Response to Reviewer 2 Comments (RC2):

Overview and general comments:
The manuscript "New approach for the determination of N_2 fixation rates by coupling a membrane equilibrator to a mass spectrometer on voluntary observing ships" describes (i) the design and performance of a GE-MIMS instrument for dissolved gas analysis in surface waters, and (ii) the scientific interpretation of the gas data in terms of the N_2 biogeochemistry. The novelty of the work is not well presented. Much of the manuscript is concerned with replicating in-depth descriptions of previously published work, sometimes without providing credit to these publications. In particular, much of the recent work that developed the GE-MIMS technique is not cited and discussed in the manuscript (for example Patent EP 4 109 092 A1 [1] and other references listed in the detailed comments and at the end of this document). Previously published work should be discussed adequately, and new work done by the authors must be presented to build or expand on these previous work. This will help the authors present the true novelty and relevance of their work (i.e., how they implemented routine analysis of dissolved N_2, O_2 and Ar in the Baltic Sea with the aim to reduce the uncertainties of previous methods to study the biogeochemical N_2 turnover). It should also be mentioned that their experimental work will not only be relevant for the Baltic Sea or for use on "voluntary" ships, and I'd suggest discussing their developments for applications in other oceanic systems, lakes, groundwaters, etc. I recommend to shorten the manuscript (a lot). I don't see the value of the in-depth (and excessive?) mathematical-theoretical treatise of the assumed gas exchange dynamics in the membrane equilibrator. It seems this treatise is based on inapplicable assumptions, and the modeled equilibration times are inconsistent with the experimental observations. The experimental tests provide all the necessary data without any dependence on the modeling exercise. Also, as the focus of the manuscript lies on the analytical techniques for dissolved gas analysis, the discussion of the theoretical concepts to disentangle the N_2 fixation from other processes in the Baltic Sea surface water (Chapter 4) seems out of place. This chapter could be removed and presented elsewhere. Overall, I can't recommend publication of the manuscript in its current form. The detailed comments below will hopefully prove useful for the authors to revise and improve the manuscript.

Reply: We sincerely appreciate the thoughtful feedback of the reviewer on our manuscript. The comments have provided valuable insights, and we are committed to addressing them thoroughly to improve our manuscript. As suggested, we will expand the existing discussion of earlier GE-MIMS work where appropriate and add further references of scientific publications. We will emphasize the novelty of our work and make it clear that our main goal (besides the pure analytical description) is to present an approach with which N_2 fixation can be monitored in higher temporal and spatial resolution (e.g. during long term observations on voluntary observing ships (VOS) in the Baltic Sea). This will include a clearer description of how our approach aims to reduce uncertainties in the determination of N_2 fixation rates.

Regarding the length of the manuscript, we agree that the mathematical modeling may be excessive and will re-organize the corresponding parts of the manuscript by moving some of the mathematical derivations into the Appendix or to the Supplement.

We will also reassess Chapter 4 to reduce its length and to highlight the novelty of our work.

Details and specific comments:

Title

I feel the title could be improved to better describe the scope of the manuscript:
• The method is targeted at the analysis of dissolved N_2, O_2 and Ar in (surface) waters, but this aspect is missing in the title
• Coupling a membrane equilibrator to a mass spectrometer allows dissolved gas analysis, but no direct quantification of N_2 fixation rates.
• The techniques described in the manuscript are by no means limited to use on (voluntary) ships

Reply: The reviewer is right that the title was too unclear. The new title has been adapted and now reads "Technical note: Testing a new approach for the determination of N_2 fixation rates by coupling a membrane equilibrator to a mass spectrometer for long term observations". From this title it is now clear that the focus is on the determination of N_2 fixation rates. It is true that we can also determine O_2 and Ar concentrations with this method. However, the focus of the new approach explained in this paper is the determination of N_2 deficits in surface water and the N_2 fixation rates that can be derived from them. That is actually the novelty about the present manuscript. We hope that the rework has succeeded in highlighting this better.

1. Introduction

The authors claim (on line 74ff) that their manuscript "introduces the GE-MIMS technique as an extension to MIMS". This is a rather puzzling statement given the extensive previous work that relies on the gas/water equilibrium in a membrane equilibrator. Some of this work is referenced in the manuscript (Cassar et al. 2009, Mächler et al. 2012, Manning et al. 2016). The methods presented in the Cassar and Manning papers allow analysis of the ratios of the partial pressures (or concentrations) of different gas species dissolved in the water. The Mächler 2012 work (who introduced the GE-MIMS term) was a first attempt at a semi-quantitative analysis of the absolute partial pressures (or concentrations), which relied on an empirical correction of the analytical data. The GE-MIMS technique was further developed as described in references [4, 5] and Patent EP 4 109 092 A1. This and other potentially relevant works [3,7,9] that established the GE-MIMS technique have been ignored in the manuscript.

Reply: We believe that there has been a misunderstanding, which may have been caused by the imprecise title. Our intention is not to claim that we were the first to use the GE-MIMS technique for determining gas concentrations in water. We acknowledged this by citing relevant studies in the introduction. To avoid further confusion, we will revise the introduction and incorporate the suggested scientific references to clearly acknowledge prior developments in the field.

Line 67

The dynamic steady state in a conventional MIMS is controlled by many more factors than just the dissolved gas concentrations and the MS pumping rate. The water flow rate, the geometry of the membrane system, water salinity, temperature, aging of the membrane material and its gas permeation properties, etc. play a crucial role.

Reply: The text will be modified: A steady state in the membrane gas room is generated by the balance between the MS pumping rate (outflow) and the diffusion of the dissolved gas across the membrane (inflow).

Line 77

Pressure can approach zero (in a vacuum system), but I don't understand how pressure can be negative ("beyond vacuum").

Reply: The reviewer is right that the sentence is misleading. It now reads: "The latter is maintained by the removal of only minor amounts of gas from the gas space of the membrane."

2.1 Membrane equilibrator

Figure 1

The gas inlet from the calibration gas tank does not seem to have a pressure controller. However, the gas pressure at the gas inlet to the MS capillary must be known accurately and precisely to allow reliable calibration of the MS data. How did they achieve this without knowing the pressure of the calibration gas?

Reply: The reviewer has misunderstood the calibration of the MS which is not (!) based on the relationship between the partial pressure of a gas and the respective MS ion current. Therefore, we will describe our calibration procedure in more detail in the revised manuscript:
To eliminate smaller temperature or pressure fluctuations within the MS, we use an internal standard (Ar) to determine calibration factors. These are obtained from the ratio I_X/I_{Ar} (ratio of the currents for gas X and Ar) divided by the ratio n_X/n_{Ar} (ratio between the molar amounts of X and Ar in the calibration gas). Calibration factors are hence given by: $F_{cal,X} = (I_X/I_{Ar})/(n_X/n_{Ar})$ where n_X/n_{Ar} are the ratios of the corresponding mole fraction in the calibration gas. From this calibration procedure it follows that elemental ratios X/Ar (N_2/Ar, O_2/Ar and N_2/O_2) are the primary outcome of our MS measurements.
The elemental ratios yield mole fractions for N_2, O_2 and Ar in the headspace of the membrane equilibrator with respect to the sum of N_2, O_2 and Ar ("incomplete" or "partial" mole fractions) (calculations are presented in Appendix A). To obtain the partial pressures for N_2, O_2 and Ar, the "incomplete" mole fractions must be multiplied with the sum of the pressures of the three gases which is given by the total pressure in the head space minus the sum of pressures of other gases. The latter is mainly given by the water vapor and is calculated from water vapor saturation in the gas room of the membrane equilibrator at the temperature and salinity of the water. The effect of other trace gases is ignored due to the minor contributions to the total pressure, e.g. the mean surface water pCO_2 is about 400 µatm and thus adds only 0.04 % to the total pressure. The total pressure in the headspace is recorded by a high precision pressure gauge (Fig. 1).
Nevertheless, we acknowledge that the ionization process within the MS is inherently pressure-dependent, leading to variations in the ionization ratios of gases under different pressure conditions. To mitigate this, the electron and ion densities in the ion formation region were effectively reduced by adjusting the emission current in the ion source. This adjustment minimizes space charge effects and improves linearity in ion

yield and fragmentation across different pressure levels. In fact we will mention in the manuscript that we observed at pressures 200 mbar above the calibration point (atmospheric pressure) the molar fraction of N_2 changes relatively by 0.4 %. However, a total equilibrium pressure (total gas tension) of surface seawater of more than 200 mbar above atmospheric pressure, e.g. by biological or temperature effects, can be excluded.

Appendix A, line 117/118

Using a pressure sensor to determine the total gas pressure and to quantify the partial pressures of the different gas species in the membrane equilibrator has been previously described in patent EP 4 109 092 A1, which should be referenced here.

Reply: As mentioned earlier, we use a different calibration method and a different method to calculate the partial pressures of the analyzed gases compared to the approach described in Patent EP 4 109 092 A1. In our setup, a pressure sensor is used to calculate partial pressures from the ("incomplete") mole fractions of gases in the mixture. This approach is standard practice in equilibrator-based systems (e.g., Schmale et al., 2019; Schneider et al., 2014; Gülzow et al., 2011) and is grounded in well-established physical-chemical principles, which are widely understood and do not require specific referencing.

Line 107

Which filter? Filter for what, where?

Reply: The term "filter cartridge" was a mistake in wording and will be corrected to "membrane equilibrator".

Line 112

How "negligible" is the gas removal? This is a crucial control for the accuracy of the analytical results and calls for a quantitative argument.

Reply: The explanation in Appendix B will be modified by using a realistic estimate of the transfer constant, k_n, that was derived from the measured equilibration time. On this basis a pressure reduction by 0.8 % was obtained by the continuous removal of gas from the gas room of the equilibrator. This is a minor effect and applies to the calibration and measurements as well.

Line 114 and 115

Why would a clogged capillary pose a risk for the MS? I'd rather argue that the clogging protects the MS from accidents with too much water.

Reply: The reviewer is right, the text is misleading and now reads:
"In addition to the Liqui-Cell membrane, we tested a membrane equilibrator from PermSelect (PermSelect 1m^2), in which the gas exchange between the water and gas phase is mediated by dense hollow silicon fibres (polydimethylsiloxane, PDMS). Since the gas exchange does not take place across pores, clogging of pores by particles that may hamper the gas flux, is avoided by these membranes. However, our tests with the

PermSelect membrane showed that the membrane is unsuitable for our application because, for some reason, water accumulates on the gas side, which could be sucked in through the gas inlet of the MS and thus block the inlet.

Line 116 and 117

Is this a confusion between accuracy and precision?

Reply: The term "accurate" will be removed.

Line 121

Pressure can approach zero (in a vacuum system), but I don't understand how pressure can be negative ("beyond vacuum").

Reply: The reviewer is right that the sentence is misleading. It now reads: "This is to prevent gravity from creating a suction effect that reduces the total pressure on the gas side of the membrane and disturbs the gas phase equilibrium."

Line 121 and 122

Why would the depressurization in the outflow tubing have an effect on the gas/water equilibrium in the membrane module? Please explain.

Reply: See previous Reply. We need an accurate determination of the gas pressure within the membrane module to calculate concentrations. A suction effect at the water outlet can interfere with this pressure measurement, as we have observed in our tests.

2.2 Mass spectrometry

Line 128

How important is gas leakage across the walls of the fused silica capillary (transfer of gases from ambient air into the low-pressure internal gas flow of the capillary)?

Reply: Fused silica capillaries are designed to have very low permeability to larger gas molecules/atoms like N_2, O_2, Ar, and any potential leakage would be minimal compared to the gas flow within the capillary itself. We have not observed significant deviations in our measurements that would indicate a gas leakage and contamination by ambient air into the system.

Line 128

Internal or external diameter?

Reply: We will add "internal" to ensure clarity and accuracy in the description.

Line 139/140

The Faraday cup and SEM are likely used not only for detection, but rather for quantification.

Reply: We will change the sentence to "…ultimately detected and quantified using a Faraday Cup."

Line 140-142

One might expect a better signal/noise ratio from the SEM, in contrast to the observation reported here. Why is this? Please elaborate.

Reply: The reasons can be manifold, with one possible factor being a greater sensitivity to temperature (Hoffmann et al., 2005; Khan et al., 2018). However, determining the reasons and their specific influence is not the focus of our manuscript. Rather, we refer here to the measurements carried out in the laboratory and their results.

Line 143/144

Quantification of the partial pressures must be based on the peak heights in the mass spectrum. To determine the peak heights, the baseline values therefore need to be subtracted from the peak-top values measured at the indicated m/z positions. Were the baseline values measured? At which m/z values?

Reply: Baseline correction was performed using values at m/z = 3. In our laboratory tests, we measured the baseline weekly over a longer period of time and could not detect any significant differences in the signal. However, the stability of the baseline may also depend on the location of the device (e.g. on the VOS) – in this case, we recommend conducting additional tests to take the conditions into account.

Line 143ff

Quantification of the partial pressures cannot be done accurately from the peak heights because their dependence on the total gas pressure at the capillary inlet follows a complicated, non-linear function [6]. With the exception of the special case where the total gas pressures of the sample gas and the calibration gas are identical, the peak-height comparison as described here will therefore not yield accurate results.

Reply: See explanation of our calibration procedure in our reply to the reviewer's comment on Figure 1.

Line 145

Why use the same measurement time for all species? Compared to N_2 and O_2, the much lower abundance of Ar results in a much smaller Ar peak intensity. It therefore seems advisable to use considerably longer measurement times for Ar to optimize the signal/noise ratio.

Reply: The reviewer raises a valid point, and this is certainly something that could be considered in future measurements. However, based on our current setup and as described in the manuscript, we were able to achieve sufficient accuracy and precision for all gases, including Ar, using the same measurement time.

Line 146

Why not use ambient air as a reference gas for routine calibration? The intermediate step of using a dedicated gas mixture that is cross-calibrated to air seems like an unnecessary step that complicates the analytical setup and potentially introduces additional uncertainty to the data calibration.

Reply: The reviewer makes a good point. However, on VOS, the composition of ambient air can vary significantly due to factors such as proximity to the engine room and other sources of contamination especially with regard to the O_2 content. To avoid potential influences, we chose a cross-calibrated gas mixture for our setup. Nonetheless, we appreciate the suggestion and will clarify in the manuscript that for other deployments with access to stable atmospheric air, the latter can certainly be used for calibration, as demonstrated in studies like Cassar et al. (2009), Mächler et al. (2012), and Manning et al. (2016).

Line 150-154

Why 60 repetitions for averaging? Why a 6 h long test period? The usual approach is to optimize the signal/noise ratio while minimizing the effect of drift. This is commonly done using an Allan plot. Is this what the authors did? Please explain.

Reply: The decision to use a 6-hour test period was based on the need to observe potential effects such as temperature variations over a sufficiently long time span. Within this period, no significant drift was observed over one hour, as shown in Figure 2. An Allan plot would indeed better illustrate the stability and drift behavior. We appreciate this suggestion and will include this statistical approach in the revised manuscript.

Appendix A, line 445

I am not convinced that the CO interference on m/z = 28 is negligible for the N_2 quantification, especially since CO_2 levels in the water may be elevated. Please quantify the potential effect of the CO interference for N_2 quantification.

Reply: Based on the manuscript of Burlacot et al. (2020), approximately 9.81% of the primary CO_2 signal at m/z = 44 is fragmented into the CO ion at m/z = 28. Assuming atmospheric CO_2 concentration, this would correspond to around 40 ppm of CO, which could potentially interfere with N_2 quantification, given that N_2 constitutes 78% of air. However, this level of interference can be considered negligible, as also confirmed by our observations. Additionally, CO_2 concentrations in the surface waters of the Baltic Sea are significantly undersaturated during periods of N_2 fixation (due to biological production, see Schneider et al. 2007), which would further reduce any potential interference. The references mentioned by the reviewer (Mächler et al., 2012; Brennwald et al., 2016) also did not report significant interference of N_2 at m/z = 28 due to CO_2 at their study conditions. Nevertheless, we acknowledge that this could be a concern in other study areas with very high CO_2 concentrations.

3.1 Accuracy and Precision

Line 168/169

Estimating the water vapor pressure by assuming saturation in the GE-MIMS equilibrator has been described in patent EP 4 109 092 A1, which should be referenced here.

Reply: This is an obvious assumption and has also been used in many studies concerning the determination of partial pressures of gases by the use of equilibrators (e.g. Schneider et al., 2007; Gülzow et al., 2011; Schmale et al., 2019). It does not need to be referenced.
Line 173-180

Using Henry's Law to convert the partial pressures to dissolved gas concentrations has been described in previous GE-MIMS work, which should be referenced here (see previous comments).

Reply: This is common practice in all approaches to derive gas concentrations from a gas phase at equilibrium with a dissolved gas. It is based on basic physical-chemical knowledge and does not need to be referenced.

Lines 182-188

Air-equilibrated water (AEW) is a good reference to assess the analytical performance, but fabrication of AEW is notoriously difficult. I would recommend comparison and validation of their GE-MIMS system with other (validated and established) methods for dissolved-gas quantification.

Reply: Through our experimental setup, we ensured the production of air-equilibrated water, as indicated by the stability of the measurement values shown in Figure 2. We have evaluated the system as described, and based on our observations, we consider additional evaluations unnecessary at this stage.

Lines 192/193

The RSD is normalized relative to the concentration value. A lower concentration value should therefore not result in a lower RSD.

Reply: We agree with the reviewer. This can also be clearly seen in Table 2.

Line 200, Tab. 2

Is the precision reported as the absolute standard deviation (*aSD*, as indicated in the Table caption) or as the 2-fold of the *aSD* (as indicated in the text)?

Reply: We will revise the table caption to explicitly state that the reported precision is based on the 2-fold absolute standard deviation.

Lines 205-208

I don't understand. What are these numbers? Where do they come from?

Reply: We understand that this section is unclear, and we will clarify in the revised manuscript by indicating in parentheses that these numbers are derived from the measured accuracy for the referenced biogeochemical concentration changes.

3.2.1 Theory of equilibration kinetics

I am not convinced that this section adds much value to the manuscript. On the one hand, it assumes that the water is stagnant inside the membrane module (it is not), and it assumes that the membrane provides the bottleneck for the gas transfer between the water and the gas phase. However, the resistance of the membrane material to the gas transfer is marginal (the authors can convince themselves about this by blowing into the water inlet of a dry module while blocking the water outlet, and observe how the air easily escapes through the membrane material into the gas headspace). In contrast, the main bottleneck for the transfer of gas species between the water and the gas headspace is expected to result from the gas exchange mechanisms at the gas/water interface (see for example [8]). The main outcome of section 3.2.1 is that the partial-pressure equilibration follows an exponential function, which comes to no surprise given the assumption of a first-order exchange kinetic, and which does not warrant any mathematical derivation. A second result is equation (27), which provides a formula to calculate the equilibration time. However, this equation relies on incorrect model assumptions (stagnant water, membrane as bottleneck for gas/water transfer) and therefore does not provide much insight.

Reply: We agree with the reviewers comment, that the crucial step for the exchange of gases across the membrane is not the diffusion of the gas along the pores of the membrane. It is rather the transfer of the gas across the water/gas interface that controls the flux. The latter depends on many variables and information for the LiquiCel membranes are not available. We have therefore moved the derivation of the equilibration time for stagnant water (no water flow) in the equilibrator, including the use of the gas-gas permeability derived from the Gurley seconds, to the Appendix. The value of this Appendix section lies in its attempt to provide a clear and accessible explanation for the reader - who may not necessarily be an expert in the field - about how equilibrium is established within a membrane equilibrator and the factors that influence this process. We aim to illustrate the underlying principles of gas transfer and equilibration dynamics, which can enhance the reader's understanding of the system.
In view of the geometric dimension of the water and gas layers within the equilibrator (thicknesses of 140 µm and 70 µm, respectively), it seems likely that equilibration between the two phases is established during the residence of the water in the equilibrator. At a water flow rates of 1 L/min - 2 L/min the residence time ranges between 7 s and 14 s. For this case that equilibrium is generated during each water renewal, we have derived a mathematical formulation for the dependency of the equilibration time on the water flow rate. This derivation, given in the main text is considered as a first approximation for the theoretical determination of the equilibration time.

Line 233

What is the "solubility constant s"? Could this be rewritten to use the Bunsen coefficient β introduced before?

Reply: We will consistently use the solubility constant s given as [mol $\cdot$ L^{-1} $\cdot$ atm^{-1}].

Equation (12)

The equilibration time τ must be a function of the transfer rate k_n, which, however, is not shown in equation (12). Please explain.

Reply: The transfer rate k_n is indeed included in Equation (12).

Equations (13) and (14)

This use of the $\partial p_{g,w}$ notation is rather awkward. By convention, the ∂ symbol is used as pairs in fractions to denote partial derivatives. They are not meaningful as isolated elements as used here. The ∂ symbols should be replaced by proper differentials ($dp_{g,w}$). This may apply to most other equations, too.

Reply: We agree with the reviewer and will make the necessary adjustments in the revised manuscript.

Line 281

The internal diameter of the X50 membrane fibers used in the 3M/Membrana membrane module is 240 µm [2]. Therefore, the water volume will be smaller than the gas volume by orders of magnitude, not just by a factor of 2.

Reply: For our model, we refer to the manufacturer's data sheet (data sheet: 3M Liquicel MM-1.7x8.75 Series Membrane Contactor, 2021), which specifies a water volume (lumen side) of 70 mL and a gas volume (shell side) of 140 mL. This indicates that the water volume is indeed smaller than the gas volume by a factor of 2. We will reference the datasheet in the revised manuscript.

Lines 285-286

This seems like a trivial finding since the removal of gas from a finite, stagnant volume of water will result in a lower dissolved-gas concentration, and hence in a lower partial pressure at equilibrium. In reality, there's a continuous flow of water through the membrane module, which means there's a (virtually) infinite amount of water available for equilibration with the gas headspace. Again, this shows that the model concept and equations are based on inappropriate assumptions.

Reply: We acknowledge the reviewer's concerns regarding the model assumptions (see reply above). The purpose of using a model that examines gas exchange with stagnant water was to provide a simplified representation for understanding the fundamental principles of gas dynamics. This approach was intended to help readers, especially those less familiar with the topic, grasp the essential mechanisms at play. We have moved this model to the appendix to clarify its role and significance in our overall analysis.

3.2.2 Measurement of τ

This section provides robust information on the time needed to attain gas/water equilibrium in the membrane module, and provides a useful basis to estimate the spatial resolution of the dissolved-gas data recorded on a moving ship. The measured equilibration times τ are approximately 50 % higher than those calculated from the model 5 in Sec. 3.2.1, which supports my impression that the model is inaccurate and seems inappropriate to optimize the operation of the GE-MIMS method for the dissolved gas monitoring described in the manuscript. To this end, the experimentally determined τ values are more suitable, and the model could be removed from the manuscript entirely.

Reply: While we acknowledge that the experimentally determined τ values are more suitable for precise monitoring, we think that it is an established scientific practice to compare experimental results with the outcome of theoretical consideration even if the latter are based on simplified assumptions. Compared with the measurements, our model results yielded the same order of magnitude for τ of the three gases. Still, significant discrepancies exist between the measured and modeled τ values which can be attributed to the simplified assumptions inherent in the model. A critical point in the model is for example the assumption that no continuous water flow exists, but that discrete water parcels are transported through the water side of the equilibrator.

Lines 324-333

This experimental setup certainly works, but I don't understand why the dissolved gas concentrations in the water were maintained at a fixed value and the disequilibrium was imposed by changing the partial pressures in the headspace. This approach is backwards to how the GE-MIMS concept works: variations in the aqueous concentrations result in a change of the partial pressures in the headspace. It would seem natural to design the test such that the aqueous concentrations are variable and the response of the partial pressures is monitored to determine the GE-MIMS equilibration time (see for example [3]). Why did the authors choose the "backwards" approach?

Reply: We do not understand why our method is a "backward approach". It is exactly the same procedure that is also used in the GE-MIMS method. At a given partial pressure on the gas side, a partial pressure difference is generated by a water flow with a different partial pressure. The equilibration process is then recorded by the change of the partial pressure in the gas phase. A similar "backward" concept was described in [3] where the gas side was filled with pure helium and the equilibration was followed by the diffusion of a gas dissolve in a flow of water into the He gas phase characterized by the flow of water and the gases dissolved in it.

Lines 340

I don't see the need for 29 equations simply to state that the partial pressures evolve exponentially towards their equilibrium value. This seems like a trivial result of the assumed first-order gas-exchange kinetic.

Reply: As mentioned above, we have moved the first part of the equations to the appendix. In addition, we believe that the 29 equations describe more than just the exponential evolution of partial pressures within the membrane equilibrator. Our aim in submitting the paper to Biogeosciences was to reach readers who may be less familiar

with the theoretical background. By providing more comprehensive derivations and explanations, we hope to give the reader a better insight into the subject.

Fig. 4

The right panel seems unnecessary, as it shows the same data as the one on the left. I'd suggest to show only the left panel and add the fitted exponential curve.

Reply: The two panels do not show the same data, although they are based on the same data set. The right panel presents only a selected segment from the left panel, focusing on a specific part of the experiment rather than the entire duration. The reviewer's suggestion may reduce clarity, so for better visualization and understanding, we prefer to keep both figures as they currently are.

Lines 349-351

The ratios of the measured and modeled τ values are 4.8/4.3 = 1.1 (N2), 3.2/2.2 = 1.5 (O2), and 3.0/2.0 = 1.5 (Ar). In other words, the true (measured) values are up to 50 % higher than those estimated from the model. I don't see how this large discrepancy can be explained by non-ideality of the gas or "impurities" of the membrane. As mentioned before, there are more fundamental flaws in model assumptions.

Reply: We refer to the comments above regarding the simplified model, which will be described more detailed in the revised version.

Lines 357-360

The membrane module used in this work is rather large and therefore exhibits long equilibration times of 12–20 min. Why did the authors not use much smaller membrane modules that would allow equilibration within about 3 min [4], which would in turn also provide approximately 5x better spatial resolution in their dissolved-gas monitoring?

Reply: The larger gas volume was intentionally chosen to ensure that the equilibrium is not disturbed, as explained in our response to the reviewer's comment on line 112. We also clarify this in our manuscript in lines 111-112. Furthermore, the equilibration time is not as critical for the intended field studies, since a reasonable data evaluation requires regional averaging.

4 Evaluation of concentration data

I feel this chapter is not well integrated in the scope of the otherwise well-structured manuscript. Similar to Sec. 3.2.1 it also provides excessive (and seemingly unnecessary) mathematical derivations that seem unnecessary for the purpose of this manuscript. Also, while I am not an expert on N_2 geochemistry in surface waters, I would be surprised if these concepts and equations have not been presented and discussed in the existing literature.

Reply: We agree that the equations in section 4.1 have already been discussed and presented in other works, which we have referenced. We will remove this part and focus solely on the new approach we developed for determining N_2 fixation rates in section 4.2. The main goal of this manuscript is to introduce a new method for determining N_2 fixation rates using GE-MIMS, based on concentration series obtained through long-

term observations, preferably on a VOS as a measurement platform. This naturally involves not only the presentation of the measurement system but also how to process the acquired data to ultimately obtain the N_2 fixation rates. Therefore, we believe that this topic must be included into our manuscript.

Lines 366-369

I don't agree. The physico-chemical properties of N2 are different to those of O2 and Ar, as demonstrated, for example, by the measurements in Sec. 3.2.2. These differences do result in fractionation of N2/Ar relative to O2/Ar.

Reply: As we have mentioned above section 4.1 will be deleted in the revised manuscript.

<u>Section 4.2</u>

The Schmidt-Number method provides a rough estimate of the gas exchange of the mixed layer with the atmosphere. However, if the Schmidt-Number model is really necessary here, I feel this discussion needs to be expanded with a quantitative assessment of the inherent uncertainties.

Reply: We do not understand, what the reviewer means by Schmidt Number method or model. The Schmidt number, Sc, does not refer to any "estimate of the gas exchange". It is simply the dimensionless ratio between the kinematic viscosity and the diffusivity of the considered gas. It is related to the gas exchange transfer velocity k by: $k \sim Sc^{-x}$ and used to convert k which in chemical oceanography is usually referring to a standard Schmidt number of $Sc = 660$ (CO_2 at 25 °C in seawater at salinity of 35), k_{660}, to any other gas and temperature (e.g., Weber et al. (2018) and many others). For the exponent x, a value of 1/2 is generally used at wind speeds above 3 m/s, but may increase at lower wind speeds (2/3).
In our case we use the change in the Ar concentration that must be driven by gas exchange to derive the N_2 gas exchange (implicitly we are determining k). This implies the use of the ratio $Sc(N_2)/Sc(Ar)$ which at a given temperature and salinity (viscosity) is given by the ratio of the corresponding diffusivities.

Lines 418-420

As I understand it, the Schmidt-Number model breaks down at low wind speed, as gas exchange rates do not tend to zero without wind. This statement therefore warrants a more quantitative argument based on observed data.

Reply: We refer to the reply above.

Lines 424-425

This has been demonstrated with a GE-MIMS instrument in previous work [9].

Reply: But Weber et al. used an entirely different approach to quantify the gas exchange.

5. Conclusion

This chapter will need to be reworked to reflect to focus and new findings of a reworked manuscript.]

Reply: We will rework the conclusions accordingly, including suggestions from the other reviewers.

References (Reviewer)

[1] Gas-equilibrium membrane inlet mass spectrometry with accurate quantification of dissolved-gas partial pressures (GE-MIMS-APP). Patent EP 4 109 092 A1, 2022.

[2] S A Ansari, S Chaudhury, P K Mohapatra, S K Aggarwal, and V K Manchanda. Recovery of plutonium from analytical laboratory waste using hollow fiber supported liquid membrane technique. Separation Science and Technology, 48(2):208–214, 2012.

[3] Matthias S Brennwald, A P Rinaldi, J Gisiger, A Zappone, and R Kipfer. Gas equilibrium membrane inlet mass spectrometry (GE-MIMS) for water at high pressure. Geoscientific Instrumentation, Methods and Data Systems, 13(1), 2024.

[4] Matthias S Brennwald, M Schmidt, J Oser, and R Kipfer. A portable and autonomous mass spectrometric system for on-site environmental gas analysis. Environmental Science and Technology, 50(24):13455–13463, 2016.

[5] Eliot Chatton, Thierry Labasque, Jérôme de La Bernardie, Nicolas Guihéneuf, Olivier Bour, and Luc Aquilina. Field continuous measurement of dissolved gases with a CF-MIMS: Applications to the physics and biogeochemistry of groundwater flow. Environmental Science and Technology, 51(2):846–854, 2017.

[6] G M Fryer. A theory of gas flow through capillary tubes. Proc. Royal Soc. London, Ser. A Math. Phys. Sci., 293(1434):329–341, 1966.

[7] S Giroud, Y Tomonaga, M S Brennwald, N Takahata, T Shibata, Y Sano, and R Kipfer. New experimental approaches enabling the continuous monitoring of gas species in hydrothermal fluids. Front. Water, 4, 2023.

[8] R P Schwarzenbach, P M Gschwend, and D M Imboden. Air-Water Exchange. Wiley, 2002.

[9] UW Weber, PG Cook, Matthias S Brennwald, R Kipfer, and TC Stieglitz. A novel approach to quantify air–water gas exchange in shallow surface waters using highresolution time series of dissolved atmospheric gases. Environmental Science and Technology, 53(3):1463–1470, 2018.

References (Authors)

Brennwald, M. S., Schmidt, M., Oser, J., and Kipfer, R.: A Portable and Autonomous Mass Spectrometric System for On-Site Environmental Gas Analysis, Environ. Sci. Technol., 50, 13455–13463, https://doi.org/10.1021/acs.est.6b03669, 2016.

Burlacot, A., Burlacot, F., Li-Beisson, Y., and Peltier, G.: Membrane Inlet Mass Spectrometry: A Powerful Tool for Algal Research, Front. Plant Sci., 11, https://doi.org/10.3389/fpls.2020.01302, 2020.

Cassar, N., Barnett, B. A., Bender, M. L., Kaiser, J., Hamme, R. C., and Tilbrook, B.: Continuous High-Frequency Dissolved O2/Ar Measurements by Equilibrator Inlet Mass Spectrometry, Anal. Chem., 81, 1855–1864, https://doi.org/10.1021/ac802300u, 2009.

data sheet: 3M^{TM} Liqui-Cel^{TM} MM-1.7x8.75 Series Membrane Contactor, Rev. 02, 2021, https://multimedia.3m.com/mws/media/1412495O/3m-liqui-cel-mm-1-7x8-75-series-membrane-contactor.pdf [20.09.2024]

Gülzow, W., Rehder, G., Schneider, B., Deimling, J. S. v., and Sadkowiak, B.: A new method for continuous measurement of methane and carbon dioxide in surface waters using off-axis integrated cavity output spectroscopy (ICOS): An example from the Baltic Sea, Limnol. Oceanogr. Methods, 9, 176–184, https://doi.org/10.4319/lom.2011.9.176, 2011.

Hoffmann, D. L., Richards, D. A., Elliott, T. R., Smart, P. L., Coath, C. D., and Hawkesworth, C. J.: Characterisation of secondary electron multiplier nonlinearity using MC-ICPMS, Int. J. Mass Spectrom., 244, 97–108, https://doi.org/10.1016/j.ijms.2005.05.003, 2005.

Khan, M. I., Lubner, S. D., Ogletree, D. F., and Dames, C.: Temperature dependence of secondary electron emission: A new route to nanoscale temperature measurement using scanning electron microscopy, J. Appl. Phys., 124, 195104, https://doi.org/10.1063/1.5050250, 2018.

Mächler, L., Brennwald, M. S., and Kipfer, R.: Membrane Inlet Mass Spectrometer for the Quasi-Continuous On-Site Analysis of Dissolved Gases in Groundwater, Environ. Sci. Technol., 46, 8288–8296, https://doi.org/10.1021/es3004409, 2012.

Manning, C. C., Stanley, R. H. R., and Lott, D. E. I.: Continuous Measurements of Dissolved Ne, Ar, Kr, and Xe Ratios with a Field-Deployable Gas Equilibration Mass Spectrometer, Anal. Chem., 88, 3040–3048, https://doi.org/10.1021/acs.analchem.5b03102, 2016.

Schmale, O., Karle, M., Glockzin, M., and Schneider, B.: Potential of Nitrogen/Argon Analysis in Surface Waters in the Examination of Areal Nitrogen Deficits Caused by Nitrogen Fixation, Environ. Sci. Technol., 53, 6869–6876, https://doi.org/10.1021/acs.est.8b06665, 2019.

Schneider, B., Sadkowiak, B., and Wachholz, F.: A new method for continuous measurements of O2 in surface water in combination with pCO2 measurements: Implications for gas phase equilibration, Mar. Chem., 103, 163–171, https://doi.org/10.1016/j.marchem.2006.07.002, 2007.

Schneider, B., Gülzow, W., Sadkowiak, B., and Rehder, G.: Detecting sinks and sources of CO2 and CH4 by ferrybox-based measurements in the Baltic Sea: Three case studies, J. Mar. Syst., 140, 13–25, https://doi.org/10.1016/j.jmarsys.2014.03.014, 2014.

Weber, U. W., Cook, P. G., Brennwald, M. S., Kipfer, R., and Stieglitz, T. C.: A Novel Approach To Quantify Air–Water Gas Exchange in Shallow Surface Waters Using High-Resolution Time Series of Dissolved Atmospheric Gases, Environ. Sci. Technol., 53, 1463–1470, https://doi.org/10.1021/acs.est.8b05318, 2019.