Review of the manuscript *Technical note: New approach for the determination of N2 fixation rates by coupling a membrane equilibrator to a mass spectrometer on voluntary observing ships*, by Sören Iwe, Oliver Schmale and Bernd Schneider, submitted to **EGUsphere**

Manuscript overview

The manuscript provides a detailed description of a new method to determine argon (Ar), oxygen (O_2) and molecular nitrogen (N_2) concentrations in seawater using a membrane contactor to establish gas equilibrium concentrations which are then measured with mass spectrometry. Here argon is used as an inactive compound to calibrate the measurements of N_2 and O_2. The manuscript also demonstrates increased accuracy of the method compared to previous methods, both in terms of percentage error but also in the time it takes to establish the equilibrium conditions for measurement. Derivation of biological quantities from these measurements are added at the end and the system has not yet been tested in actual operation on a voluntary observation vessel.

Review overview

The presented manuscript is very detailed and well written. It is very thorough in its derivation process, set-up and testing description. The method is explicitly presented as suitable for ships of opportunity but this has not been implemented yet. I realise this is presented as a Technical Note, but still I would like to see a bit more context there, i.e. a bit more discussion on actual implementation onboard as well as on the resulting biological quantifications this would allow. I should note that I am not an expert on observational techniques for marine chemistry, and as such, I cannot provide an expert opinion on the presented method though the derivation process seems correct and complete to me.

More detailed comments are provided below.

Recommendation

Minor revision

Detailed Comments

1. Lines 7-9: here in the abstract some context is mentioned with respect to the importance of N2 fixation as a source for biological activity. Yet this statement is not repeated in the text and references for the assertion are missing. In my opinion, this provides a good context for the presented work and should merit a paragraph in the Introduction, elaborating on the statements and providing references. Now the values are given in line 61 but no context. What are the numbers for riverine N discharge? What for atmospheric deposition of N? And if these are of the same order of magnitude, can we expect a spatial differences in riverine nutrients dominating coastal waters and N2 fixation being a more dominant source offshore? In any case, the abstract cannot contain statements that the manuscript does not substantiate.
2. Line 60: I agree, but even with a larger number of voluntary observational vessels a spatial extrapolation will still be necessary. Using ferry routes is a good start to address the temporal data scarcity, much more than the spatial scarcity.
3. Line 85: missing subscripts in N_2 and O_2.
4. Line 111: This is the first mention of an appendix, so should be A and not B. Appendix A is only mentioned on line 148.
5. Line 188: there is no explanation of what aSD and rSD actually are. I can guess it, but it should be explicitly mentioned in the text.

6. Table 2: here aSD is explained but rSD still is not, even though it appears in the table.
7. Line 205: the presented accuracy for determining the N_2 concentration is high at 0.2% for the used concentration, but the much smaller value representing a "*moderate-strong N_2 fixation episode*" generates a related accuracy of 20%. Yet the method is presented as a way to do exactly that: measure N_2 fixation to derive biological production based on N_2 fixation. Given the derivations in Section 4, how do the authors see this 20% accuracy impacting the ability of the method to quantify the role of N_2 fixation in biological N drawdown?
8. Line 316: as the method is specifically aimed at voluntary observational ships, what is the expected impact of varying marine temperature and salinity levels? That is, what part of the technique is sensitive to T, S changes (e.g. solubility constants) and what would that mean for application in other areas? I would prefer to see this discussed in a separate section aimed more explicitly at marine application on ships of opportunity.
9. Line 359-360: the averaging needed over larger spatial scales due to the measurement technique make it suitable for comparison with process-based model results, with usually have a spatial resolution of several km. Point measurements are much less suitable for this. It can also be used to estimate the representativeness of point measurements taken in the vicinity of the transect.
10. Line 386: if 2 articles both used both methods, what are the results from that work? Is one better than the other, or do they differ in accuracy under different circumstances? Now the 2 methods for estimating the biological activity through O_2 are mentioned only, leaving the reading guessing what the included references found.
11. Line 394: any N_2 input to the surface mixed layer across the thermocline is ignored. Can the authors provide any references for this claim? N_2 production through denitrification can occur at depth in low oxygen zones and in sediments. The Baltic is known for the occurrence of extensive "dead zones" due to the limited circulation in the deep basins and the limited exchange with the North Sea. So I would expect N_2 production to occur there.
12. Line 408: can the authors provide a reference or explanation for the statement that N_2 fixation coincides with a significant increase in surface temperature leading to Ar gas exchange?
13. Line 425: as the aim is to apply this technique on voluntary observational ships, how do the authors propose to estimate the mixed layer depth? Will that be done in situ or afterwards using model results or earth observation tools?
14. Section 4: the authors provide two quantifications using O_2 of a proxy for net community production and one estimate for N_2 fixation rate (which is stated to be virtually equal to the measured change in N_2). It may be outside of the scope of this Technical Note, but it would be good to see some real life testing here using controlled set-ups that allow for an independent quantification of primary production. In the very least this should be proposed as a next step, and could be included in more text about the actual application of the proposed technique onboard. Now these derivations are simply presented as stand-alone results, rather than being tied to the stated objectives and actual implementation of onboard, continuous measurements. Which method of quantification of biogeochemical effects would they recommend for their proposed application? How accurate is the method if first biogeochemical processes (used as a proxy for biological activity) are quantified and then the N2 fixation rate is determined quantifying the role of N_2 fixers within the N drawdown associated with primary production?
15. Line 493: again, how do different temperatures affect the equilibrator? 18 ^{o}C seems quite warm for the Baltic and will not represent normal water temperatures entering the water chamber.