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Interactive comment on "A multi-year observation of nitrous oxide at the Boknis Eck Time-Series Station in the Eckernförde Bay (southwestern Baltic Sea)" *by* Xiao Ma et al.

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Thank you very much for the comments. They are thought-provoking and helpful to improve our manuscript.

General comments: The present paper examined the seasonal and annual variations of dissolved N2O in a time-series station located in the southwestern Baltic Sea. The results show the coupled variations between the N2O anomalies, the oxygen concentrations, and nutrients. The paper presents a valuable new dataset of N2O and related biogeochemical parameters in a marine region subject to extensive human activities and so nutrients inputs, responsible of the deoxygenation in the Baltic Sea. After the

revision, I consider that the manuscript is highly interesting and provide relevant information about processes occurring to the N2O in the Boknis Eck. The paper is well written and structured, with an appropriate description of the state of the art, objectives are clearly outlined and discussion precisely referenced. The main strength of the paper is the monthly sampling undertaken during twelve years. However, there are several weaknesses in the paper. First, the authors make the discussion of the results based on data that are included in this study. There are references to data that exist but are not shown. But, in other to discuss about upwelling and hydrographic changes, about algal blooms and ammonium changes, the salinity, temperature, chlorophyll and ammonium data should be included and shown in this paper.

Reply: Both reviewers requested to show additional temperature, salinity, chlorophyll a and ammonium data. These data were not explicitly shown in our ms because they have been published already in Lennartz et al.: Long-term trends at the Boknis Eck time series station (Baltic Sea), 1957–2013: does climate change counteract the decline in eutrophication? Biogeosciences, 11, 6323–6339, https://doi.org/10.5194/bg-11-6323-2014.). However, in order to provide this obvious lacking information, we decided to include the seasonal and annual variations of temperature, salinity, chlorophyll a and ammonium in a new supplement to our manuscript.

Secondly, the paper lack of a proper description of the water masses presents at BE and their temporal variability.

Reply: Considering that all the measurements were conducted at one fixed location, it is difficult to investigate the water masses based on our data. However, the hydrological condition at BE are not complicated. As is written in Lines 86-87, there is no pronounced river input, and saline water from the North Sea plays a dominant role. By showing the seasonal and annual variations of temperature, salinity, dissolved oxygen and other parameters, readers gain a comprehensive idea about the hydrographic conditions at BE during 2005-2017. We rewrite the lines 86-87 which read now: There is no significant river runoff to Eckernförde Bay. Hence, the hydrographical conditions are mainly dominated by saline water input from the North Sea and less saline water from the Baltic Proper, which is typical for that region.

Specific comments: -Lines 129-130: How did you shifted the data to the 15th? Include procedure and assumptions in the text.

Reply: Since the time of sampling varied every month (usually 20-40 days interval), it would be easier for comparison and data analysis if all the samples were collected with a regular spacing. In this case, we ignored the slight time difference and assumed that all of the samples were collected on the same day every month. We have replaced lines129-130 with the following sentence: Sampling time varied for every month (usually 20-40 day interval), but for the statistical analysis, data was assumed to be regularly spaced as differences on weekly scales were minor.

Line 170: Could you explicitly explain in the text how did you computed Sc, instead just give the reference? What is the equation for computing Sc?

Reply: Sc was computed as: Sc =v/D_N2O

D_N2O =3.16×10ˆ(-6) eˆ(-18370/RT)

where v is the kinematic viscosity of seawater, which is calculated from the empirical equations given in Siedler and Peters (1986), and DN2O is the diffusion coefficient of N2O in seawater. R is the universal gas constant and T is the water temperature in K. We used the DN2O from Rhee (2000). We have incorporated this part into section 2.4.

Lines 176-184: The comparison of the range of concentrations found between Boknis and other time-series would be better move later in the text, since the reader at this point does not have enough information about the causes that differentiate it from other time-series. The authors should better discuss not only the different magnitudes of the N2O concentrations, but also the site-specific processes responsible of such differences.

Reply: Thank you for the suggestion. The purpose of the comparison is just to give a

general idea about the values of the few time-series N2O measurement published so far, because it might be different from the normal cruises which only last for days or months. A comparison of N2O concentrations between different time-series analysis is not the major topic of the manuscript, and a discussion about the site-specific processes requires detailed information on the environmental variability of the time-series stations, which does not fit in the scope of the manuscript. In this case, we keep this part in section 3.1.

Lines 207…: In case there is additional information in the BTS, such as chlorophyll, during the study period, show the data in figures instead to refer to previous studies.

Reply: Chlorophyll a data were added and are now shown in a new supplement.

Lines 235: are there NH4 data available at the study site during the study period? In that case, it would be better to show them for the discussion instead to appeal to a reference.

Reply: NH4+ data were added and are now shown in a new supplement.

Lines 238-239: “Denitrification is inhibited by the presence of O2 and thus nitrification is presumably responsible for the high N2O concentrations in winter/early spring.” This statement is not correct at all. The production of N2O by denitrification can occur at suboxic and hypoxic environments. Please, modify this sentence.

Reply: Thank you for pointing out the problem. We modified the text to “Denitrification is inhibited by the presence of high concentrations of dissolved O2 (> 20 μmol L-1) and…”

Line 239-240: The authors should normalized the N2O and pH to a constant temperature. Otherwise, temperature changes can be the responsible of this relationship because of thermodynamics changes and not necessarily due to nitrification. In fact, it is not as clear the positive correlation between the N2O and pH in figure 5, since for pH higher than 7.6, there is no apparent trend between N2O and pH. The relationship between pH and N2O obtained during incubations experiments described by Rees et al. (2016) cannot be directly compare to this study, since the experimental conditions and approaches are completely different. The authors should rewrite the entire paragraph.

Reply: We need to delete this part from the manuscript because after double-checking the data, we realize that some of the pH values were not calibrated properly. After re-calibration, the relationship between N2O and pH no long exists. We are very sorry about the mistake.

Lines 263-269: Again, the temperature salinity and Chla information at Boknis are mentioned in the text, but data are missed. If data for these parameters exist, the authors should include in the manuscript. It would reinforce some of the statement that now could look only speculative.

Reply: Temperature, salinity and Chlorophyll a data were added and are now shown in a new supplement.

Lines 287-288: "Although the observed temperatures and salinities during October 2016–April 2017 were comparable to other years,..". Please, show temperature and salinity.

Reply: Data is now shown in the supplement (see replies above).

Lines 295-296: "Considering the classical view of N2O consumption via denitrification under hypoxic and anoxic conditions". This is contrary to the statement done at lines 238-239. Consider to rewrite the first one.

Reply: Thank you pointing this out. We have revised the first one as suggested.

Lines 304-306; 308-309: The authors should make use of temperature, salinity or density to show changes in water masses.

Reply: Temperature and salinity data can be found in the supplement. Mixed layer variations can be seen in Fig. 4. As is mentioned above, it is difficult to show the changes

in water masses. We suggested that the low-N2O water was a result of advection because vertical exchange can be excluded. However, we do not have any evidence since we did not measure dissolved N2O from adjacent waters.

Lines 313: Instead of "presence" it would be more correct "concentration/level"

Reply: We have revised it as suggested.

Lines 320: "We did not observe an exceptional spring algae bloom in 2017". Please, consider to include Chla or POM to support this statement.

Reply: Chlorophyll a data is now shown in the supplement (see replies above). Unfortunately, POM data are not available. Secchi depth, a proxy of water transparency, is slightly lower in March 2017 than the average value. This could be used to support the statement. We modified the text to "Secchi depth, a proxy of water transparency, was 3.8 m in March 2017, which is only slightly lower compared to the monthly average value for March (4.5 ± 1.8 m). There was no exceptional spring algae bloom and thus we infer that assimilative uptake of nutrients by phytoplankton was not responsible for the low nutrients concentrations."

Lines 319: Why can not be shown the Chla data?

Reply: Chlorophyll a data is now shown in the supplement.

Lines 331-335: The author should also discuss the potential dependence of rates on temperature and its impact on the seasonal variations of N2O production/consumption trough the text.

Reply: Unfortunately, we did not measure N2O production/consumption rates at BE. A discussion about the potential temperature dependence of rates is, thus, too speculative. Besides, there is no significant temperature anomaly during the low-N2O-event. In this case, we suggest that the impact of temperature on the low-N2O event could be excluded.

Lines 356-357: Please, consider to support this statement with the salinity data 371-373. Please, show the density (or temperature and salinity) record to track the upwelling event in autumn 2017. Lines 377-378: Please, show the chlorophyll data. Lines385_386: Please, show the ammonium data.

Reply: The data are now shown in the supplement.

Lines 394-399: This is a very speculative paragraph as it is written. Could you give any evidence for these potential explanations of the homogeneous distribution of N2O?

Reply: Although the oxic/anoxic interface, where enhanced N2O production occurs, lasts for several months, the high N2O concentrations were usually observed only in late autumn (Fig. 4). We agree this paragraph is speculative. There are just some "potential explanations" for why there is no enhanced N2O in early autumn. Unfortunately, we do not have any further evidence to support the conjecture.

-Section 3.5: The author should evaluate in the results the impact of the dissolved gas analysis uncertainty in the air-sea flux computation and the uncertainty introduced in the net seasonal and annual air-sea NO fluxes.

Reply: The uncertainty of flux density, which is mainly derived from KN2O, with a minor contribution from the error of trace gas analysis, was estimated to be 20% (Wanninkhof, 2014). The average flux density at BE was 3.5$\pm$12.4 μmol m-2 d-1. With a large uncertainty in the flux density, it is difficult to compute meaningful seasonal/annual fluxes. In this case, we only discussed the variation of flux density in section 3.5. We have added the uncertainty of flux density in section 3.5.

Lines 416-424: The authors show that N2O concentration change seasonally, but the saturation stay almost constant. So, how can the author affirm that emissions are controlled by temperature?

Reply: There is a seasonality in surface N2O concentrations but not for the N2O saturation. During the transformation of concentrations into saturations, the effect of tem-

perature on the saturation is more essential than the effect of salinity. In summer when surface N2O concentrations are low, N2O saturations are increased by the relative high temperature (because the equilibrium concentration is decreased). In winter the N2O concentrations are high, but N2O saturations are decreased because of the high N2O solubility at low temperature condition. Temperature is "buffering" the variation of saturation and thus affecting N2O emissions, and this is our point of "a modulating role". To clarify this point we rewrite the paragraph: We found a weak seasonal cycle for surface N2O concentrations, with high N2O concentrations occurring in winter/early spring and low concentrations occurring in summer/autumn, but no such cycle for N2O saturation. The seasonality in concentration but not in saturation could be largely attributed to the effect of temperature on N2O solubility: In summer when surface N2O concentrations are low, N2O saturations are increased by the relative high temperature; and vice versa in winter. Although salinity also affects N2O solubility, its contribution is negligible compared to temperature. Temperature alleviated the fluctuation of surface N2O saturation and thus affected the sea-to-air N2O fluxes. We conclude that temperature plays a modulating role for N2O emissions.

Lines 476-484: Unless the author do not include salinity and temperature, they should not used them to conclude the hydrographic conditions at Boknis Eck. Further studies about the hydrography at the BE would complete the picture together with the biogeochemical data at the BE time-series station.

Reply: We agree that changing hydrographic conditions will affect N2O cycling at Boknis Eck as well. This, however, will require modeling studies which need to take into account the ongoing environmental changes of temperature, deoxygenation, changing frequency of North Sea water inflow etc. We think that a detailed discussion of potential future projections of the environmental variability of Boknis Eck/Eckernförde Bay is beyond the scope of the manuscript.

Please also note the supplement to this comment:

https://www.biogeosciences-discuss.net/bg-2019-165/bg-2019-165-AC1-supplement.pdf

Interactive comment on Biogeosciences Discuss., https://doi.org/10.5194/bg-2019-165, 2019.