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A Fast-Response Automated Gas Equilibrator (FaRAGE) for continuous in situ measurement of 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 coupling 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.

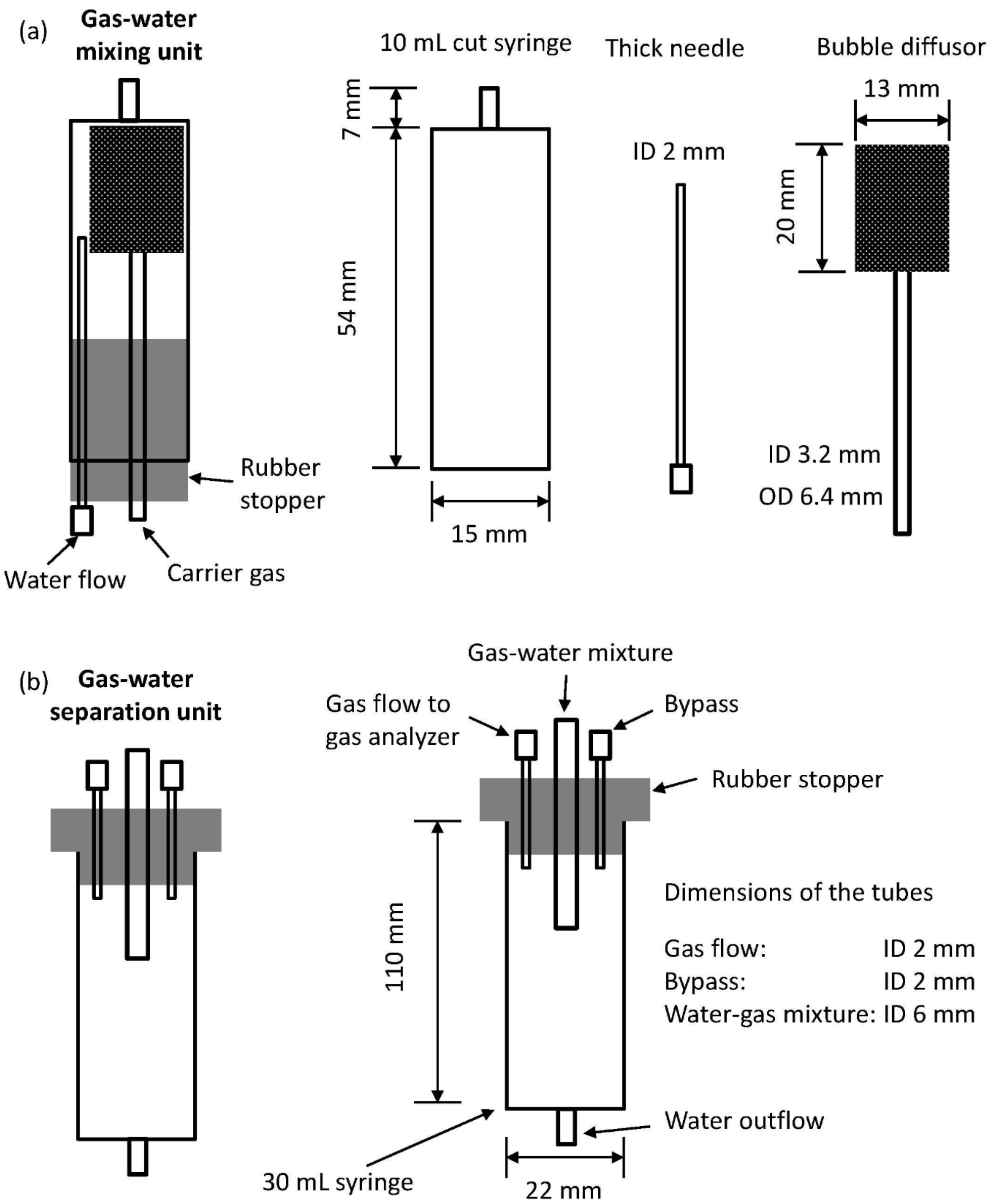

Fig. S1 Technical drawings of FaRAGE key components. (a) Gas-water mixing unit and (b) gas-water separation unit. Note: ID and OD are the abbreviations of inner diameter and outside diameter, respectively.

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	10 mL	Cut to 9 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 drierite, 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 $\delta^{13}C$-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.

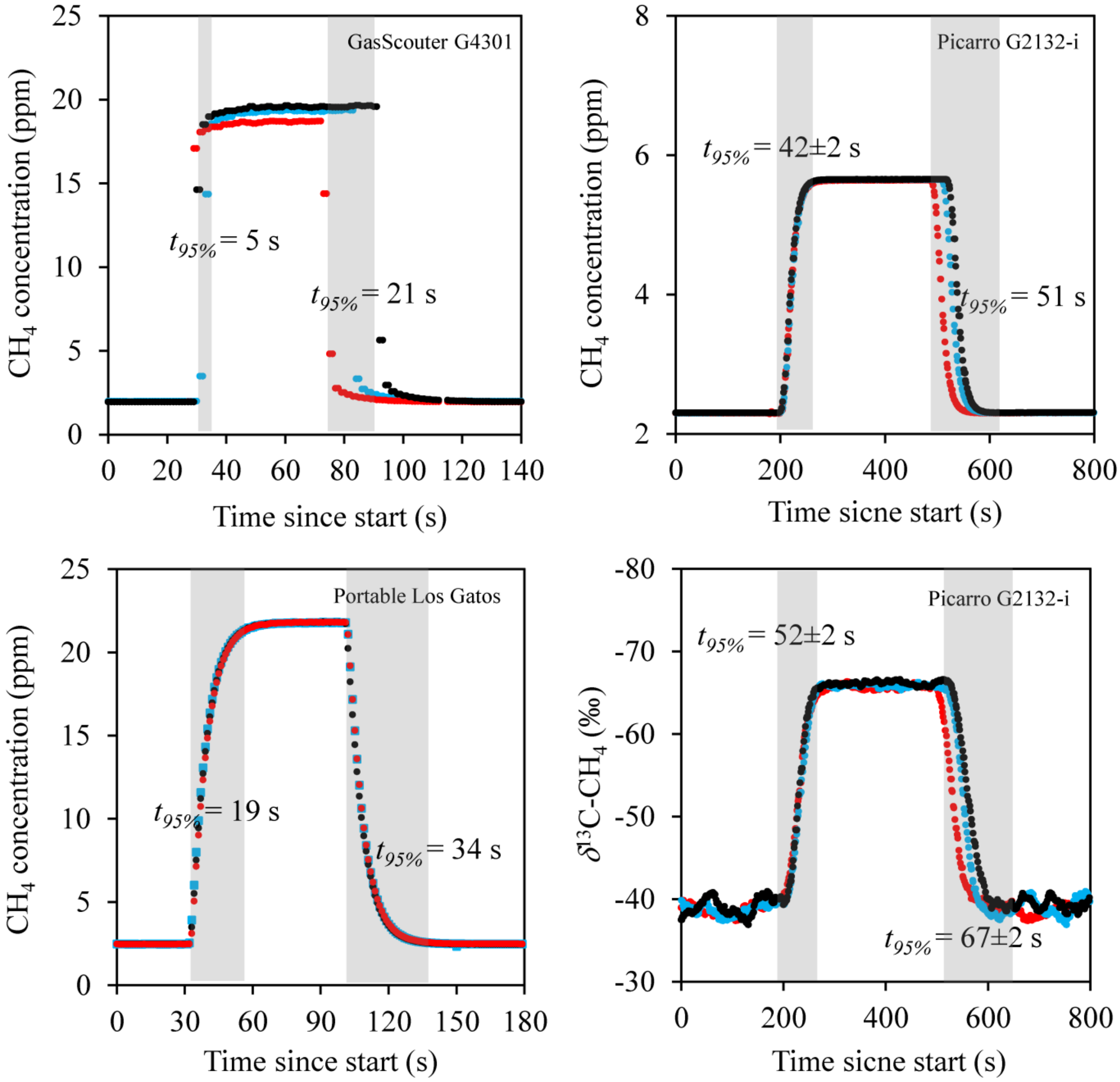

Fig. S2 Response times of gas analyzers. Triplicated measurements were performed. Low-to-high and high-to-low concentration changes were investigated. The response time was determined by taking the time when 95% of final concentration was reached. For $\delta^{13}C$-CH_4, 30 s moving average data was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

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

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:

$$K = \frac{C_{pe}-C_{eq}}{C_{ini}-C_{eq}} \tag{4}$$

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:

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

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. 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 the presence of high phytoplankton biomass (represented by Chl-a) within the surface 20 m water depth in the both study lakes.

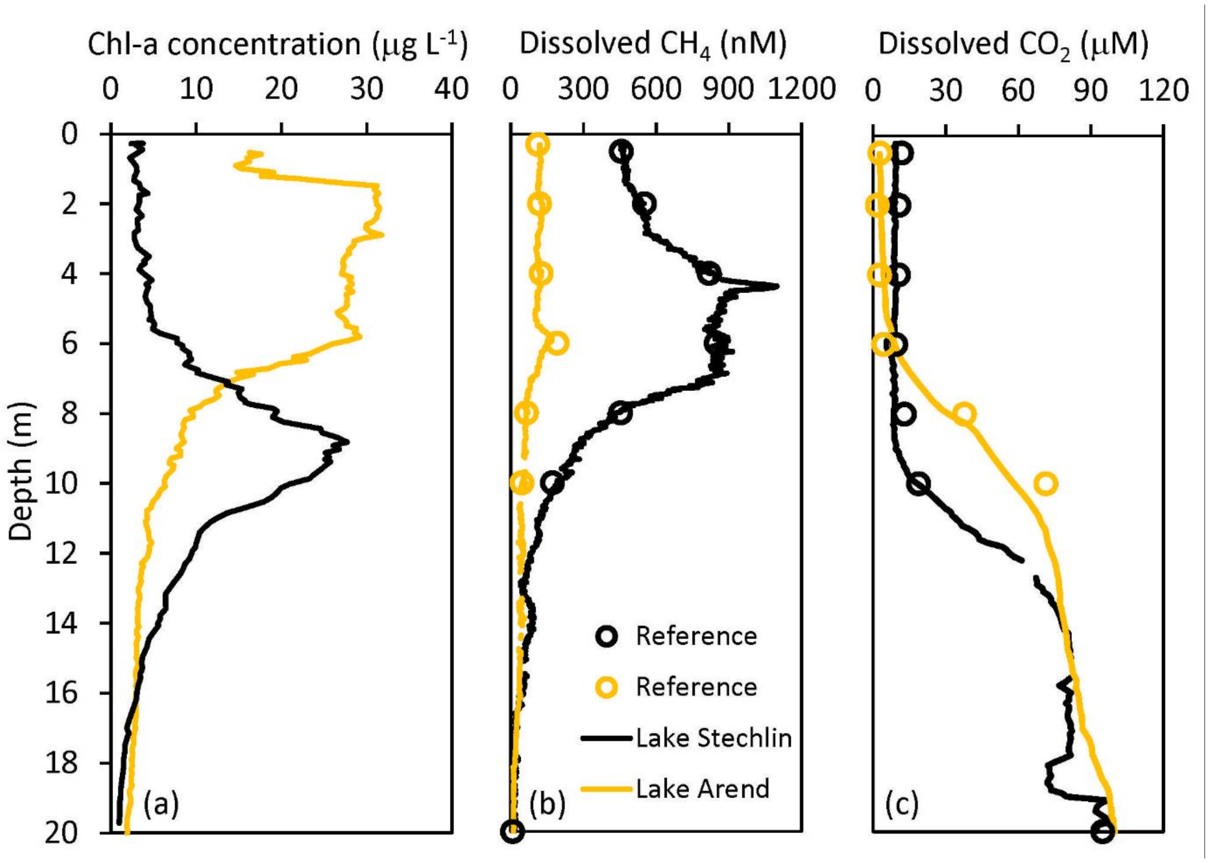

Fig. S3 Depth profiles of Chlorophyll-a (Chl-a) at Lake Arend and Lake Stechlin on June 17 and July 23, 2019 with (b)-(c) dissolved CH_4 and CO_2 profiles. The profiles were measured using a BBE FluoroProbe (Moldaenke, Germany) simultaneously with dissolved gas profiles.

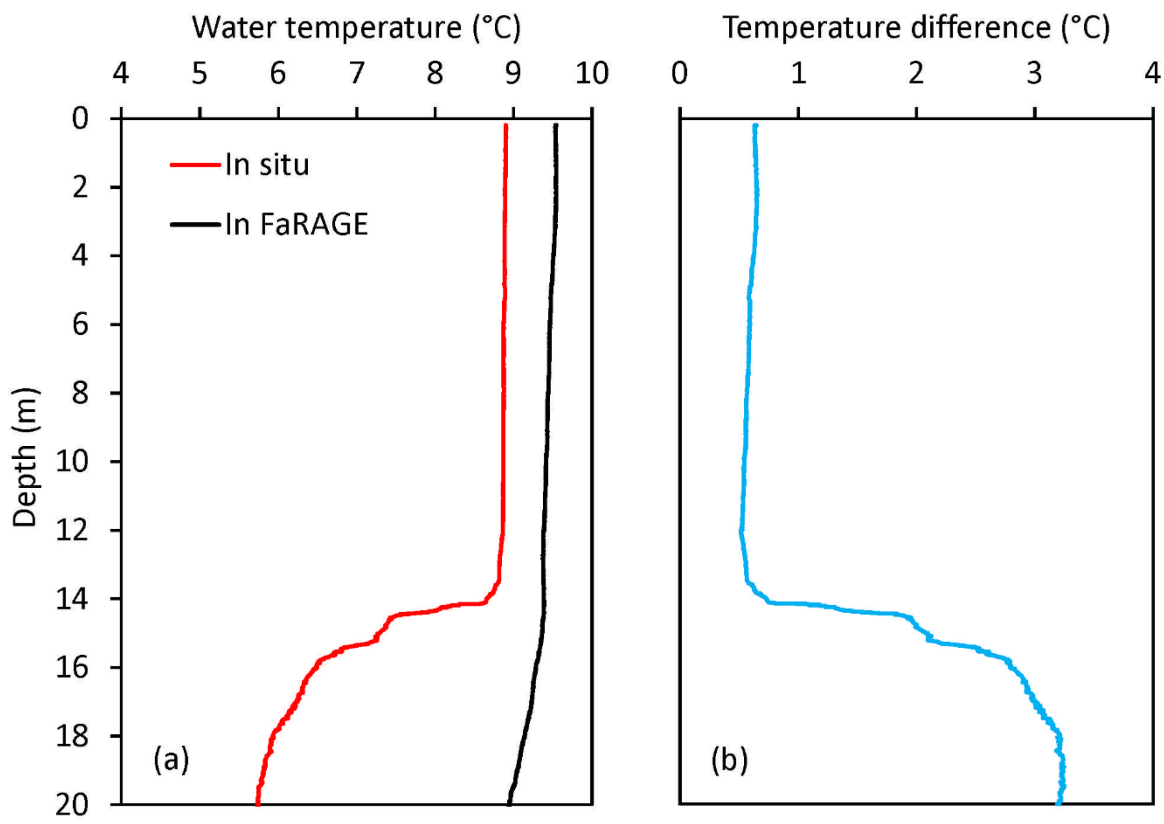

Fig. S4 An example of altered depth profile of water temperature at Lake Stechlin in autumn 2019. (a) Comparison of in situ water temperature (red line) with water temperature measured in the FaRAGE (black line). (b) The difference between the two temperature measurements (In FaRAGE - In situ).

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