Review of manuscript os-2019-1
"Photoproduction of nitric oxide in seawater"
by Ye Tian et al.

1. General comments

This manuscript presents original data on NO photoproduction from nitrite in seawater samples from the northwestern Pacific Ocean. The two cruise tracks add substantially to the rather scant data coverage in open ocean waters so far. NO photochemistry is linked to the production of reactive species such as the hydroxyl radical and is therefore of wider interest for ocean scientists. The manuscript is therefore relevant to the scope of Ocean Science.

The methods used for the photochemical irradiations and sample analyses largely seem sound although their description requires some additional detail (see specific comments below).

Aspects of the authors' interpretation of the irradiation results suffer from a rather narrow perspective which neglects that nitrite and nitric oxide dynamics are tightly linked to a host of reactive nitrogen and oxygen species in seawater. Authors should consider the available literature in this regard in more detail, see for example Mack and Bolton (1999) who reviewed nitrate and nitrate photolysis pathways and their interconnections. Given the complexity of the reaction schemes in Mack and Bolton (1999) the absence of straightforward relationships between nitrite and NO production is not surprising. The authors discussions of variability in NO photoproduction rates could also be enhanced by considering factors other than nitrite concentration and light intensity (e.g. NO_3^-, ocean optics, organic reactants, see e.g. De Laurentiis et al. (2015)).

I am also concerned about some aspects of wider interpretation in section 3.6. Estimates of NO sea-to-air flux were based on steady state concentrations calculated from laboratory-derived photoproduction rates and a poorly constrained scavenging rate with not discussion of the uncertainties involved. As far as I can see, laboratory rates were not adjusted to ambient conditions, although daily averaged irradiances in the tropical North Pacific are likely very different from those in the solar simulator. Applying laboratory conditions here significantly overestimated relevant photoproduction rates and therefore resulted in artificially enhanced NO steady state concentrations and sea-to-air fluxes. This section will require thorough revision before publication.
Furthermore, the manuscript neglects to justify the validity of their approach to estimate NO steady state concentrations from 'surface rates' (aka those measure in the laboratory) rather than from depth integrated production rates for the upper mixed layer. This approach might be fine if the timescales of mixing significantly exceed the timescales of photoproduction and scavenging. However, this discussion is missing here. Furthermore, in the absence of photoproduction during night time hours sea surface NO levels will be determined by the interplay

between turbulent mixing and scavenging, and mixing is bound to lower NO levels at the sea surface. This should also be considered by the authors.

Further specific comments are detailed below.

2. Specific and editorial comments

Abstract: The abstract is rather vague, does not give any quantitative information, does not spell out how many irradiations were carried out and what oceanic regions were covered. Please add the relevant detail.

Introduction

The introduction is exceedingly brief and gives hardly any context regarding inorganic nitrogen photochemistry in aquatic systems. Again, authors should refer to Mack and Bolton (1999), and refer to key pathways involved. For example, it would be well worth mentioning that nitrate photolysis to nitrite and nitrite photolysis to NO occur in parallel and that there are various NO consumption pathways.

lines 33 ff: This sentence merely lists previous papers on NO photoproduction without any discussion of available results. To provide adequate context, the authors should add relevant quantitative information on the variability of NO production rates and discuss suggested reasons for this variability.

Methods

Lines 57 ff, Detection limits: Please explain how you calculated these – are they based on triplicate analyses?

Lines 65 ff, Temperature control: It is unclear how samples were irradiated, and how temperature was controlled. Please describe irradiation flasks/ cuvettes used (material, dimensions, optical pathlength) and explain if they were immersed in a water bath or if they were water jacketed to allow for water cooling. If samples were immersed did you correct for the effects of immersion on irradiance?

Line 74: How were subsamples collected?

Lines 80, irradiance: I understand that the Suntest CPS+ solar simulator provides 765 W m^{-2} as per manufacturer specifications. Measured lamp output is then given in units of Lux, which is a photometric unit only. Please convert 60000 lx to units of W m^{-2} for the spectral output of your system. How did the actual solar simulator output compare to ambient sea surface irradiances during the cruise?

Lines 103 ff, broadband filters: please spell out the cut-off wavelengths of the 2 filter materials used and add appropriate references.

Lines 122 ff, seawater sampling: please describe here how water samples were obtained.

Lines 139 ff, sample storage: please give the maximum storage time from sample collection to subsequent laboratory analysis.

Results and Discussion

Lines 169 ff, comparison with Anifowose et al. (2015): your statement "*The difference might be explained by different experimental set–ups such the different light sources used in the irradiation experiments*" is too vague. Please give details on irradiance levels, and other possible differences such as sample self-shading.

Lines 172 ff, pH dependence: while data on the pH dependence of NO photoproduction from nitrite may be scant, there is substantial information available on hydroxyl radical production which – as the authors state – is linked to NO:

$$NO_2^- + H_2O \rightarrow NO + \bullet OH + OH^- \qquad \text{(equation 1)}$$

Again please refer to the review in Mack and Bolton (1999) and to other more recent relevant literature, and give further detail on previous findings.

Lines 179 ff, temperature dependence: Again, the description of results and their discussion are too brief and lack detail. It would be interesting to see Arrhenius parameters, a note on the fact that NO production at 0.5mM nitrite did not increase from 20 to 30ºC, and some plausible explanations for that.

Lines 182 ff, salinity dependence: Again, this is too brief and lacks detail. At the very least there should be some quantitative statement on the observed salinity dependence, if not some parameterization.

Lines 187 ff, broadband wavelength dependence: Again, some additional detail would be useful. What are the percentage contributions to the various wavelength ranges (UVB, UVA, Vis)?
Another minor niggle: The nitrite absorption maximum according to Zuo and Deng (1998) is at 354 nm, not at 356 nm as stated in line 192. Please clarify.

Lines 195 ff, NO yield: The statement that differences in yield may be due to "*(unknown) nitrogen-containing substrates*" seems rather speculative. Can the

authors explain what N-bearing components could be present in pure laboratory water or artificial seawater?
Another much more plausible explanation would be that some nitrite reacts to N_2O_4 which then disproportionates to nitrite and nitrate (Mack and Bolton, 1999).

Line 210, DIN: Please clarify if you tested for correlations with DIN only or also with its individual components.

Line 211, CDOM: What measure of 'colored dissolved organic matter did you use?

Lines 214 ff, correlations between NO production rates and nitrite: Please give a quantitative comparison between nitrite concentrations found in your and in previous work.
Also, given that you compare your own open ocean data to results from coastal and estuarine waters, you should consider factors other than nitrite. For example, how could salinity changes or to changes in DOM levels and composition affect the relationship between nitrite and NO production?

Lines 220 ff, NO production rates: Please refer to Table 1 at the start of this paragraph. Also, I would expect some quantitative statements here, e.g. how much lower are your rates compared to previous work. What other factors may have contributed to these differences (e.g. sea surface irradiance, light attenuation?).

Lines 230 ff, air-sea flux densities: This section raises several issues.
Firstly, you will need to give at least a brief statement summarizing your approach even if details of calculations were provided elsewhere. This summary must contain references to the air-sea gas exchange parameterization used and to the source of the Henry constant.
Secondly, it is very unfortunate that no onboard wind speeds were available. Given that, the next best solution would have been to use something like the ECMWF reanalysis data sets (e.g. ERA-5, https://cds.climate.copernicus.eu/cdsapp#!/dataset/reanalysis-era5-single-levels?tab=overview)
which give hourly winds at 10 m above sea level.
Thirdly, equation (3) for calculating the steady state NO concentration uses NO photoproduction rates ***without adjustment to ambient conditions!*** This will have caused significant bias due to regional and diurnal changes in sea surface irradiance and requires revision. The authors also don't discuss uncertainty in the scavenging rate. Their calculations are based on Olasehinde et al. (2010) who conducted their work with seawater collected from the Seto Inland Sea. Is it plausible to assume that scavenging rates in the Seto Inland Sea and the tropical Pacific are comparable? Please discuss this issue.

And, finally, this section requires quantitative comparisons to previous work (=> NO concentration?, flux densities?).

See also my above **General Comments** on this issue.

Lines 253 ff, Depth integrated photoproduction: In the absence of apparent quantum yield the broadband approach taken here may be legitimate. However, there are various issues with the data used:
Firstly, it is unclear if the irradiance data used reflect the conditions in the study area. Ideally, the authors should use global irradiance levels recorded during their transects, but again – if this was not possible – ECMWF ERA-5 data could be used. Solar simulator intensity is given as 725 W m^{-2}, which contradicts the statement in Methods (765 W m^{-2}).
Secondly, K_D could have been estimated from CDOM absorbance, but no observations were reported (apart from the vague statement in Line 211). However, in the absence of CDOM or attenuation data, the authors could have used recent models such as that of Smyth (2011). The 10% residual light level depths given in Smyth (2011) suggest $K_{D(365)}$ values near 0.05 m^{-1} for the study area, two times lower than the assumed value of 0.1 m^{-1}.
Thirdly, the text in this section only gives the range of observed MLDs and does not clarify what MLD value was used in the calculations.
And, finally, it is unclear why 365 nm was used. The choice of 365 nm here contradicts the earlier statement on spectral nitrite absorbance (lines 187 ff). Chu and Anastasio (2007) (wrongly cited here as Liang and Cort 2007) suggest maximum nitrite photolysis closer to 340 nm although depth integration likely will lead to a red shift. This requires clarification.

Editorial:

The wording could be improved by careful editing.

References

Chu, L. and Anastasio, C.: Temperature and Wavelength Dependence of Nitrite Photolysis in Frozen and Aqueous Solutions, Environ. Sci. Technol., 41, 3626-3632, 2007.

De Laurentiis, E., Minella, M., Berto, S., Maurino, V., Minero, C., and Vione, D.: The fate of nitrogen upon nitrite irradiation: Formation of dissolved vs. gas-phase species, Journal of Photochemistry and Photobiology A: Chemistry, 307-308, 30-34, 2015.

Mack, J. and Bolton, J. R.: Photochemistry of nitrite and nitrate in aqueous solution: a review, J. Photochem. Photobiol. A-Chem., 128, 1-13, 1999.

Olasehinde, E. F., Takeda, K., and Sakugawa, H.: Photochemical Production and Consumption Mechanisms of Nitric Oxide in Seawater, Environ. Sci. Technol., 44, 8403-8408, 2010.

Smyth, T. J.: Penetration of UV irradiance into the global ocean, J. Geophys. Res.-Oceans, 116, 2011.

Zuo, Y. and Deng, Y.: The near-UV absorption constants for nitrite ion in aqueous solution, Chemosphere, 36, 181-188, 1998.

End of review