Response to reviewer #1

Comments from reviewer #1 are in black while our response in red and changes in the manuscript are in blue.

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).

Thank you very much for your advice. 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.

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)).

Reports about nitrite and nitric oxide dynamics have been added to the Introduction and the Results and Discussion parts (not showed here, showed in later part). The possible factors like NO_3^-, ocean optics, organic reactants in natural seawater (like CDOM) and other influences in artificial seawater were considered, and relevant references were also added like Mack and Bolton (1999); Kieber et al. (1999); Minero et al. (2007), and so on.

"Apart from (micro)biological processes, NO can be produced photochemically from dissolved nitrite (NO_2^-) in the sunlit surface ocean (Zafiriou and True, 1979; Zafiriou and McFarland, 1981):

$$NO_2^- + H_2O \xrightarrow{h\nu} NO + OH + OH^- \quad \text{(R 1)}$$

Mack and Bolton (1999) had reviewed the possible subsequent reaction, for example: the produced NO and OH could react to produce HNO_2 reversely (R2), and some reactions that consumed NO like R4 to R7

$$NO + OH \rightarrow HNO_2 \quad \text{(R 2)}$$

$$NO + NO_2 \rightarrow N_2O_3 \quad \text{(R 3)}$$

$$N_2O_3 + H_2O \rightarrow 2H^+ + 2NO_2^- \quad \text{(R 3)}$$

$$NO + NO \rightarrow N_2O_2 + O_2 \rightarrow N_2O_4 \quad \text{(R 4)}$$

$$2NO_2 \rightarrow N_2O_4 \quad \text{(R 5)}$$

$$N_2O_4 + H_2O \rightarrow 2H^+ + NO_2^- + NO_3^- \quad \text{(R 6)}$$

In natural sunlit seawater, photolyzed dissolved nitrate (NO_3^-) could also be a potential source of NO through NO_2^- (R 8)

$$NO_3^- \xrightarrow{h\nu} NO_2^- + \frac{1}{2}O_2 \quad \text{(R 7).}$$

In addition to NO_3^-, dissolved organic matter sometimes could be a potential source of NO_2^- (Kieber et al., 1999;Minero et al., 2007)."

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.

We agreed that laboratory results overestimated relevant photoproduction rates. Thank you so much for the advice on the ERA-5 data, the laboratory-derived photoproduction rates were adjusted into

the ambient photoproduction rates, based on the following added assumption: the rate of nitrite photoproduction into NO was proportional to the irradiance flux in order to adjust the rates under simulator light into ambient light at the sampling time (Zafiriou and McFarland, 1981). After the adjustment, the rates became lower, which was understandable.

"Since the measured NO concentrations were not available from the cruise we estimated [NO] by assuming that (1) NO production is mainly resulting from NO_2^- photodegradation, (2) the NO photoproduction R_{NO} as measured in our irradiation experiment is balanced by the NO scavenging rate R_s, (3) the rate of nitrite photoproduction into NO was proportional to the irradiance flux in order to adjust the rates under simulator light into ambient light at the sampling time (Zafiriou and McFarland, 1981;Olasehinde et al., 2010):

$$R_{NO} \times \frac{I_{ambient}}{I_{simulator}} = [NO] \times R_s, \quad \text{(EQ 1)}$$

where R_s represents the sum of the rate constants for the scavenging compounds reacting with NO times the concentrations of the scavenger compounds."

Furthermore, the manuscript neglects to justify the validity of their approach to estimate NO steady state concentrations from 'surface rates' (aka those measured 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.

On the one hand, the scavenging rates in our study were adopted from previous literatures (Zafiriou and McFarland, 1981), and most scavenging rates were measured in the surface water samples. Actually, the scavenging rates would change with the depth in the upper mixed layer. On the other hand, the NO_2^- photolysis was the mainly source of NO because some reactions like nitrification in the surface water was inhibited by light in the surface water. Thus, the NO concentration was estimated from the photolysis of surface samplers. Furthermore, according to our study results in the Yellow Sea and Bohai Sea, the photoproduction rates of NO were far higher than that of sea-to-air exchange rates in the surface water (unpublished data), which suggested that many NO radicals were scavenged and there were no significant difference between the surface NO concentration and bottom NO concentration. Therefore, it seems reasonable to assume that the photoproduction rates

and the scavenging rates were faster than the mixing rates.

We add the following text to justify the validity of their approach.

"Tian et al (2018) found that NO concentration in the surface water showed no significant difference with that in the bottom water (average depth: 43 m), so it seems reasonable to estimate the steady state NO concentration with the NO concentration in the mixed layer."

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.

According to the study of Zafiriou and McFarland (1981) and relevant studies, NO in the surface seawater seemed under detection limit after sunset, thus when adjusting into the ambient light intensity, the rates and NO concentration were estimated to 0.

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.

The abstract has been rewritten with quantitative data results from the present study.

"Nitric oxide (NO) is a short–lived intermediate of the oceanic nitrogen cycle. However, our knowledge about its production and consumption pathways in oceanic environments is rudimentary. In order to decipher the major factors affecting NO photochemical production, we irradiated artificial seawater samples as well as 31 natural surface seawater samples in laboratory experiments. The seawater samples were collected during a cruise to the western tropical North Pacific Ocean (WTNP, a N/S section from 36 to 2 °N along 146/143 °E with 6 and 12 stations, respectively, and a W/E section from 137 to 161 °E along the equator with 13 stations) from November 2015 to January 2016. NO photoproduction rates from dissolved nitrite in artificial seawater showed increasing trends with decreasing pH, increasing temperatures and increasing salinity. In contrast, NO photoproduction in the natural seawater samples from the WTNP did not show any correlations with

pH, water temperature and salinity as well as dissolved nitrite concentrations. NO photoproduction rates (average: 0.5 ±0.2 $\times 10^{-12}$ mol L^{-1} s^{-1}) in the WTNP were significantly larger than the NO air–sea flux densities (average: 1.8 $\times 10^{-12}$ mol m^{-2} s^{-1}) indicating a further NO loss process in the surface layer."

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.

The background about inorganic nitrogen photochemistry in aquatic systems has been included in the introduction part. The key pathways of NO scavenging and the following reactions were added:

"Apart from (micro)biological processes, NO can be produced photochemically from dissolved nitrite (NO_2^-) in the sunlit surface ocean (Zafiriou and True, 1979; Zafiriou and McFarland, 1981):

$$NO_2^- + H_2O \xrightarrow{h\nu} NO + OH + OH^- \quad \text{(R 8)}$$

Mack and Bolton (1999) had reviewed the possible subsequent reaction like the produced NO and OH could react to produce HNO_2 reversely (R2), and some reaction that consumed NO like R4 to R7

$$NO + OH \rightarrow HNO_2 \quad \text{(R 9)}$$

$$NO + NO_2 \rightarrow N_2O_3 \quad \text{(R 3)}$$

$$N_2O_3 + H_2O \rightarrow 2H^+ + 2NO_2^- \quad \text{(R 10)}$$

$$NO + NO \rightarrow N_2O_2 + O_2 \rightarrow N_2O_4 \quad \text{(R 11)}$$

$$2NO_2 \rightarrow N_2O_4 \quad \text{(R 12)}$$

$$N_2O_4 + H_2O \rightarrow 2H^+ + NO_2^- + NO_3^- \quad \text{(R 13)}$$

In natural sunlit seawater, photolyzed dissolved nitrate (NO_3^-) could also be a potential source of NO through NO_2^- (R 8) (Carpenter and Nightingale, 2015; Benedict et al., 2017)

$$NO_3^- \xrightarrow{h\nu} NO_2^- + \frac{1}{2}O_2 \quad \text{(R 14).}$$

In addition to NO_3^-, dissolved organic matter sometimes could be a potential source of NO_2^- (Kieber et al., 1999; Minero et al., 2007)."

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.

The sentence has been amended to include some quantitative information about NO production rates, the relevant NO concentration and NO lifetime, and previous papers were discussed.

"Table 1 summarized studies about photochemical production of NO measured in the surface waters of the equatorial Pacific Ocean (Zafiriou et al., 1980; Zafiriou and McFarland, 1981), the Seto Inland Sea (Anifowose and Sakugawa, 2017; Olasehinde et al., 2009; 2010), the Bohai and Yellow Seas (Liu et al., 2017, Tian et al., 2018) and the Kurose River (Japan) (Olasehinde et al., 2009; Anifowose et al., 2015). NO photoproduction rates varied among different seawater samples, it seems the rates in Kurose River (average: 499 $\times 10^{-12}$ mol L^{-1} s^{-1}) was biggest, which was possibly due to an increase of nitrite being released into the river in agricultural activity during the study time. However, NO concentration was about 1.6 $\times 10^{-12}$ mol L^{-1}, at lowest level, which was because of higher scavenging speed in river water (lifetime :0.25 s). The lifetime of NO showed increasing trend from river (several seconds) to inland sea (dozens of seconds) to open sea (dozens to hundreds of seconds), reviewed in Anifowose and Sakugawa (2017). NO also showed higher concentration level in coastal waters than open sea, higher photoproduction rates might account for this."

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

Further detail has been added about the detection limit. The detection limit and relative standard error were based on 7 times. The detection limit concentration was determined by S/N=3 (3×0.03) with 7 blank samples (only DAF-2 in artificial seawater) and the slope (0.101) in the low concentration range (3.3 – 33×10^{-10} mol L^{-1}).

"The detection limit concentration was determined by S/N=3 (3×0.03) with the blank samples (7) and the slope (0.101) in the low concentration range (3.3 – 33×10^{-10} mol L^{-1})."

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?

The irradiation experiment has been amended as suggested. Fig. R1 is a simple profile figure of the SUNTEST CPS+ solar simulator (ATLAS, Germany) with a thermostatic pump ((LAUDA Dr. R. Wobser Gmbh & Co. KG, Germany) in a water bath. The SUNTEST CPS+ was lifted on a steel shelf, and there was a box with a lifting platform. Bottom of the box, there was another tiled steel with a lot of square hole, and the test-tube rack was tied to the tiled steel. The hole on the second floor of the test-tube rack was filled with silica gel flower pat which could prevent the cuvettes floated (Fig. R2). The height of the cylindroid quartz cuvette was 70 mm and inner diameter was 14 mm with the volume about 10 mL (optical pathlength was the height about 70 mm). During the experiment, the 10 mL sample in the quartz cuvette was blocked by PTFE stopper, and the mouth of the quartz cuvette was wrapped by parafilm to avoid leak and being polluted. In our experiments, the samples were installed in the SUNTEST CPS+ solar simulator and a little higher than the water bath surface.

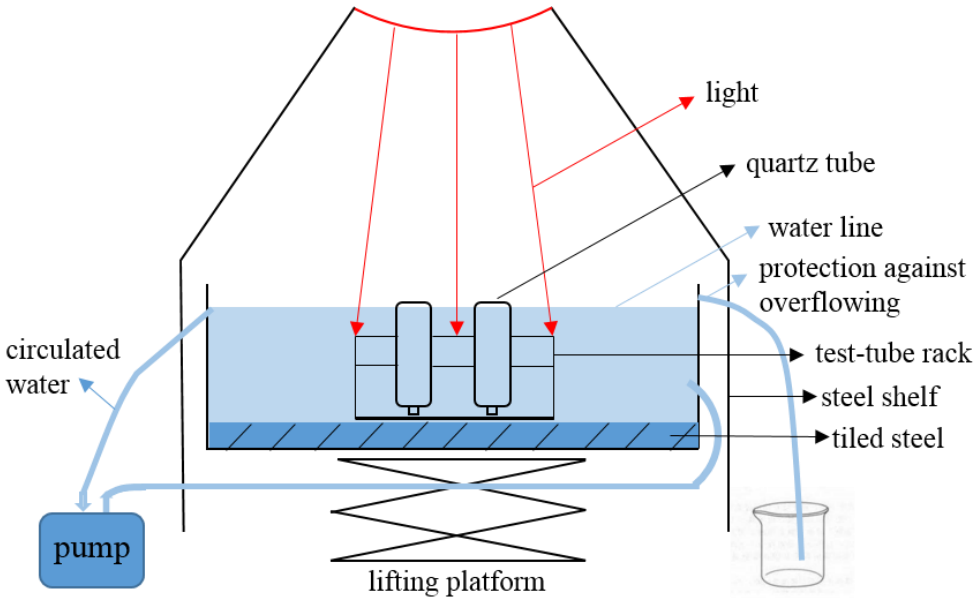

Figure R1. Simple profile figure of the SUNTEST CPS+ solar simulator with the thermostatic pump.

Figure R2. The test-tube rack.

"The temperature of the photochemical reaction was 20 ℃, controlled by a thermostatic pump ((LAUDA Dr. R. Wobser Gmbh & Co. KG, Germany). The height of cylindroid quartz cuvette used for irradiation was 70 mm and the inner diameter was 14 mm with the volume about 10 mL. The optical pathlength was about 70 mm. During the experiment, the quartz cuvette, filled with 10 mL sample and blocked by PTFE stopper, was a little higher than the water bath surface."

Line 74: How were subsamples collected?

When sampling, the SUNTEST CPS+ was turned off and triplicate subsamples were collected from each sample in dark with microsyringe (50 μL), and then the cuvettes were quickly put back into the water bath to continue the experiment until two hours.

"Triplicate samples from each treatment were collected every 0.5 h with an entire irradiation time of 2 h. At the sampling time, the SUNTEST CPS+ was turned off and triplicate subsamples were collected from each sample in dark with microsyringe (50 μL), and then the cuvettes were quickly put back into the water bath to continue the experiment until two hours."

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?

In our system, the light irradiated on the sample was maintained at light intensity about 765 W m^{-2} (measured by internal radio meter), which is spectral output of our system. The illuminance was

measured about 60000 lx using (illuminance meter TP201704017, Zhejiang Top Cloud–Agri Technology Co., Ltd, China). To avoid ambiguity, we would delete this description. The ERA-5 hourly data of our study cruise ranged from 0 (night)–873 W m^{-2}, with an average of 259 W m^{-2}, which was lower than the simulator. Thus, the laboratory-derived photoproduction rates were adjusted into the ambient photoproduction rates as described above.

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

In the study by Li et al. (2010), the films were described as: (1) full ambient sunlight (not wrapped), (3) UV-A+Vis (wrapped with UV-B block film), (3) Vis (wrapped with UV block film). In the study by Wu et al. (2015), the film were described as: Mylar film, which was purchased from United States Plastic Cor. (Lima, Ohio), could only shield UVB. The other film, obtained from CPFilm Inc., USA, was a kind of car insulation film, which could shield both UVA and UVB. According to the specification, the CPF film could shelter 99.7% UV (280–400nm) while Mylar film could shelter UVB (280–320nm).

In order to compare the contributions of ultraviolet A (UVA), ultraviolet B (UVB) and visible light to the NO photoproduction, two kinds of film light filters were used (wrapped around the quartz glass tubes): (i) a Mylar plastic film (from United States Plastic Cor., Lima, Ohio) which can only shield UVB (275–320nm) and (ii) a film, always used as car insulation film (from CPFilm Inc., USA) shielding both UVA and UVB (280–400nm) (Li et al., 2010;Wu et al., 2015).

The following references were added.

Li, Y., Mao, Y., Liu, G., Tachiev, G., Roelant, D., Feng, X., and Cai, Y.: Degradation of methylmercury and its effects on mercury distribution and cycling in the Florida Everglades, Environ. Sci. Technol., 44, 6661-6666, 2010.

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

The seawater sampling description was added to the section, as indicated below:

"A 750 mL black glass bottle was rinsed with in situ seawater three times, and then was filled with seawater quickly through a siphon directly from the Niskin bottles. When the overflowed sample reached the half volume of the bottle, the siphon was withdrawn rapidly, and the bottle was sealed

quickly."

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

It was about two months from the first sampling time to the laboratory analysis. Samples were stored in darkness at 4 ℃.

"the maximum storage time was about two months."

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.

The irradiance in Anifowose et al. (2015) was about 2/3 as powerful as natural sunlight (at noon under clear sky conditions in Higashi-Hiroshima city (34° 25′ N) on May 1, 1998), but they don't give exact value of irradiance level. The lamp power in our system was higher (1500 W), however, the set-up should also be considered. In Anifowose et al. (2015), the quartz photochemical reaction cell was 3 cm in diameter, 1.5 cm in length, and had a 6.5 mL capacity while in our study, the quartz cuvette was 70 mm height and inner diameter was 14 mm with the volume about 10 mL, thus it seemed that there are more sample self-shading effect in our study.

"The difference might be explained by different experimental set–ups such as sample self-shading, in our study, the quartz cuvette was 70 mm height and inner diameter was 14 mm with the volume about 10 mL while in Anifowose et al. (2015), the quartz photochemical reaction cell was 3 cm in diameter, 1.5 cm in length, and had a 6.5 mL capacity."

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: $NO_2^- + H_2O \rightarrow NO + {\bullet}OH + OH^-$ (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.

It is agreed that the reactions of N_2O_4 and N_2O_3 hydrolysis reaction should be considered as repoted

in Mack and Bolton (1999), and some new literatures were cited.

Carpenter, L. J., and Nightingale, P. D.: Chemistry and Release of Gases from the Surface Ocean, Chem. Rev., 115, 4015-4034, 2015.

Benedict, K. B., Mcfall, A. S., and Anastasio, C.: Quantum Yield of Nitrite from the Photolysis of Aqueous Nitrate above 300 nm, Environ. Sci. Technol., 51, 4387-4395, 2017.

"Tugaoen et al. (2018) also found the effect of lowering pH to conjugate NO_2^- to HONO allowed for HONO photolysis (pH = 2.5). Besides, higher pH could also inhibit N_2O_4 and N_2O_3 hydrolysis reaction (R4 and R7) as reported by Mack and Bolton (1999). However in previous studies of Chu and Anastasio (2007) and Zellner et al. (1990), the quantum yield of OH (which equals to the quantum yield of NO) was constant at the pH ranges from 6.0 to 8.0 and 5.0 to 9.0 under the condition of single wavelength light in nitrite solution. This might indicate that decreasing pH in our study mainly reduced NO consumption rather than increased NO production."

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 0.5 µM nitrite did not increase from 20 to 30 ℃, and some plausible explanations for that.

This section was amended to show results and their discussion. The Arrhenius formula parameters were as following description. The plausible explanation of the rates from 20 to 30 ℃ was that NO_2^- concentration here was the main influencing factor, NO_2^- might be run out at 20 ℃. If NO_2^- concentration increased, like up to 5.0 µmol L^{-1}, the temperature could make a noticeable difference.

"Higher temperatures led to increasing NO photoproduction rates according to the temperature dependence of chemical reactions given by the Arrhenius formula:

$$R = A \times \exp\left(-\frac{E}{R \times T}\right) \quad \text{(EQ 2)}$$

where A is an Arrhenius prefactor and T is the temperature (K). This indicates that an increasing temperature results in a higher rate, Chu and Anastasio (2007) also found that the quantum yield of OH or NO showed a decreasing trend from 295K, 263K to 240K. Moreover, this equation can be used to consider the difference of the rates at two temperatures $T1$ and $T2$:

$$R_{T2} = R_{T1} \times \exp\left(\frac{E}{R} \times \left(\frac{1}{T1} - \frac{1}{T2}\right)\right) \quad \text{(EQ 3)}$$

If it was assumed that E was a constant in the temperature ranges of 10 to 30 ℃ when NO_2^- = 0.5 μmol L^{-1}, and plotting ln*R* against 1/*T*, the E value was obtained as 57.5 kJ mol^{-1} K^{-1}. Using the photoproduction rate at 20 ℃ (293.15 K) as our reference point (T1), an expression of the R_T with the temperature was as follows:

$$R_T = 2.7\times10^{-10} \times \exp\left(6920 \times \left(\frac{1}{293.15} - \frac{1}{T2}\right)\right) \quad \text{(EQ 4)}$$

Similarly, we could conclude expression of the R_T with the temperature when NO_2^- = 5.0 μmol L^{-1},

$$R_T = 7 \times 10^{-10} \times \exp\left(11026 \times \left(\frac{1}{293.15} - \frac{1}{T2}\right)\right) \quad \text{(EQ 5)}$$

However, the NO production rate at 0.5 μM nitrite did not increase from 20 to 30ºC. The reason could be attributed to that NO_2^- concentration here was the main influencing factor, NO_2^- might be run out at 20 ℃. If NO_2^- concentration increased, like up to 5.0 μmol L^{-1}, the temperature could make a noticeable difference."

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.

Salinity dependence has been discussed and the quantitative statement was added, as indicated below.

"Higher salinity obviously enhanced photoproduction rates of NO in both Milli–Q water and artificial seawater samples with the initial NO_2^- concentrations of 0.5 or 5.0 μmol L^{-1}. The linear regression relationship is y = 0.37 x – 4.55 for 0.5 μmol L^{-1} NO_2^- and y=2.3 x – 39.5 for 5.0 μmol L^{-1} NO_2^-, respectively, where x is the salinity (‰) and y is the photoproduction rate (× 10^{-10} mol L^{-1} s^{-1}). This result indicates that with the increasing ion strength NO production is enhanced, however, the exact mechanism is unknown and need further study. Zafriou and McFarland (1980) also demonstrated that artificial seawater comprised with major and minor salts showed complex interactions. However, Chu and Anastasio (2007) reported that added Na_2SO_4 (4.0–7.0 mmol L^{-1}) in solution had no effect on the quantum yield of OH."

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.

The contribution of visible band, UVA band and UVB band were <1.0%, 30.7 % and 85.2 % for 0.5 µmol L^{-1} NO_2^-, respectively (sum>1 because of experimental error) and <1%, 34.2 % and 63.1 % for 5.0 µmol L^{-1} NO_2^-. The nitrite absorption maximum of 356 nm was corrected to 354 nm.

"The highest NO photoproduction rates were observed with full wave length band whereas the lowest NO rates were observed with UVB. The NO photoproduction rates approached zero at wave lengths in the visible. The contribution of visible band, UVA band and UVB band were <1%, 30.7 % and 85.2 % (sum>1 because of experimental error) and <1%, 34.2 % and 63.1 % for 0.5 and 5.0 µmol L^{-1} NO_2^-, respectively. Our results are in line with the findings of Zafiriou and McFarland (1981) who found that samples exposed to (UV+visible) wave lengths lost NO_2^- more rapidly than those exposed only to visible wave lengths alone. Chu and Anastasio (2007) found that under single wavelength light, quantum yield of OH decreased with the wavelength (280 nm to 360 and plateau until 390) which meant that single wavelength light of UVB had higher photoproduction rate than UVA. Since it might be because of the wider band of UVA (320–420 nm) that lead to the total higher rates under UVA than UVB (in our system 300-320). Moreover, the photochemical NO_2^- degradation, as described in reaction (R 1), proceeds at wave lengths of 300–410 nm with a λ_{max} of 354 nm, which is in the range of UVA (320–420 nm) (Zuo and Deng, 1998; Zafiriou and McFarland, 1981)."

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).

The explanation was added to the revised manuscript as following statement. Besides, the average $\%f_{NO}$ value in natural water samples was calculated based on the J_{NO} in artificial seawater.

"Another plausible explanation would be that during the photoproduction of NO_2^-, some NO were

oxidized into NO_2, then NO_2 dimerized (R5) and the dipolymer N_2O_4 would hydrolyze into NO_2^- and NO_3^- (R6), which actually reduce the concentration of NO_2^- (Mack and Bolton, 1999)."

"In our study, the average $\%f_{NO}$ value in natural water was 52%, indicating that there are other unknown nitrogenous compounds, for example, NO_2^- produced from NO_3^- photolysis (R7) or other organic matters which could further lead to NO production (Benedict et al., 2017;Goldstein and Rabani, 2007;Kieber et al., 1999;Minero et al., 2007)."

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

Individual components correlation with rates were analyzed.

"Photoproduction rates did not show significant correlations with NO_2^-, NO_3^- or NH_4^+"

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

Absorbance spectra of CDOM in natural seawater samples were measured from 200 to 800 nm at 1 nm increment against a Milli-Q water reference using a UV-2550 UV-VIS spectrophotometer (Shimadzu, Japan) with a quartz cell of 10 cm path length. A baseline correction was applied by subtracting the absorbance value which was an average absorption from 700 nm to 800 nm from all the spectral values mainly because of negligible CDOM absorption at this spectra range (Babin et al., 2003). Absorption coefficient (α) were calculated as

$$\alpha = (2.303 \times A)/L,$$

where A is absorbance and L is the cell's light path length in meters (Loh et al., 2004;Yang et al., 2011), the absorption coefficient at 355 nm wavelength was assigned to CDOM concentration in the present study (Blough et al., 1993;Zhu et al., 2017).

"Photoproduction rates did not show significant correlations with NO_2^-, NO_3^- , NH_4^+, pH, salinity, water temperature as well as colored dissolved organic matter (data not shown, the same method with Zhu et al (2017))(statistics computed with SPSS v.16.0)."

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.

368 Relevant nitrite concentrations were added to Table 1 and minor modifications were made: Liu et
369 al. (2017) and Anifowose and Sakugawa (2017) were added.

370 "In Table 1, the NO_2^- concentration of 0.06 μmol L^{-1} in our study was lower than most of other study
371 area like Qingdao coastal waters (0.75 μmol L^{-1}) and the Seto Inland Sea (0-0.4 μmol L^{-1} or 0.5-2 μmol
372 L^{-1}). In the study of Anifowose et al. (2015), since the NO_2^- concentration of upstream K1 station was
373 similar to ours (0.06 μmol L^{-1}), the higher R_{NO} might attributed to lower pH (7.36) as mentioned above."

374 **Table 1** Photoproduction rates (*R*), methods, average NO concentrations, NO_2^- concentrations and
375 average flux densities of NO in different regions.

Regions	*R* (mol L^{-1} s^{-1})	Methods	NO (mol L^{-1})	NO_2^- (μmol L^{-1})	Flux (mol m^{-2} s^{-1})	Sampling date	References
Seto Inland Sea, Japan	$8.7–38.8\times10^{-12}$	DAF-2	120×10^{-12}	0.5-2	3.55×10^{-12}	Oct 5–9, 2009	Olasehinde et al., 2010
Seto Inland Sea, Japan	$1.4\text{-}9.17\times10^{-12}$	DAF-2	$3\text{-}41\times10^{-12}$	~0.02-0.4	0.22×10^{-12}	Sep, 2013 and Jun, 2014	Anifowose and Sakugawa, 2017
Kurose River, Japan	$9.4–300\times10^{-12}$	DAF-2	–	-	–	–	Olasehinde et al., 2009
Kurose River (K1 station), Japan	4×10^{-12}	DAF-2	1.6×10^{-12}	0.06	–	Monthly, 2013	Anifowose et al., 2015
Jiaozhou Bay	–	DAN	157×10^{-12}	-	7.2×10^{-12}	Jun, Jul and Aug, 2010	Tian et al., 2016
Jiaozhou Bay and its adjacent waters	–	DAN	$(160\pm130)\times10^{-12}$	-	10.9×10^{-12}	Mar 8–9, 2011	Xue et al., 2011
Coastal water off Qingdao	1.52×10^{-12}	DAN	260×10^{-12}	0.75	-	Nov, 2009	Liu et al., 2017
Central equatorial Pacific	$>10^{-12}$	Chemiluminescence	46×10^{-12}	0.2	2.2×10^{-12}	R/V Knorr 73/7	Zafiriou and Mcfarland., 1981
Northwest Pacific Ocean	$0.5\pm0.2\times10^{-12}$	DAF-2	49×10^{-12}	0.06	1.8×10^{-12}	Nov 15, 2015 to Jan 26, 2016	This study

376 Also, given that you compare your own open ocean data to results from coastal and estuarine waters,
377 you should consider factors other than nitrite. For example, how could salinity changes or to changes
378 in DOM levels and composition affect the relationship between nitrite and NO production?

Salinity and other influencing factors were added.

"In the study of Anifowose et al. (2015), since the NO_2^- concentration of upstream K1 station was similar to ours (0.06 μmol L^{-1}), the higher R_{NO} might attributed to lower pH (7.36) as mentioned above. Or it might be because of the discrepancy between the river water and the seawater, considering lower nitrite level of K1, the higher R_{NO} might be attributed to dissolved organic matter. Because of its conservative mixing behavior with salinity, dissolved organic matter always showed higher level in river than open sea (Zhu et al., 2017), which could could photodegrade itself to produce NO_2^-, finally to promote R_{NO}."

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?).

Some quantitative statements were added here, for example, "the average photoproduction rate of NO measured in our cruise (0.5 $\times 10^{-12}$ mol L^{-1} s^{-1})" and NO_2^- (0.06 μmol L^{-1}) in our study area.

"Seen from Table 1, we can find that the average photoproduction rate of NO measured in our cruise (0.5 $\times 10^{-12}$ mol L^{-1} s^{-1}) was lower than that of the Seto Inland Sea (1.4–38.8 $\times 10^{-12}$ mol L^{-1} s^{-1}) and Kurose River (9.4–300 $\times 10^{-12}$ mol L^{-1} s^{-1}) which could be ascribed to higher background NO_2^- in the inland sea and river waters (Olasehinde et al., 2009; 2010), in addition to our lower photoproduction rates during nighttime. Our result is slightly lower than the R_{NO} from the central equatorial Pacific Ocean (> 10^{-12} mol L^{-1} s^{-1}), the lower concentration of NO_2^- (0.06 μmol L^{-1}) in our study area might account for this (Zafiriou and McFarland, 1981). In the study of Anifowose et al. (2015), since the NO_2^- concentration of upstream K1 station was similar to ours (0.06 μmol L^{-1}), the higher R_{NO} (4 $\times 10^{-12}$ mol L^{-1} s^{-1}) might attributed to lower pH (7.36) as mentioned reason above. Or it might be because the difference between the river water and the seawater, considering lower nitrite level of K1, the higher R_{NO} might be attributed to dissolved organic matter. Because of its conservative mixing behavior with salinity, dissolved organic matter always showed higher level in river than in open sea (Zhu et al., 2017), which could photodegrade itself to produce NO_2^-, finally to promote R_{NO}."

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.

Brief summarized statement about study approach and used references were included, as indicated below.

"The NO flux densities were computed with (EQ 6):

$$F = k_{sea}([NO] - pNO_{air} \times H^{cp}) \quad \text{(EQ 6)}$$

$$pNO_{air} = x'NO_{air} \times (p_{ss} - p_w) \quad \text{(EQ 7)}$$

here F stands for the flux density (mass area^{-1} time^{-1}) across the air-sea interface, k_{sea} is the gas transfer velocity (length time^{-1}), c_{sea} is the measured concentration of NO in the surface seawater (mass volumn^{-1}), x'NO_{air} is the mixing ratio of atmosphere NO (dimensionless). The p_{ss} is the barometric pressure while p_w was calculated after Weiss and Price (1980):

$$\ln p_w = 24.4543 - 6745.09/(T + 273.15) - 4.8489 \times \ln(T + 273.15)/100) - 0.000544 \times S) \quad \text{(EQ 8)}$$

H^{cp} is the Henry's law constant which is calculated after Sander (2015) as:

$$H^{cp}(T) = H^{\Theta} \times \exp(-\Delta sol\, H/R \times (1/T - 1/T^{\Theta})) \quad \text{(EQ 9)}$$

where $-\Delta sol \frac{H}{R} = \frac{dlnH}{dln(\frac{1}{T})}$, H^{Θ}, and $-\Delta sol\, H/R$ are tabulated ($-\Delta sol\, H/R$=1600 and H^{Θ}=1.9 ×10^{-5} mol m^{-3} pa^{-1}) in Sander (2015). Sander (2015) reviewed several literatures about NO H^{Θ} and the values in different literatures were similar. In our calculation, the value in the Warneck and Williams (2012) were used.

Then k_{sea} was calculated after Wanninkhof (2014) as (EQ 10),

$$k_{sea} = k_w (1 - \gamma_a) \quad \text{(EQ 10)}$$

γ_a is the fraction of the entire gas concentration gradient across the airside boundary layer as a fraction of the entire gradient from the bulk water to the bulk air (dimensionless), k_a is the air side air-sea gas transfer coefficient (length time^{-1}) of NO according to (Mcgillis et al., 2000;Jähne et al., 1987;Sharqawy et al., 2010) for the details of the calculation of k_w and γ_a see Tian et al. (2018)."

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-singlelevels? tab=overview) which give hourly winds at 10 m above sea level.

Thank you very much for your advice. We have got the wind speed data (wind speed near the hourly time was adopted, average: 5.55 m s^{-1}) and the irradiance data (light intensity at the sampling time was estimated with interpolation method, average: 259 W m^{-2}).

Table R1: The wind speed and the light intensity from ECMWF reanalysis data sets (ERA-5)

Station	Wind speed (m s^{-1})	Light intensity (W m^{-2})
S0301	5.90	153.34
S0303	6.41	450.50
S0305	3.88	196.00
S0307	0.95	0.00
S0309	6.33	0.00
S0310	3.50	711.53
S0313	4.33	0.00
S0315	4.58	666.00
S0317	2.55	3.90
S0319	2.49	0.00
S0321	3.19	441.36
S0323	3.84	12.41
S0325	4.55	0.00
S0701	8.44	0.00
S0704	10.64	260.97
S0707	2.75	623.04
S0709	1.46	657.65
S0711	2.51	593.52
S0713	5.86	0.00
S0715	10.43	0.43
S0717	5.76	0.00
S0719	6.31	0.00
S0721	6.90	0.00
S0723	7.64	0.00
S0724	10.11	727.17
S0725	8.03	0.00
S0727	9.76	762.90
S0729	7.49	0.00
S0730	7.57	873.16
S0733	5.47	563.87
S0735	2.43	335.56

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 local sea surface irradiance flux (0-873 W m^{-2}) from ECMWF reanalysis data sets were used, and we assumed that nitrite photoproduction rates into NO was proportional to the irradiance flux (Zafiriou and McFarland, 1981), which means the rates could be adjusted to the ambient condition through the solar simulator irradiance flux we have got. The average photoproduction rates of our sample under local conditions were about 0.5×10^{-12} mol L^{-1} s^{-1}. Besides, the pH and temperature influence were ignored (firstly, the linear relationship between temperature with rates was not significant; secondly, for lower nitrite concentration, the photoproduction rates seemed not so influenced by temperature from 20 ℃ to 30 ℃)

"Since the measured [NO] were not available from the cruise, we estimated [NO] by assuming that (1) NO production is mainly resulting from NO_2^- photodegradation and (2) the NO photoproduction R_{NO} as measured in our irradiation experiment is balanced by the NO scavenging rate R_s (3) rates of nitrite photoproduction into NO was proportional to the irradiance flux in order to adjust the rates under simulator light into ambient light at the sampling time (Zafiriou and McFarland, 1981; Olasehinde et al., 2010):

$$R_{NO} \times \frac{I_{ambient}}{I_{simulator}} = [NO] \times R_s, \quad \text{(EQ 11)}$$

where R_s represents the sum of the rate constants for the scavenging compounds reacting with NO times the concentrations of the scavenger compounds."

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.

The uncertainty in the scavenging rate of and the lifetime of NO in seawater was discussed as below:

"In the study of Zafiriou et al. (1980) and Anifowose and Sakugawa (2017), they reviewed the NO lifetime in the different area for the Kurose River (0.05–1.3 s), the Seto Inland sea (1.8–20 s), and

the central Equatorial Pacific (40-200 s, 170 ℃ Equatorial regions), which showed an increasing trend from river to open sea. It seemed that NO lifetime in our study area should be most similar to the central Equatorial Pacific. Considering part of our sampling stations were in open sea while some stations were closer to continent like New Guinea Island and Japan, we think that average lifetime about 100 s, however the uncertainty was not reported in the literature, but estimated uncertainty about 30% might be appropriate."

And, finally, this section requires quantitative comparisons to previous work (=> NO concentration?, flux densities?). See also my above **General Comments** on this issue.

Table 1 summarized NO concentrations and NO flux densities. Besides, we also add quantitative comparisons to previous work in revised manuscript as follows:

"[NO] was estimated to range from 0 to 292×10^{-12} mol L^{-1} (0 means that sampling time during nighttime), with an average of 49×10^{-12} mol L^{-1}, which was consistent with previous results in the central equatorial Pacific (46×10^{-12} mol L^{-1}), while it was lower than near continent seawater like the Seto Inland Sea (up to 120×10^{-12} mol L^{-1}) and the Jiaozhou Bay (157×10^{-12} mol L^{-1}), which might be because of higher nitrite concentration. NO showed lowest concentration in the Kurose River, which might because of less nitrite, and shortest life time might also accounted for this in river water than seawater (Anifowose and Sakugawa, 2017).

The resulting flux density of NO for WTNP ranged from 0 to 13.9×10^{-12} mol m^{-2} s^{-1}, with an average of 1.8×10^{-12} mol m^{-2} s^{-1}, which is in good agreement with that in the central equatorial Pacific (see Table 1), while it was lower than that in costal seawater such as the Seto Inland Sea or the Jiaozhou Bay, consistent with NO concentration distribution."

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}).

The solar simulator intensity 725 W m^{-2} was corrected to 765 W m^{-2}. As mentioned above, we got the ECMWF ERA-5 hourly.

"I_{ocean} was set to 185 W m^{-2}, while I_{ss} was 765 W m^{-2} in our study"

Secondly, KD 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 KD (365) values near 0.05 m^{-1} for the study area, two times lower than the assumed value of 0.1 m^{-1}.

The CDOM absorbance was measured according to the method mentioned above, we tried to search the calculation using CDOM to estimate the Kd (354), and we found that Kd was derived from the slope of log-transformed *E*d (z, λ) versus depth (Kieber et al., 2009) In Uher (1996), where Kd = $^4/_3\,(a + a_w)$, a is the light absorption coefficient of CDOM and a_w= 0.0463 m^{-1} is the light absorption coefficient of pure seawater at 350 nm. However in this way, average Kd was about 0.24 m^{-1}, which was higher than the expected value. Besides, we tried to find other methods to estimate the Kd value but failed. So the value of 0.05 m^{-1} (354 nm) in the suggested literature of Smyth, (2011) was adopted.

"In Smyth (2011), $K_{D\text{-}340}$ to $K_{D\text{-}380}$ derived from 10% residual light level depths ranged from 0.04 m^{-1} to 0.07 m^{-1} for our study area (Smyth, 2011), we used the average value of 0.05."

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.

MLD is the estimated mixed layer depth at the sampling station. The MLD was taken as the layer depth where the temperature was 0.2 ℃ lower than the 10 m near–face seawater layer (Montégut, 2004), ranging from 13–77 m with an average of 37 m. Actually, we calculated R_{ocean} respectively and then we get an average value of R_{ocean} and we don't use the average MLD value in the calculations.

"The MLD was taken as the layer depth where the temperature was 0.2°C lower than the 10 m near–face seawater layer (Montégut, 2004), ranging from 13–77 m with an average of 37 m."

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.

The 365 value was corrected to 354 as Chu and Anastasio (2007) and Zuo and Deng (1998). It was an error that we used the value of 356 nm (the most maximum absorption wavelength of nitrite) as the chosen wavelength value of the K-d, but we wrote it wrong as 365 nm.

About spectral nitrite absorbance experiment, we found that the rates under full-band>UVA>UVB>visible, which was not consistent with single wavelength characteristic in the study by Chu and Anastasio (2007), under single wavelength light, quantum yield of OH decreased with the wavelength (Figure 2: 280 nm to 360 and plateau until 390) which meant that single wavelength light of UVB had higher photoproduction rate than UVA. Since it might be because of the wide band of UVA (320–420 nm) that lead to the total higher rates under UVA than UVB (in our system 300-320).

"As described above, UVA is the most influencing wavelength and it is reported that 354 nm is primarily responsible for NO production (Chu and Anastasio, 2007; Li et al., 2011; Zafiriou and McFarland, 1981)"

Editorial: The wording could be improved by careful editing.

We would carefully modify our manuscript and make it improved.

The following references were added.

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