommended value.

2) All gas analyzers are sensitive to liquid-phase water, therefore a hydrophobic filter is normally placed before the gas intake to protect instrument from being flooded.

3) According to Picarro, interference can occur for concentrations of H_2O and CO_2 well above normal ambient levels, as well as other organics, ammonia, ethane, ethylene, or sulfur containing compounds.

S2. Re-evaluation of response time of gas analyzers

While response time for each gas analyzer has been provided by its manufacturer (Table S2), a large difference was found when they were re-evaluated (Fig. S2). Picarro GasScouter has the fastest response to concentration increase, in comparison to four-fold and eight-fold slower response for portable Los Gatos and Picarro G2132-i, respectively. All three gas analyzers were seen longer response time when concentration changed from high to low. The Picarro GasScouter still has the best performance compared to the other two.

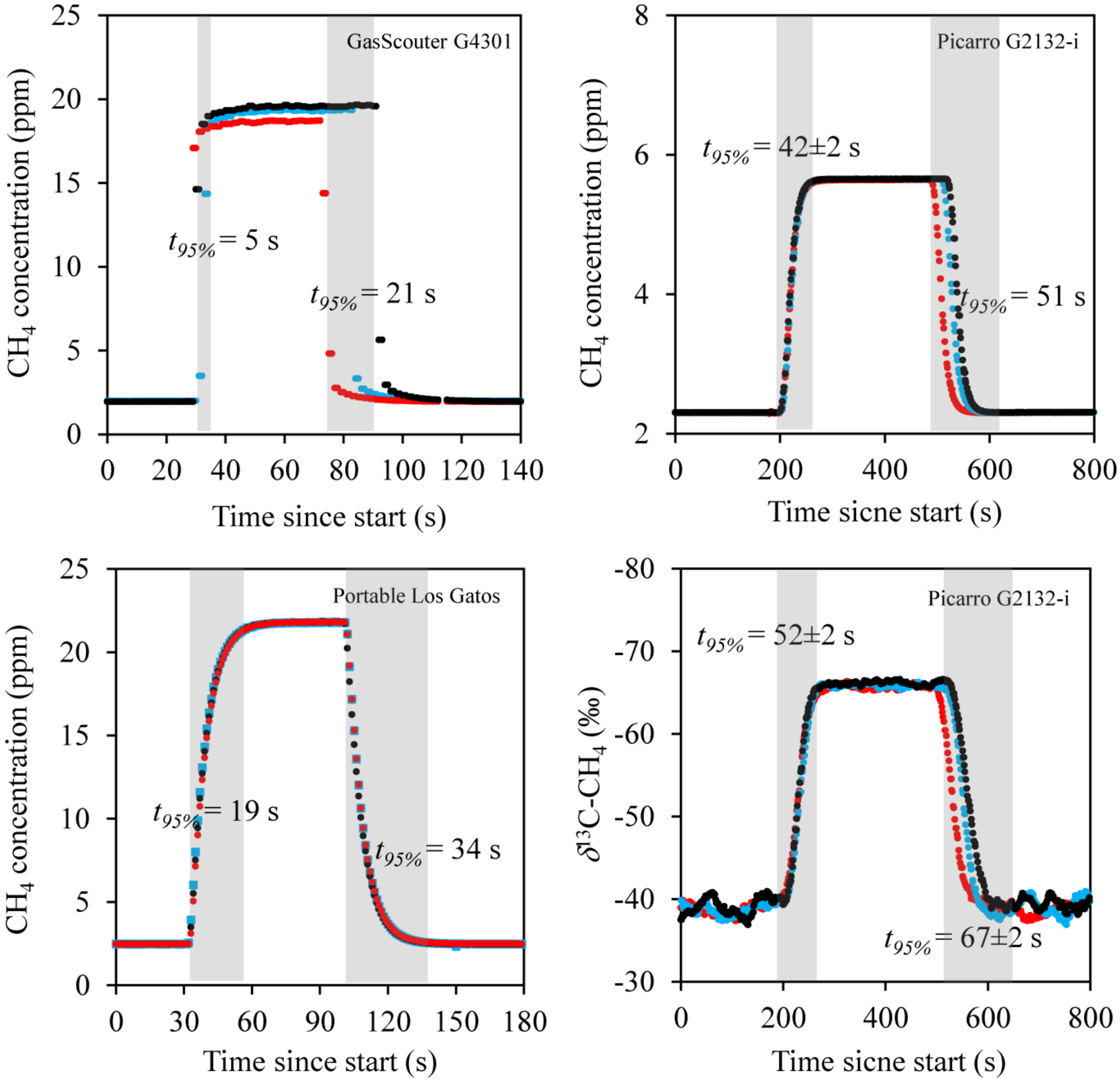

Fig. S2 Response times of gas analyzers. Triplicated measurements were performed. Low-to-high and high-to-low concentration changes were investigated. The response time was determined by taking the time when 95% of final concentration was reached. For δ^{13}C-CH_4, 30 s moving average data was used.

S3. Theoretical background

With the present design of the **Fast-Response Automated Gas Equilibrator (FaRAGE)**, a continuous dynamic gas-water mixing occurs and the carrier gas is partially equilibrating with the CH_4 dissolved in water sample. The gas composition reaching the gas analyzer depends on equilibration time and flow rates. The equilibration between the carrier gas and the water sample during flowing through the FaRAGE depends on the concentration difference between the gas stream (C in µmol L^{-1}) and the dissolved (aqueous) concentration in the sample water (C_a):

$$\frac{dC}{dt} = k \times (\frac{1}{HRT} C_a - C) \qquad (1)$$

Where H is the temperature-dependent Henry constant (mol L^{-1} atm^{-1}), R the universal gas constant (8.31 J mol^{-1} K^{-1}), T is temperature (K) and k (s^{-1}) is an exchange coefficient. The equilibrium gaseous concentration $C_{eq} = \frac{1}{HRT} C_a$ corresponds to the headspace concentration of a fully equilibrated water sample. k is expected to depend on the relative flow rates of gas and water as well as on the flow regime and mixing of both phases in the FaRAGE. For an initial concentration of CH_4 in the carrier gas C_{ini}, the time-dependent concentration during the passage through the equilibrator is:

$$C(t) = \left(C_{ini} - C_{eq}\right)e^{-kt} + C_{eq} \qquad (2)$$

After a device-specific partial equilibration time t_e, the CH_4 concentration in the carrier gas has changed to C_{pe}, which is measured by the gas analyzer

$$C_{pe} = C(t_e) = K\left(C_{ini} - C_{eq}\right) + C_{eq} \qquad (3)$$

With $K = e^{-kt_e}$ being a device-specific coefficient, which can be obtained by calibrating the FaRAGE with at least one water sample of known dissolved concentration (C_{eq}) through:

$$K = \frac{C_{pe} - C_{eq}}{C_{ini} - C_{eq}} \qquad (4)$$

The equilibrium headspace concentration of CH_4 in the water sample and the corresponding dissolved concentration can be estimated from the initial and final carrier gas concentration as:

$$C_{eq} = \frac{1}{HRT} C_a = (KC_{ini} - C_{pe})/(K - 1) \qquad (5)$$

For a high flow rate of the carrier gas, the response time of the system to changing dissolved concentrations at the sample intake is predominantly determined by the gas venting rate, i.e. by the total volume of carrier gas that is in contact with the water sample, divided by the volumetric gas flow rate (cf. level two model of Johnson (1999)), as well as by the response time of the gas analyzer.

Table S3. Response times when adapting to different gas analyzers. Tests were performed with a water/gas mixing ratio of 0.5. Triplicates were made and mean values are shown here.

Gas analyzer	**Treatment**	**$t_{95\%}$ response time (s)**		
		CH_4	**CO_2**	**$^{13}\delta$C-CH4**
Gas Scouter G4301	Low-to-high	13	6	-
	High-to-low	13	6	-
Ultraportable Greenhouse Gas Analyzer 915-0011	Low-to-high	34	32.3	-
	High-to-low	37	30	-
Picarro G2132-i	Low-to-high	53	53	53
	High-to-low	65.3	60.7	65.3

Note: Response time for Picarro G2132-i was determined without using a desiccant. ~~Repeated tests were done to examine the effect of desiccant. The response time was extended by 150 s when the 20 mL desiccant was used.~~A desiccant should be used to keep the moisture content in gas samples < 1%. Drierite and magnesium perchlorate ($Mg(ClO_4)_2$) are recommended for such a purpose due to their high performance. It was shown by Webb et al. (2016) that both types of dryer had no effect on CH_4 and CO_2, except for a 1.5 min delay in response time for CO_2 when using Drierite.

Table S4. Comparison of response times for simultaneous measurement of dissolved CH_4 and $\delta^{13}C$-CH_4 in water from previous studies using different devices (after Webb et al., 2016, Hartman et al., 2018) compared with response times in this study. Response time was unified here to $t_{95\%}$ to allow for meaningful comparison. The $t_{95\%}$ values were taken from literature by applying $t_{95\%} = 3\tau$ and the mean were used.

Device	$t_{95\%}$ response time (s)	Study
Weiss-type (small)	6744	Li et al. (2015)
General oceanics	6123	Webb et al. (2016)
Shower head	4971	Webb et al. (2016)
Weiss-type (large)	3600	Rhee et al. (2009)
Marble	2679	Webb et al. (2016)
Bubble-type	2034	Gülzow et al. (2011)
Liqui-Cel (medium)	1251	Webb et al. (2016)
Liqui-Cel (small)	531	Webb et al. (2016)
Liqui-Cel (large)	351	Webb et al. (2016)
Liqui-Cel (small) in vacuum mode	171	Hartmann et al. (2018)
Combined Weiss-type with bubble-type	53	This study

S4. The depth profiles of phytoplankton biomass at Lake Arend and Lake Stechlin

As in most freshwater lakes phytoplankton is a large component of suspended solids in water column, the effect of phytoplankton biomass on the performance of the gas equilibrator was evaluated. Fig. S3 shows ~~that~~ the presence of ~~in both study lakes~~ high phytoplankton biomass (represented by Chl-a) within the surface 20 m water depth in the both study lakes.

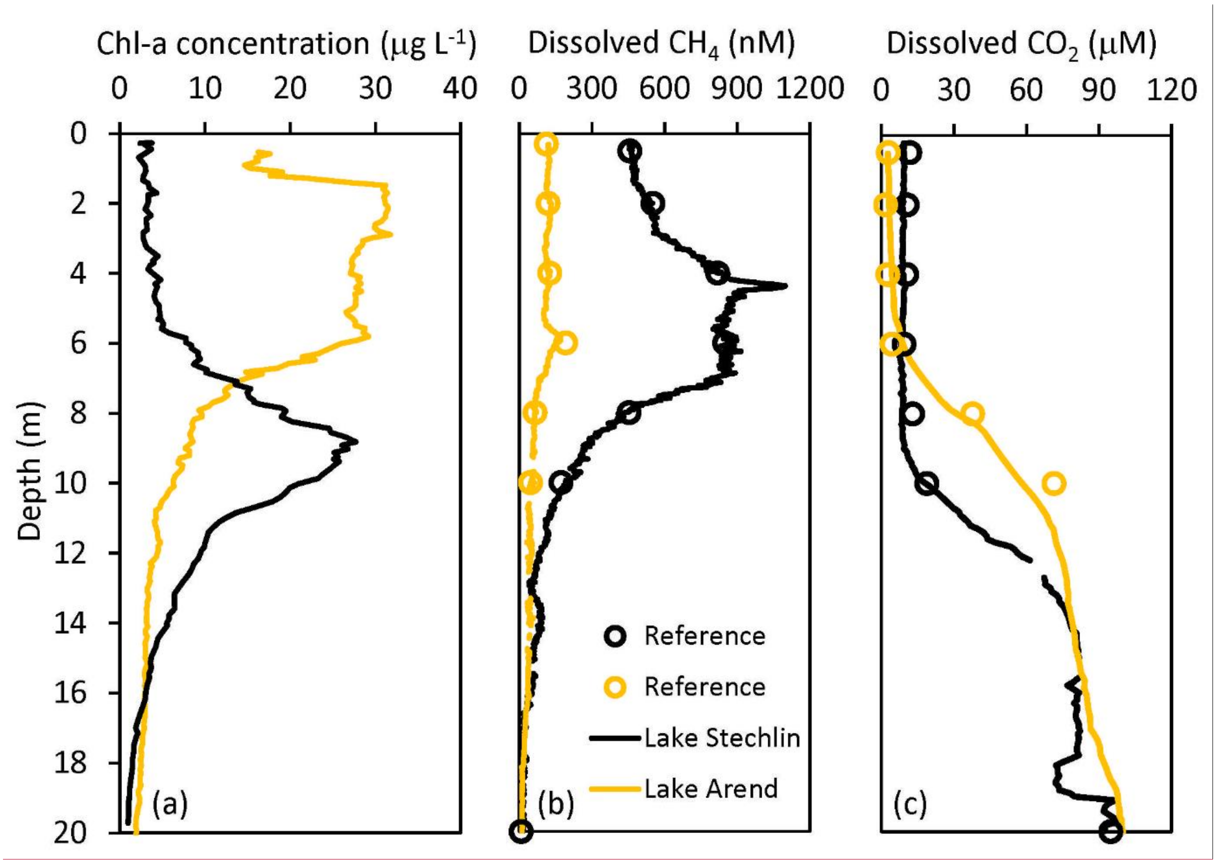

Fig. S3 Depth profiles of Chlorophyll-a (Chl-a) at Lake Arend and Lake Stechlin on June 17 and July 23, 2019 with (b)-(c) dissolved CH_4 and CO_2 profiles. The profiles were measured using a BBE FluoroProbe (Moldaenke, Germany) simultaneously with dissolved gas profiles.

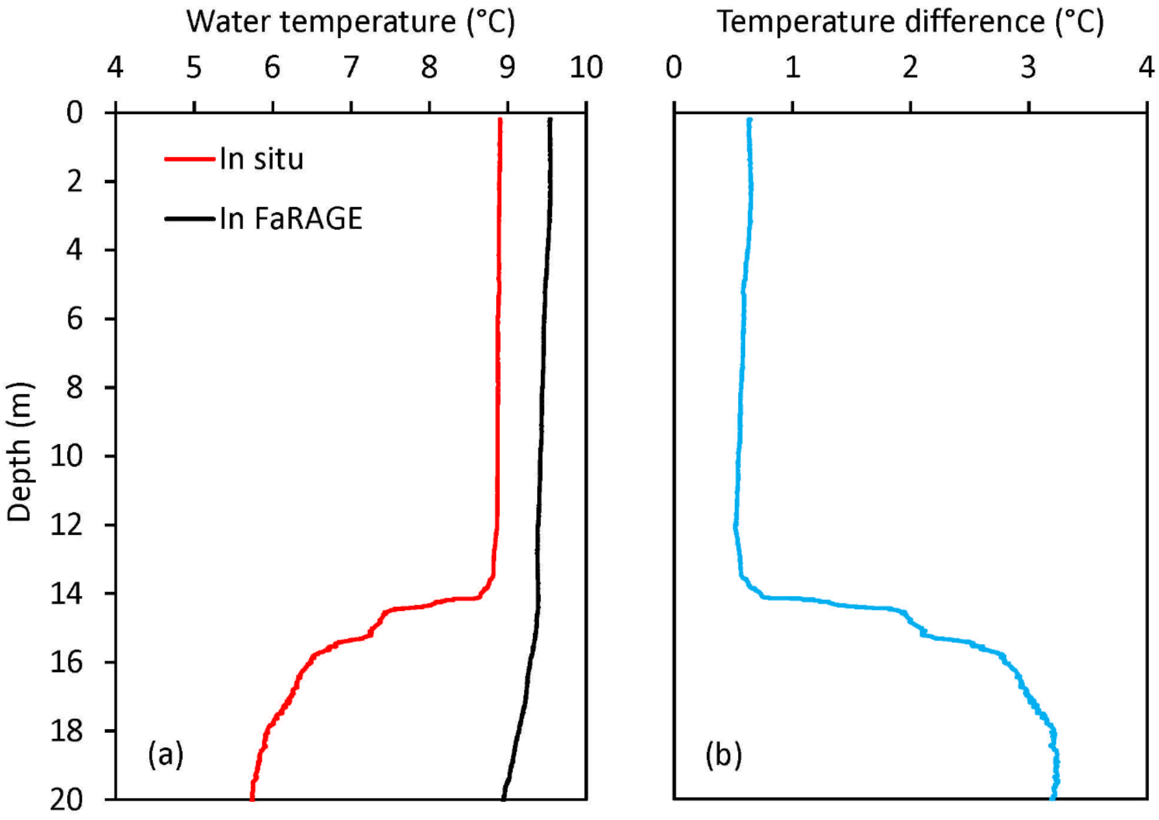

Fig. S4 An example of altered depth profile of water temperature at Lake Stechlin in autumn 2019. (a) Comparison of in situ water temperature (red line) with water temperature measured in the FaRAGE (black line). (b) The difference between the two temperature measurements (In FaRAGE - In situ).

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