

Reply to Prof. Carolin Löscher.

Comments from Prof. Carolin Löscher are in black while our response in red and changes in the manuscript in blue.

The manuscript by Ye Tian et al on NO distribution in the Bohai and Yellow Sea is a first report on the distribution of this intermediate of the nitrogen cycle, complemented with a model on production sources and pathways. The paper is well-written and straight forward to understand, it will certainly be interesting to the readers of Biogeosciences.

Thank you very much for your comments and suggestions. The manuscript was amended, and you will find a detailed description in how we took all the comments and suggestions into account in the preparation of the revised manuscript.

I have some comments of rather technical nature, as well as some questions to the authors, which I hope to be perceived constructive for the quality of the manuscript. Generally, I am wondering why there hasn't been any discussion of the NO<sub>x</sub> rates from anthropogenic sources as they were mentioned three times in the paper. This would possibly be important to do, particularly in the context of production pathways, which leads me to my second point.

In our manuscript 3.4 "sea-to-air fluxes of NO" part, we describe the anthropogenic source from the ship engine in the Bohai and Yellow Seas as "Ding et al. (2018) report a satellite-derived average NO<sub>x</sub> emission estimate for June over the BS and the YS in the period from 2007 to 2016 of about  $1.3 \times 10^{10}$  g N month<sup>-1</sup>. The obvious very large discrepancy between the satellite-derived emission estimate and the one presented here results from the fact that Ding et al.'s (2018) estimate is dominated by the NO<sub>x</sub> emissions from ships' diesel engines. This indicates that oceanic NO emissions to the atmosphere only account for a negligible fraction (~0.6%) of the NO<sub>x</sub> emissions observed over the BS and YS."

Most of the production seems to be photochemical in surface waters. A possible change in dust particles or a change in UV intensity could both alter this production, I assume, to a more or less significant extent- could that be discussed?

We have added the discussion about dust particles, however, we did not do the detailed researches about this, thus we cited Olasehinde et al. (2010) and Liu et al. (2017) to elaborate the influence of the dust particles.

Besides, Olasehinde et al. (2010) found that filtered and unfiltered seawater samples collected from the Seto Inland Sea showed no significant difference in NO• photoformation rates, which suggested a negligible contribution of NO• produced by photobiological processes from particle matter in seawater. However, Liu et al. (2017) reported that the rates difference between filtered ( $0.45 \mu\text{m}$ ,  $1.46 \times 10^{-12}$  mol L<sup>-1</sup> s<sup>-1</sup>)

and unfiltered ( $1.52 \times 10^{-12}$  mol L<sup>-1</sup> s<sup>-1</sup>) seawater samples from coastal waters of the Yellow Sea indicated that particles in seawater could increase the NO production rate. The difference might be due to the composition of sample, filter membrane, etc. Thus, further research is needed.

We used the UV data from ECMWF reanalysis data sets (ERA-5 hourly mean surface downward UV radiation flux data) and analyzed the photoproduction rates with UV data. The NO photoproduction rates showed a positive relationship with the mean surface downward UV radiation flux ( $p < 0.01$ ,  $r = 0.865$ ,  $n = 26$ ),

Overall, the NO photoproduction rates showed a positive relationship with illuminance ( $p < 0.01$ ,  $r = 0.884$ ,  $n = 26$ ) and the mean surface downward UV radiation flux ( $p < 0.01$ ,  $r = 0.865$ ,  $n = 26$ ) indicating that the NO concentrations in the surface layer during daylight were dominated by photochemical production.

The average photoproduction rate in the NYS was obviously lower than those in the BS and the SYS, consistent with the average illuminances of 22450, 20433, and 27825 lx and the mean surface downward UV radiation flux 34.7, 32.1, and 40.6 W m<sup>-2</sup> for the BS, the NYS and the SYS, respectively.

In addition, there is this mysterious pathway producing NO during dark periods. One option would be nitrification, which is in some steps light sensitive- this needs to be discussed from my perception.

We have added some discussion like nitrification process and some chemical process into our manuscript.

This suggests that there was also a non-photochemical NO dark production in the surface layer like nitrification process or other chemical processes like the process of ammonium (NH<sub>4</sub><sup>+</sup>/NH<sub>3</sub>) oxidation into NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> (Joussotdubien and Kadiri, 1970). Caranto and Lancaster (2017) found that NO was an obligate bacterial nitrification intermediate produced by hydroxylamine oxidoreductase. Ward and Zafiriou (1988) also found that NO might play as an intermediate of a soluble byproduct of nitrification such as hydroxylamine.

The obvious pathway, denitrification, does not seem to contribute anything here- why is that?

In our study area, DO fluctuated from 178 to 271 μmol L<sup>-1</sup> in the surface water and 147 to 266 μmol L<sup>-1</sup> in the bottom water (added into the manuscript), which indicated that the water was well-oxygenated thus it seemed that denitrification could not occur. In our manuscript, “The water columns of the BS and YS were well-oxygenated during our study and, thus, no suboxic or anoxic conditions were detected. Therefore, we did not found any enhancement of NO concentrations in the bottom layers with low DO or NO<sub>2</sub><sup>-</sup> concentrations as observed in the OMZ of the eastern tropical South Pacific Ocean off Peru (Lutterbeck et al., 2018)”, which partly explained this.

Technical considerations:

P1

L. 12 change 'pathways' to 'turnover'

We have corrected it and thank you.

however, our knowledge about its oceanic distribution and turnover is rudimentary.

L. 17 and throughout the text: There is a dot between mol and L, please remove

Thank you, we have removed the dot between mol and L throughout the text.

L. 21 and throughout the text, the commas are incorrect. Replace 'unknown' by 'unidentified'.

We have corrected it and thank you.

The persistent nighttime NO supersaturation pointed to an unidentified NO dark production.

L. 23 The last sentence is repeated later in the manuscript and is not particularly informative as part of the abstract, I recommend removing it, here.

We have removed it as you advised.

p. 2

L. 3 What would be the impact of NO in the atmosphere?

We have added the NO environmental influence to the revised ms.

Zafiriou and McFarland (1981) suggested that photochemically produced NO is a potential source of atmospheric NO during daylight, which could further lead to ozone hole, acid precipitation and photochemical smog (Bange, 2008).

L. 14 'The current understanding...'

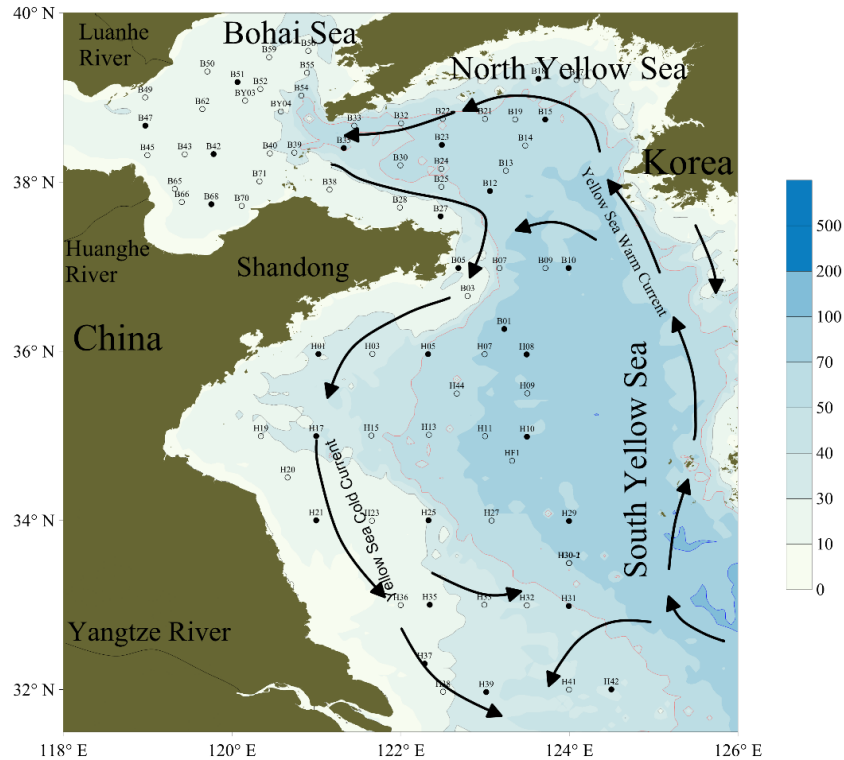
We have revised it and thank you.

The current understanding of the oceanic NO distribution is mainly limited to the ocean surface (Zafiriou and McFarland, 1981; Olasehinde et al., 2009; 2010; Liu et al., 2017) and oxygen minimum zones (Ward and Zafiriou, 1988; Lutterbeck et al., 2018).

P. 3

L 13 ff. Please remove this list and show the stations on the map in Figure 1.

We have corrected it and thank you.



**Figure 1.** Locations of the sampling stations in the BS and the YS during summer. Solid dots (●) represent the stations for incubation experiments.

L. 22 Please explain what those chemicals are added for.

The  $\text{NaN}_3$  solutions were added to remove the microbial influence while DAN were added to react with NO (process of trapping NO) and the fluorescence of the product was measured using a method described by Liu et al., 2017.

Then 200  $\mu\text{L}$   $\text{NaN}_3$  solutions were added to remove the microbial influence. After adding 10  $\mu\text{L}$  of  $1 \times 10^{-3} \text{ mol L}^{-1}$  2, 3-diaminonaphthalene (DAN, trap NO) solution and gentle mixing, the fluorescence of the mixed solution was measured before irradiation (Liu et al., 2017).

p. 4

L. 1 replace ‘were’ by ‘was’

We have corrected it and thank you.

The concentrations of dissolved inorganic nitrogen (nitrate, nitrite, and ammonium) was analyzed using a nutrient automatic analyzer (Auto Analyzer 3, SEAL Analytical, USA) in the laboratory.

L. 3 the statement of the precision sounds weird, rephrase please.

We have revised “higher” to “better than”.

The detection limits were  $0.14 \mu\text{mol L}^{-1}$  for nitrate, nitrite, and ammonium, with the precision of the method better than 3% (Liu et al., 2005).

p. 5

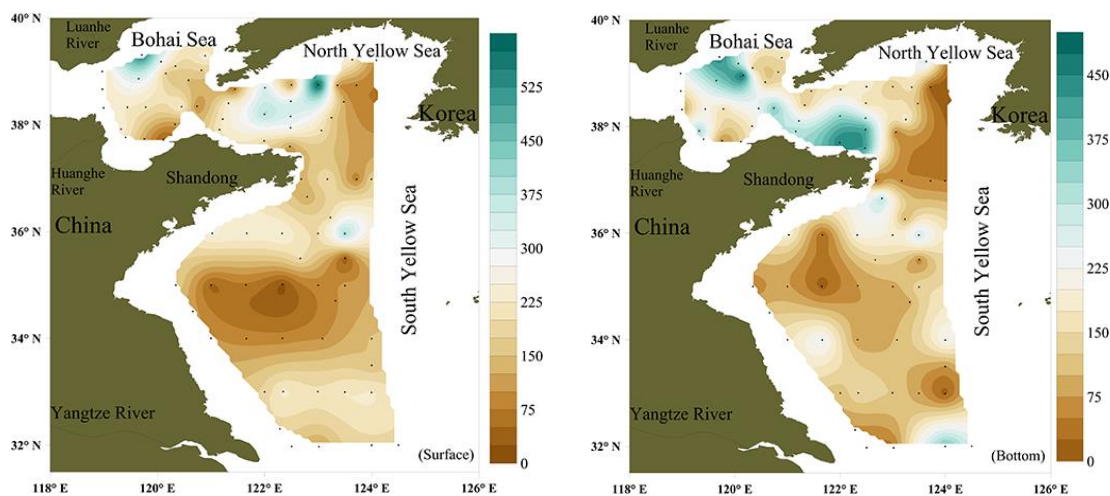
L. 16 This could still be explained, here and not only presented as a table, also the table content should be submitted to PANGAEA and a doi should go into the text, here.

We have added some information and explanation here and the data was submitted to Pangaea and we are still waiting for the doi (<https://issues.pangaea.de/browse/PDI-21749>).

In the study area, temperature varied from 8.8 to 21.7 °C and salinity varied from 29.57 to 32.73‰ in the surface water. DO fluctuated from 178 to 271  $\mu\text{mol L}^{-1}$ . The average concentrations of  $\text{NH}_4^+\text{-N}$ ,  $\text{NO}_2^-\text{-N}$ , and  $\text{NO}_3^-\text{-N}$  were 2.11, 0.20, and 2.59  $\mu\text{mol L}^{-1}$ , respectively. While temperature varied from 3.8 to 21.6 °C, salinity varied from 30.00 to 33.71‰, and DO varied from 147 to 266  $\mu\text{mol L}^{-1}$  in the bottom water.

Fig. 2 The panels could be smaller and shown side by side, also a colored figure would be beneficial, here.

We have redrawn the colored figure and made them side by side.



**Figure 2.** Horizontal distributions of NO ( $\text{pmol L}^{-1}$ ) in the surface and bottom layers.

L. 26 How would a correlation to depth make sense if we are talking about surface samples?

We have removed the description of the correlation between the depth and the NO concentration in the surface water.

p. 7

L. 11 replace 'was' by 'were'

We have corrected 'was' into 'were' and thank you.

Overall, the NO photoproduction rates showed a positive relationship with illuminance ( $p < 0.01$ ,  $r = 0.884$ ,  $n = 26$ ) and the mean surface downward UV radiation flux ( $p < 0.01$ ,  $r = 0.884$ ,  $n = 26$ ) indicating that the NO concentrations in the surface layer during daylight were dominated by photochemical production.

L. 13 Here, a discussion on the different biological pathways would fit in well.

Thank you for your suggestion. We have revised this part about the nitrification process here.

This suggests that there was also a non-photochemical NO dark production in the surface layer like nitrification process or other chemical processes like the process of ammonium ( $\text{NH}_4^+/\text{NH}_3$ ) oxidation into  $\text{NO}_2^-$  and  $\text{NO}_3^-$  (Joussotdubien and Kadiri, 1970). Caranto and Lancaster (2017) found that NO was an obligate bacterial nitrification intermediate produced by hydroxylamine oxidoreductase, Ward and Zafiriou (1988) also found that NO might play as an intermediate of a soluble byproduct of nitrification such as hydroxylamine.

L. 19 dot after ) is missing.

We have corrected it and thank you.

p. 8

L. 17/ 18 Awkward sentence, please rephrase

We rephrased it as “The horizontal distribution of NO concentration in both the surface and bottom layers were highly variable, however, there was no significant difference between the mean NO concentrations in the surface and bottom layers.”

L. 21, same comma situation as in the abstract. Again, it’s only unidentified, but possibly known. As no genetic or biological data is presented such a statement is not possible.

We have corrected “unknown” into “unidentified” and the comma situation has also been revised.

The persistent nighttime NO supersaturation pointed to a non-photochemical (so far unidentified chemical and/or biological) NO dark production.

L. 24 This is the same sentence as in the abstract, the whole idea should be discussed, before, otherwise the statement is somewhat unfounded.

As mentioned above,  $\text{NO}_x$  emissions from ship’s diesel engines were described as “Ding et al. (2018) report a satellite-derived average  $\text{NO}_x$  emission estimate for June over the BS and the YS in the period from 2007 to 2016 of about  $1.3 \times 10^{10} \text{ g N month}^{-1}$ . The obvious very large discrepancy between the satellite-derived emission estimate and the one presented here results from the fact that Ding et al.’s (2018) estimate is dominated by the  $\text{NO}_x$  emissions from ships’ diesel engines. This indicates that oceanic

NO emissions to the atmosphere only account for a negligible fraction (~0.6%) of the NO<sub>x</sub> emissions observed over the BS and YS.”

**Added references:**

Joussotdubien, J., and Kadiri, A.: Photosensitized Oxidation of Ammonia by Singlet Oxygen in Aqueous Solution and in Seawater, *Nature*, 227, 700-701, <https://doi.org/10.1038/227700b0>, 1970.