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Hydrology and
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Discussions

Interactive comment on “A Fast-response automated gas equilibrator (FaRAGE) for continuous in situ measurement of methane dissolved in water” *by* Shangbin Xiao et al.

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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 will add these data into the revised draft.

Also, we performed additional laboratory tests for high concentrations (e.g., 33 microM) and will add these to the new revision. The measured concentration is about 245 ppm with the FaRAGE. For the Gas Scouter 4301 we use, a linearity can only be guaranteed up to 500 ppm. Adjustment of water-gas mixing ratio is needed for mM CH4 concentrations. Therefore, we agree with the reviewer’s suggestion. We will rephrase 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 150 s extension in response time was observed (Line 108-109 in SI). 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. I reproduced their results below. They show both dryers have no effect on CH4 except 1.5 m time delay on CO2 was caused by using Drierite.

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

So the numbers in table S4 and the statement in line 274 are all valid. We understand it is not well clarified. We will clarify this in the revised draft.

Reference Webb, J. R., Maher, D. T., and Santos, I. R.: Automated, in situ measurements of dissolved CO2, CH4, and δ13 C values using cavity enhanced laser absorption spectrometry: Comparing response times of airâĂŘwater equilibrators, Limnol. Oceanogr.: Methods, 14, 323-337, https://doi.org/10.1002/lom3.10092, 2016.

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 will check this carefully and make sure the

terms of parts 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 will add CO2 as well and incorporate throughout the full text.

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 will mention this explicitly in abstract and also in text. The potential use what the reviewer suggested is very interesting!

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 will include an example in SI to show that how different the water temperature (water flow inside the gas-water separation unit) can be 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 install 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 will rephrase this sentence and replace “filthy”.

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

Response: Thanks. Yes, a copper scrubber can help removing H2S gas 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. I also reproduced the figure they included in the publication. We will add this reference to the revised manuscript.

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.

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

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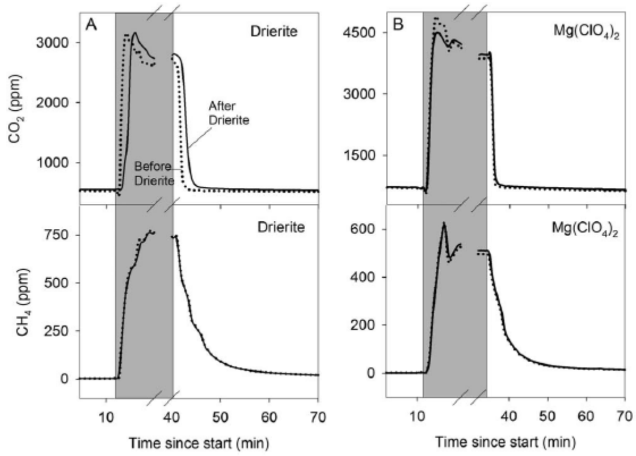

Fig. 2. Step experiments carried out to determine the effect of two desiccants, Drierite (**A**) and magnesium perchlorate ($Mg(ClO_4)_2$) (**B**), on the response times of CO_2 and CH_4 through a showerhead equilibrator. A time delay of 1.5 min was observed for CO_2 concentrations when Drierite was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

Fig. 1. The effect of dryers on response time

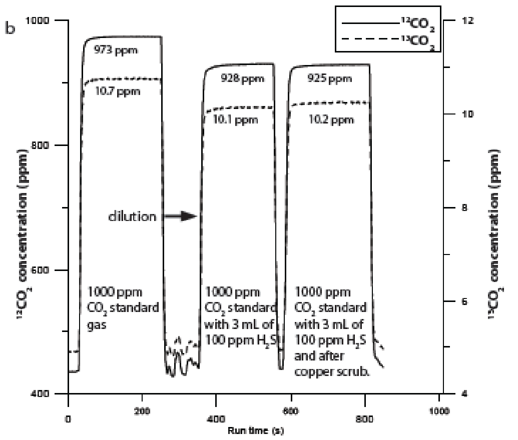

Figure 3. Change in the $^{12}CO_2$ and $^{13}CO_2$ concentrations with addition of H_2S to the standard gas. **(a)** Plot showing the percentage change in CO_2 concentration between gas with H_2S and gas scrubbed of H_2S. There is a visible increase in the $^{12}CO_2$ concentration and a decrease in 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.

Fig. 2. The effect of copper scrubber on response time