Review of 'Seasonal variability of nitrous oxide concentrations and emissions along the Elbe estuary' 12/03/2023

This work presents five years (two years of new data) of seasonal (winter v summer) data on dissolved N2O concentrations in the Elbe River Estuary. The insights this can provide into interannual variations in aquatic N2O is relatively unique. The site of the study itself, which encompasses a large industrial port, is also important in terms of better understanding anthropogenic impacts on aquatic N2O emissions. The authors show that, even though the source of N2O seems to be strongly seasonal, emissions remain relatively consistent over the year. This is a new and interesting finding. Overall this is a nice study with the potential to be a useful contribution to both the journal and scientific understanding of aquatic N2O.

However, there are a few weaknesses with the data analysis and discussion that need to be addressed to ensure that the emissions are accurately represented and the findings are clearly conveyed.

<u>Data analysis:</u>

1. <u>Converting dissolved concentrations to emissions:</u> Like many studies, here the authors measured the dissolved concentration of the gas (N2O), and then converted this into water-air emissions based on a gas transfer velocity (k). Gas transfer velocities can be highly variable, especially in estuaries where the importance (and magnitude) of factors like wind, flow velocity, and water depth can all vary a lot over space and time. This complexity is reflected in the wide range of empirical k value parameterisations that have been developed for estuaries (see e.g., Rosentreter et al. (2021), also Hall and Ulseth (2019) for a good review of the topic, albeit for freshwater systems). However, here the authors convert measured concentrations to emissions using a single parameterisation (L116-125). This creates considerable uncertainty, which is not reflected in the reported estuary emissions estimates. Emissions should be recalculated using 3-5 k parameterisations, and the variability of these outputs reported in the results / figures. More information should also be supplied on the wind speed data used in the parameterisations. It is important to understand how the values measured during the campaigns compare to 'average' conditions around the estuary when considering the upscaled seasonal emissions values (e.g., are emissions estimates likely to be on the low side because cruises were only done on low-wind days?).
2. <u>Relationship between N2O and N inputs:</u> As discussed in the paper intro here, aquatic N2O emissions are generally predicted based on N loads to the system (i.e., leaching of N, inputs from WWTPs, etc). While here N2O emissions are discussed and presented, the N inputs side of the equation is not clear to me. In the site description it says that annual N load were ~80 Gg y-1 (L67) – but does this mean the estuary *receives* this much N, or discharges this much N? And how does this break down between sources (WWTPs v river discharge)? On L231 it says that N2O emissions were low relative to other high N input estuaries. But how do N inputs into the Elbe stack up compare to these other estuaries? I particularly wonder how the 'point source' N loads around the port might stack up with those in other urban estuaries where N2O emissions have been measured, e.g., (Wells et al., 2018). Constraining the other side of the N2O emissions v N inputs equations is critical for placing these findings into a more global context. Within the study, more information on N loads will also be important for picking apart the seasonal emissions drivers. How much N enters the estuary at the port? Is this input seasonally variable? Did it vary between the sampled years? Do these variations correspond with variations in emissions (particularly the size of the winter N2O-excess excursion)?

Paper structure:

1. Introduction: It is not entirely clear how studying N2O in the Elbe estuary will advance understanding of aquatic N2O emissions / fill a needed research gap. A stronger transition between the penultimate and last paragraphs of the discussion is needed (how does the present study relate to the broader literature). Stating a testable hypothesis, rather than just site-specific study objectives, in the last paragraph may also help make the study more clearly relevant to the broader scientific community. Is this just a case study or will the data help us understand estuary N cycling and gaseous emissions in a more fundamental way?
2. Discussion: While I think overall the data interpretation makes sense, the discussion section currently reads as a bit descriptive and could go further to place these findings in a broader context (rather than just the context of how we understand the Elbe River Estuary). This could include in particular more discussion of N cycling in urban estuaries / where there are point N pollution. Where else in the world would the observed seasonal patterns be expected to be found? I also think there is missing some discussion of 'alternative hypotheses' – work through the logic of why denitrification is not thought to be the primary driver of N2O in the estuary, and why benthic production (e.g., (Chen et al., 2022)) is also ruled out. Also please carefully edit to ensure that you are not repeating results in this section.
3. Conclusion: This is currently very focused on untangling what exactly is happening within the Elbe River Estuary, but the implications for broader understanding of aquatic N2O production and emissions are not clear.

Line comments

L17-19: This sentence is not clear (how does N2O 'compensate' for decreasing N loads?), please reword.

L22-24: "In winter, high riverine N2O concentrations led to high N2O emissions from the estuary, whereas in summer, estuarine biological N2O production led to equally high N2O emissions." This is I think getting at a crucial point (that although seasonal magnitude of N2O fluxes did not differ the drivers of these fluxes did), the meaning is not clear. What is the difference between winter 'high N2O concentrations' and summer 'high N2O production'? Reword to be more precise about these differences.

L70: How often is 'on a regular basis'? e.g., weekly, yearly, every three years?

L86: Suggest changing 'steaming upstream' to 'travelling upstream' (steaming sounds a bit antiquated)

L101-104: More information on number of nutrient samples collected per survey, as well as method detection limits and precision, would be useful.

L109: How often was 'regularly'? e.g., before each cruise?

L116: How often, and how, was dry air sampled during each cruise?

L122: The term 'flux densities' is not one I'm familiar with – more common to see something like 'water-air fluxes' or 'evasion'.

L123-125: Please provide some clarification on the upscaling approach used to calculate whole-estuary emissions. From the description it sounds like the mean flux was multiplied by the estuary surface area? Or were these calculations area-weighted, and if so at what resolution?

L127-128: Citation?

L148: Low relative to what?

L163-189: Separating the N2O data into different sections for the different units (molar concentrations, % saturation, water-air fluxes) is confusing as these are all inter-related. For instances, it is hard to make sense of the meaning of the molar concentrations without also considering whether these reflect changes in percent saturation (i.e., changes due to water temperature / salinity v source / production). I suggest integrating these lines of data (and thinking) to provide a clearer picture of estuary N2O patterns.

L204: High relative to what?

L209-218: The AOU v N2O-excess relationship really highlights the importance, and seasonality, of the port for estuary N2O emissions, with distinct peaks in the winter and consumption in the summer. Given that this underpins the discussion around seasonal N2O source switching, I wonder if there is a way to include more than just these 'representative' plots in the main text. For instance, a table with info on AOU v N2O-excess slopes, and min-max range for the port? I think if the port data is excluded something like an ANCOVA could be used to compare shifts in slope relationships.

L256-260: Interesting relationship between NO2- and N2O. This could be connected to previous work, e.g., (Sharma et al., 2022; Smith and Bohlke, 2019; Wertz et al., 2018)

L314-316: This should be in the results section

L318-324: Interesting! I wonder if the algae themselves could also be contributing to the N2O production, e.g., (Fabisik et al., 2023)

L330-332: This makes sense, but is this the only possible explanation for high emissions around the port area? What about wastewater inputs, enhanced benthic production, and/or enhanced groundwater connectivity due to dredging? Some discussion of these points will make this conclusion stronger.

L357-358: How extreme was this rain event, i.e., was it more extreme than any rainfalls over the other five years of sampling? This will help verify the attribution, and also put the pulse into context. It would then be instructive to recalculate the seasonal budget with and without this pulse.

L392: If large riverine loads were the main driver, wouldn't there be a ~continuous decrease in concentration over distance? But instead emissions peak in the port.

Table 2: Standard deviations for the air N2O concentrations would be helpful

Fig. 1: The most important pieces of info in this map (where sampling points are, where the port is, where the MTZ is) don't really stand out. Can you adjust colours, font size, etc to better highlight these key features? A scale bar for the main map would also be helpful.

Fig. 2: I'm not sure that there is much value in showing N2O concentrations (in nM) here – the % saturation information in the subsequent figure is much more effective for showing fluctuations between seasons and over the salinity gradient, given the relatively low concentrations and the impact of both temperature and salinity on N2O solubility. It would also be helpful to have 'summer' and 'winter' headings at the top of the two columns to make the point of difference more immediately obvious.

Fig. 3: A unified y axis scale would be helpful for picking out seasonal differences

Fig. 4: As above, unified axes scales would make differences between sampling dates much clearer.

Fig. 5: Different y axes are needed for the different variables (N2O, O2, TN), if not different plot panels

Fig. 6: I found this to be too many variables on the same plot to make much logical sense out of. I suggest separating into two panels, one for all of the N species (y axis unit is uM N), and then another with two y axes, one for PN and one for C/N.

Fig. 7: It would be helpful to use a different pattern or colour scheme to distinguish the winter v summer cruises.

References (included to be helpful, not as required citations)

Chen, J.-J., Wells, N.S., Erler, D.V. and Eyre, B.D. (2022) Land-use intensity increases benthic N_2O emissions across three sub-tropical estuaries. J. Geophys. Res.: Biogeosci. 127, e2022JG006899.

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Hall, R.O. and Ulseth, A.J. (2019) Gas exchange in streams and rivers. WIREs Water 0, e1391.

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Sharma, N., Flynn, E.D., Catalano, J.G. and Giammar, D.E. (2022) Copper availability governs nitrous oxide accumulation in wetland soils and stream sediments. Geochim. Cosmochim. Acta 327, 96-115.

Smith, R.L. and Bohlke, J.K. (2019) Methane and nitrous oxide temporal and spatial variability in two midwestern USA streams containing high nitrate concentrations. Sci. Total Environ. 685, 574-588.

Wells, N.S., Erler, D.V., Maher, D.T., Rosentreter, J., Hipsey, M.R. and Eyre, B.D. (2018) Estuaries as sources and sinks of N_2O across a land-use gradient in subtropical Australia Global Biogeochemical Cycles 32, 877-894.

Wertz, S., Goyer, C., Burton, D.L., Zebarth, B.J. and Chantigny, M.H. (2018) Processes contributing to nitrite accumulation and concomitant N_2O emissions in frozen soils. Soil Biol. Biochem. 126, 31-39.