Response to Reviewer 1 Comments (RC1):

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.

Reply: We thank the reviewer for the constructive feedback and positive remarks! The manuscript will be revised in order to clarify the biochemical implications of N_2 fixation. Furthermore, we will present a more detailed explanation of the practical implementation of the measurement system on a voluntary observing ship (VOS).

Lines 7-9:

here in the abstract some context is mentioned with respect to the importance of N_2 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_2. And if these are of the same order of magnitude, can we expect a spatial differences in riverine nutrients dominating coastal waters and N_2 fixation being a more dominant source offshore? In any case, the abstract cannot contain statements that the manuscript does not substantiate.

Reply: We agree with the reviewer's comments and will make the necessary changes. We will remove the N-budget numbers from the abstract and instead revise the manuscript to ensure better alignment and consistency between the abstract and the main text. Therefore, we will expand the introduction to provide more facts regarding the importance of N_2 fixation relative to other nitrogen sources, such as riverine discharge and atmospheric deposition, and include relevant references.

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.

Reply: We agree with the reviewer. Nonetheless, the use of a single VOS represents already considerable progress compared to conventional point measurements in space and time typically conducted from research vessels. The following publications provide an example of such added value: Schneider et al., 2015; Jacobs et al., 2021; Gülzow et al., 2011.

Line 85:

missing subscripts in N2 and O2.

Reply: We will correct it in the revised manuscript.

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.

Reply: The appendices will be restructured and the order of the references will be adjusted.

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.

Reply: It will be clarified in the revised manuscript.

Table 2:

here aSD is explained but rSD still is not, even though it appears in the table.

Reply: We will add the missing information in the table caption.

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?

Reply: As mentioned by the reviewer the accuracy of the measurement system is considered high. The current accuracy of 20% for moderate-strong N_2 fixation episodes is a limitation we must accept, but it reflects the performance of our method. While other methods may not necessarily be more accurate (Wasmund et al., 2005), our approach offers the advantage of higher temporal and spatial resolution. Our main purpose is to measure N_2 concentration differences to determine the contribution of N_2 fixation to the N budget. The role of the N_2 fixation for the total seasonal biological N draw down, including the 20 % uncertainty, will briefly addressed in the revised manuscript.

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.

Reply: Since many years we are running a fully automated measurement system for the determination of surface water trace gas (CO_2, CH_4, N_2O, CO) concentrations (e.g. Schneider et al., 2014b, and references mentioned above). Therefore, our GE-MIMS system will be integrated into an existing infrastructure. Variables that affect the chemical-physical properties of dissolved gases such as N_2, O_2 and Ar will of course be measured with high accuracy (e.g., temperature, salinity, pressure, see Fig. 1). Still, we will add a short paragraph to the introduction to indicate some of the challenges we are facing when operating our GE-MIMS on a VOS.

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.

Reply: We agree with the reviewer and will address this in the conclusion of the revised manuscript.

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.

Reply: Since the focus of our manuscript is on the determination of the N budget/fixation, section 4.1 will be deleted. Herewith we are following the recommendation of Reviewer #2.

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.

Reply: N_2 fixation in the Baltic Sea takes place during mid-summer when a shallow surface layer at z < 20 m separates the surface from water below. The development of the cyanobacteria bloom starts at low wind speeds which lead to increasing temperatures up to 22 °C, stabilize the thermocline and suppress mixing with

underlying water layers. The underlying water, called intermediate water, may affect the N_2 depletion in the surface layer, however, dentrification, oxygen depletion and related phenomena occur below the permanent halocline which prevents mixing with surface water.

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?

Reply: See e.g. Schneider et al. (2014) and Schmale et al. (2019) which will be adressed in the revised manuscript.

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?

Reply: The estimation of mixed layer depth is based on temperature and salinity modeling (Gräwe et al., 2019), rather than in situ measurements. However, the accuracy of these estimations can be validated using research vessel transects (CTD profiles) or data from Argo floats. We will ensure to make this point clearer in the revised manuscript and reference the relevant literature.

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 N_2 fixation rate is determined quantifying the role of N_2 fixers within the N drawdown associated with primary production?

Reply: As we mentioned above section 4.1 will be deleted to better highlight our novel approach in section 4.2. We appreciate the suggestion and recognize that the effect of N_2 fixation can be viewed as a trigger for biological production, which could be compared with other measurement methods, especially with already existing pCO_2 measurements onboard of the VOS, where our system could be deployed (e.g., Schneider et al., 2014).
Additionally, we argue that combining our Technical Note, focused on a new method for the determination of N_2 fixation, with a discussion concerning possible methods for the quantification of primary production would exceed the scope of this paper. Therefore, we have chosen to focus on the testing of the new method in this Technical Note, however, adding plans to use it on a VOS.

Line 493:

again, how do different temperatures affect the equilibrator? 18 °C seems quite warm for the Baltic and will not represent normal water temperatures entering the water chamber.

Reply: During the period of N_2 fixation, sea surface temperatures are most likely higher than 18 °C (up to 22 °C). While varying temperatures do not affect the system's functionality, they can lead to condensation in the gas room of the equilibrator if the water temperature exceeds the ambient air temperature. In this case, temperature insulation of the membrane equilibrator is required.

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