

Interactive comment on “Nitrogen and oxygen availabilities control water column nitrous oxide production during seasonal anoxia in the Chesapeake Bay” by Qixing Ji et al.

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[Referee] The paper reports an experimental study of rates and pathways of nitrous oxide production in Chesapeake Bay waters. Water was sampled on three occasions (spring, summer, autumn) and incubated with N-15 labelled nitrate or nitrite under anoxic conditions. Additional incubations were made with oxygen added back to investigate the oxygen sensitivity of the processes. Based on the results, the authors draw conclusions about the controls of N₂O emissions from the Bay. The paper addresses an interesting subject and the experimental work is of good quality. However, the results do not provide strong support for the conclusions because the experimental

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conditions do not sufficiently reflect the environmental conditions in the Bay.

Also, although there are few previous experimental studies from comparable environments, the paper largely neglects the large number of previous studies on N₂O dynamics in estuaries, although these do provide some insight to the controls of N₂O emission.

Importantly, the literature points to nitrification (ammonium oxidation) as a major N₂O source in estuaries whereas the present study only investigates N₂O production through denitrification. Without data on the rates and controls of N₂O production by ammonia oxidation (i.e. experiments with N-15 labelled ammonia at different oxygen concentrations), no conclusions can be drawn about the controls of N₂O emissions from Chesapeake Bay.

Based on the mismatch between the experiments and the conclusions, I recommend that the paper be rewritten to focus on what the experiments can actually tell us, i.e. how N₂O production during denitrification is affected by oxygen, and how production from nitrate and nitrite seem to function independently, which is novel and interesting.

I also warn against trying to translate the results into understanding denitrification as a N₂O source in the Bay as a whole, and the role of anoxia in this, because denitrification is an interface process there, and the anoxic water body might serve as net sink for N₂O, drawing it down from the overlying oxycline. Here, fine scale profiling of N₂O across the interface might be more informative than the experimental approach.

[Response] The reviewer's major criticism is that the manipulated experimental conditions led to the conclusion of the Chesapeake Bay being a N₂O source, whereas the static concentration profile suggested the Bay as a N₂O sink. We shall explain as follows:

(1) Our work of environmental control of N₂O production is motivated by previous studies that identified the Chesapeake Bay as a N₂O source (Elkins et al. 1978; McElroy

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et al., 1978).

(2) Through incubation experiments, it is straightforward to draw the conclusion from the results: Adding nitrogen substrates and removing oxygen stimulate N₂O production in summer and autumn. Thus the Bay is potentially a N₂O source when pulses of nitrogen enters the water body that is experiencing summertime anoxia. Conditions in estuaries are highly variable, in both time and space, which is one of the motivations for investigating the control mechanisms on N₂O production. Failure to detect efflux at this time does not mean that intense efflux does not occur at this site at other times, or in other parts of the Bay.

(3) Indeed there's a large body of literature reporting the variation of N₂O fluxes in estuaries around the world. Many of them applied the traditional methodology: By quoting surface N₂O supersaturation, wind speed, temperature, water turbulence, etc. and measure N₂O fluxes, which is then related to water column oxygen and nitrogen availability. A small number of work applied nitrogen isotopic approach to study the mechanism of N₂O production. The isotopic approach reveals the dynamic, potential N₂O production that is masked by the static concentration profile. In addition, the isotopic approach allows to quantify the environmental controls of N₂O production in the water column.

We disagree with the reviewer about the lack of similarity between experimental and actual conditions. Our incubation experiments were designed to study the effects of oxygen and nitrogen availability on N₂O production, by changing experimental nitrogen (1 – 10 μ M) and oxygen concentrations (0 – 10 μ M) that occur regularly in the Chesapeake Bay (Lee et al., 2015).

As we have stated in the Introduction, nitrification is another important pathway for N₂O production. The focus of the manuscript is N₂O production under naturally occurring and laboratory anoxic condition. It is unlikely that nitrification could occur, and thus nitrification is beyond the scope of this manuscript. We thank the reviewer for pointing

out one possible future research direction: study the N₂O production via nitrification and denitrification and their environmental controls with extended spatial and temporal coverage across the Chesapeake Bay.

The scope of this manuscript is to examine the control of N₂O production by nitrogen and oxygen availability during denitrification under naturally occurring and laboratory anoxic condition. It is another future research direction that study the N₂O dynamics by fine scale profiling of N₂O across the interface so as to demonstrate whether the anoxic Chesapeake Bay serves as a net sink or source for N₂O. We will revise accordingly in the next version.

Specific comments [Referee] 3, 3: Why pilot? – to me this indicates preliminary results

[Response] We chose “pilot” because we are the first group to study N₂O production using ¹⁵N tracer at a single station in the Chesapeake Bay, and we examined the environmental control of denitrification pathway for N₂O production. This is a small scale study and the results are important for a larger scale, more comprehensive study in the future.

[Referee] 7, 10: The detection limit for H₂S by smell is $\sim 10\mu\text{M}$. It seems strange if no sulphide was present at all, if all more favourable oxidants were depleted.

[Response] It would be more helpful if the reviewer list the reference. First, the odor threshold of H₂S is ~ 0.5 ppb [1], and Henry's Law constant of H₂S is ~ 0.1 mol/kg/bar [2]. Under atmospheric pressure with 0.5 ppb H₂S, the equilibrium concentration of a H₂S solution is 0.5×10^{-9} bar $\times 0.1$ mol/kg/bar = 0.05×10^{-9} mol/kg ≈ 0.05 nM.

The calculation shows the detection limit for H₂S by smell is on the order of sub-nanomolar range. Under such a low concentration, the statement “sulphide compounds were most likely not present” is still robust.

[1] Iowa State University Extension (May 2004). The Science of Smell Part 1: Odor perception and physiological response. PM 1963a. [2] NIST Chemistry WebBook,

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[Referee] 9, 5: I would leave out this back-of-the-envelope estimate of denitrification. It does not add new, robust insight to N loss in C. B.

[Response] Indeed. We will remove this paragraph in the next version.

[Referee] 9, 23 and onwards: This is an important finding, which requires elaboration. I suggest calculating the direct contribution from nitrate to N₂O for all the different combinations of nitrate and nitrite concentrations instead of just one example. If rates are assumed to be constant during the incubation, a simple model can describe the concomitant production and consumption of nitrite and hence how N-15 should accumulate in the extracellular nitrite pool if the intermediate nitrite were exchanging freely.

[Response] The reviewer points out the need to quantify intracellular nitrite exchange during nitrate reduction. We think it is impossible, and beyond the scope of this paper, to quantify the actual percentage of nitrite using the data presented here. We attempted to examine one hypothesis: nitrite is fully (100%) exchanged during nitrate reduction to N₂O. And the calculation result shows that 15N-fraction labeled of N₂O from the calculation does not match our measurements. Therefore, we reject the hypothesis. More elaborate experiments can be conducted in the future to tackle this question.

[Referee] 10, 9: I don't understand this formula. How can the amount of 15N-nitrite produced depend on either the total nitrate and the total nitrite concentration? Shouldn't it simply be: Rate of NO₂⁻ production from NO₃⁻ × incubation time × initial fraction labelled of NO₃⁻?

[Response] The formula was incorrect. Now the formula has changed to "Rate of NO₂⁻ production from NO₃⁻ × incubation time × initial fraction labelled of NO₃⁻". The result is $0.2 \mu\text{mol-N L}^{-1} \text{ hr}^{-1} \times 2 \text{ hr} \times 0.16 = 0.064 \mu\text{mol-N L}^{-1}$. And the revised value will be inserted to the subsequent calculations. The resulting 15N fraction of N₂O will be 0.0087. This value is still much lower than measured value (>0.02) and our conclusion

is still robust.

[Referee] 12, 1: don't understand this. Oxygenation will just shift the zone of denitrification and N₂O consumption to greater depth (until it reaches the sediment). It won't necessarily inhibit it.

[Response] Good point. The N₂O concentration profile in July indicates that N₂O consumption is occurring. Our incubation experiment showed N₂O production is occurring at the oxic-anoxic interface. These results demonstrate denitrification is responsible for N₂O production and consumption in different layers of water column. Whether the Chesapeake Bay is net N₂O source or sink requires further evaluation, and will be one of the future research directions. We'll add these in the next version of the manuscript.

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