

# Review of EGUSPHERE-2024-2049 Manuscript

## 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.

## 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

### 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.

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.

Line 77 Pressure can approach zero (in a vacuum system), but I don't understand how pressure can be negative (“beyond vacuum”).

### 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?

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.

Line 107 Which filter? Filter for what, where?

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.

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.

Line 116 and 117 Is this a confusion between accuracy and precision?

Line 121 Pressure can approach zero (in a vacuum system), but I don’t understand how pressure can be negative (“beyond vacuum”).

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.

## 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)?

Line 128 Internal or external diameter?

Line 139/140 The Faraday cup and SEM are likely used not only for detection, but rather for quantification.

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.

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?

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.

Line 145 Why use the same measurement time for all species? Compared to N<sub>2</sub> and O<sub>2</sub>, 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.

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.

Lines 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.

Appendix A, line 445 I am not convinced that the CO interference on  $m/z = 28$  is negligible for the N<sub>2</sub> quantification, especially since CO<sub>2</sub> levels in the water may be elevated. Please quantify the potential effect of the CO interference for N<sub>2</sub> quantification.

### **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.

Lines 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).

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.

192/193 The RSD is normalized relative to the concentration value. A lower concentration value should therefore not result in a lower RSD.

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)?

Lines 205–208 I don't understand. What are these numbers? Where do they come from?

#### **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 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.

Line 233 What is the “solubility constant  $s$ ”? Could this be rewritten to use the Bunsen coefficient  $\beta$  introduced before?

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

Equations (13) and (14) This use of the  $\partial p_{g,w}$  notation is rather awkward. By convention, the  $\partial$  symbol is used as pairs in fractions to denote partial derivatives. They are not meaningful as isolated elements as used here. The  $\partial$  symbols should be replaced by proper differentials ( $dp_{g,w}$ ). This may apply to most other equations, too.

Line 281 The internal diameter of the X50 membrane fibers used in the 3M/Membrana membrane module is  $240\ \mu\text{m}$  [2]. Therefore, the water volume will be smaller than the gas volume by orders of magnitude, not just by a factor of 2.

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.

### 3.2.2 Measurement of $\tau$

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  $\tau$  are approximately 50 % higher than those calculated from the model

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  $\tau$  values are more suitable, and the model could be removed from the manuscript entirely.

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?

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.

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.

Lines 349–351 The ratios of the measured and modeled  $\tau$  values are  $4.8/4.3 = 1.1$  ( $\text{N}_2$ ),  $3.2/2.2 = 1.5$  ( $\text{O}_2$ ), and  $3.0/2.0 = 1.5$  ( $\text{Ar}$ ). 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.

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 5× better spatial resolution in their dissolved-gas monitoring?

## 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  $\text{N}_2$  geochemistry in surface waters, I would be surprised if these concepts and equations have not been presented and discussed in the

existing literature.

Lines 366–369 I don't agree. The physico-chemical properties of N<sub>2</sub> *are* different to those of O<sub>2</sub> and Ar, as demonstrated, for example, by the measurements in Sec. 3.2.2. These differences *do* result in fractionation of N<sub>2</sub>/Ar relative to O<sub>2</sub>/Ar.

Section 4.2 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.

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.

Lines 424–425 This has been demonstrated with a GE-MIMS instrument in previous work [9].

## 5. Conclusion

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

## References

- [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 high-resolution time series of dissolved atmospheric gases. *Environmental Science and Technology*, 53(3):1463–1470, 2018.