Dear Mario Hoppema,

we would like to thank you and the anonymous reviewer and Prof. Oliver Zafiriou for their comments which helped us to improve our manuscript. Please find a point-by-point responses (in red) to all comments (in black) in this document. The line numbers mentioned by the reviewers refer to the original version of the manuscript while the line numbers in our replies refer to the revised version of the manuscript.

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 (lines 33–49).

“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):

\[
\text{NO}_2^- + \text{H}_2\text{O} \rightarrow \text{NO} + \text{OH} + \text{OH}^- \quad \text{(R 1)}
\]

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:

\[
\begin{align*}
\text{NO} + \text{OH} & \rightarrow \text{HNO}_2 \quad \text{(R 2)} \\
\text{NO} + \text{NO}_2 & \rightarrow \text{N}_2\text{O}_3 \quad \text{(R 3)} \\
\text{N}_2\text{O}_3 + \text{H}_2\text{O} & \rightarrow \text{2H}^+ + 2\text{NO}_2^- \quad \text{(R 3)} \\
\text{NO} + \text{NO} & \rightarrow \text{N}_2\text{O}_2 + \text{O}_2 \rightarrow \text{N}_2\text{O}_4 \quad \text{(R 4)} \\
2\text{NO}_2 & \rightarrow \text{N}_2\text{O}_4 \quad \text{(R 5)} \\
\text{N}_2\text{O}_4 + \text{H}_2\text{O} & \rightarrow \text{2H}^+ + \text{NO}_2 + \text{NO}_3^- \quad \text{(R 6)}
\end{align*}
\]

In natural sunlit seawater, photolyzed dissolved nitrate (NO$_3^-$) could also be a potential source of NO through NO$_2^-$ (R 8):

\[
\text{NO}_3^- \xrightarrow{\text{hv}} \text{NO}_2^- + \frac{1}{2}\text{O}_2 \quad \text{(R 7)}.
\]

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 irradiiances 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 (lines 356–364).

“Since the measured NO concentrations were not available from the cruise we estimated [NO] by assuming that (1) NO production is mainly resulting from NO₂¹⁻ 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 (lines 373–379)

“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 (lines 11–24).

“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 rates (average: 0.5 ± 0.2 ×10^{-12} mol L^{-1} s^{-1}) in the natural seawater samples from the WTNP did not show any correlations with pH, water temperature and salinity as well as dissolved inorganic nitrite concentrations. The flux induced by NO photoproduction in the WTNP (average: 13 ×10^{-12} mol m^{-2} s^{-1}) were significantly larger than the NO air–sea flux densities (average: 1.8×10^{-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 (See line 33–54.):

“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):

\[
\text{NO}_2^- + \text{H}_2\text{O} \xrightarrow{\text{hv}} \text{NO} + \text{OH} + \text{OH}^- \quad (\text{R}8)
\]

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

\[
\text{NO} + \text{OH} \rightarrow \text{HNO}_2 \quad (\text{R}9)
\]
In natural sunlit seawater, photolyzed dissolved nitrate (NO₃⁻) could also be a potential source of NO through NO₂⁻ (R 8) (Carpenter and Nightingale, 2015; Benedict et al., 2017).

\[
\text{NO}_3^- \xrightarrow{h\nu} \text{NO}_2^- + \frac{1}{2} \text{O}_2
\] (R 14).

In addition to NO₃⁻, dissolved organic matter sometimes could be a potential source of NO₂⁻ (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 (line 55–66).

“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: \(499 \times 10^{-12} \text{ mol L}^{-1} \text{ s}^{-1}\)) 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 \(1.6 \times 10^{-12} \text{ mol L}^{-1}\), 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}) (lines 93–96).

“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 (lines 103–110).
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°C, 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 (lines 115-118).
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) (lines 145-149).

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.


**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 (lines 177-179):

“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 (line 185). Samples were stored in darkness at 4°C.

“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 (lines 216-219).

“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: \( \text{NO}_2^- + \text{H}_2\text{O} \rightarrow \text{NO} + \cdot \text{OH} + \text{OH}^- \) (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 \( \text{N}_2\text{O}_4 \) and \( \text{N}_2\text{O}_3 \) hydrolysis reaction should be considered as reported in Mack and Bolton (1999), and some new literatures were cited (lines 228-235).


“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 \( \text{N}_2\text{O}_4 \) and \( \text{N}_2\text{O}_3 \) 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 \( \cdot \text{OH} \) (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 \( \mu \text{M} \) nitrite did not increase from 20 to 30°C, 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°C was that NO₂⁻ concentration here was the main influencing factor, NO₂⁻ might be run out at 20°C. If NO₂⁻ concentration increased, like up to 5.0 μmol L⁻¹, the temperature could make a noticeable difference (lines 236–254).

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

\[ R = A \times \exp \left( -\frac{E}{RT} \right) \]  \hspace{1cm} (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 \( T_1 \) and \( T_2 \):

\[ R_{T_2} = R_{T_1} \times \exp \left( \frac{E}{R} \times \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \right) \]  \hspace{1cm} (Eq 3)

If it was assumed that \( E \) was a constant in the temperature ranges of 10 to 30°C when NO₂⁻ = 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°C (293.15 K) as our reference point (T1), an expression of the \( R_T \) with the temperature was as follows:

\[ R_T = 2.7 \times 10^{-10} \times \exp \left( 6920 \times \left( \frac{1}{293.15} - \frac{1}{T} \right) \right) \]  \hspace{1cm} (Eq 4)

Similarly, we could conclude expression of the \( R_T \) with the temperature when NO₂⁻ = 5.0 μmol L⁻¹,

\[ R_T = 7 \times 10^{-10} \times \exp \left( 11026 \times \left( \frac{1}{293.15} - \frac{1}{T} \right) \right) \]  \hspace{1cm} (Eq 5)

However, the NO production rate at 0.5 μM nitrite did not increase from 20 to 30°C. The reason could be attributed to that NO₂⁻ concentration here was the main influencing factor, NO₂⁻ might be run out at 20°C. If NO₂⁻ 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 (lines 255–263).

“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 \( y = 0.37x - 4.55 \) for 0.5 μmol L$^{-1}$ NO$_2^-$ and \( y = 2.3x - 39.5 \) 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$_2$SO$_4$ (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 (lines 264–275).

“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 summational higher rates under UVA than UVB (in our system 300–320). Moreover, according to the UV–visible absorption spectra of NO₂⁻, \( \lambda_{\text{max}} \) was 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 \( \text{N}_2\text{O}_4 \) which then disproportionates to nitrite and nitrate (Mack and Bolton, 1999).

The explanation was added to the revised manuscript as following statement (lines 280–283). Besides, the average \( f_{\text{NO}} \) value in natural water samples was calculated based on the \( J_{\text{NO}} \) in artificial seawater (lines 323–330).

“Another plausible explanation would be that during the photoproduction of NO₂⁻, some NO were oxidized into NO₂, then NO₂ dimerized (R5) and the dipolymer \( \text{N}_2\text{O}_4 \) would hydrolyze into NO₂⁻ and NO₃⁻ (R6), which actually reduce the concentration of NO₂⁻ (Mack and Bolton, 1999).”

“In our study, the average \( f_{\text{NO}} \) value in natural water was 52%, indicating that there are other unknown nitrogenous compounds, for example, NO₂⁻ produced from NO₃⁻ 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.(line 296)

“Photoproduction rates did not show significant correlations with NO₂⁻, NO₃⁻ or NH₄⁺”

**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

\[ \alpha = \frac{2.303 \times A}{L} \]

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).

Line 296–298:

“Photoproduction rates did not show significant correlations with NO\textsubscript{2}, NO\textsubscript{3}, NH\textsubscript{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.

Relevant nitrite concentrations were added to Table 1 and minor modifications were made: Liu et al. (2017) and Anifowose and Sakugawa (2017) were added (line 309–312).

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

<table>
<thead>
<tr>
<th>Regions</th>
<th>( R ) (mol L\textsuperscript{-1} s\textsuperscript{-1})</th>
<th>Methods</th>
<th>NO (mol L\textsuperscript{-1})</th>
<th>NO\textsubscript{2} (µmol L\textsuperscript{-1})</th>
<th>Flux (mol m\textsuperscript{-2} s\textsuperscript{-1})</th>
<th>Sampling date</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seto Inland Sea, Japan</td>
<td>8.7–38.8×10\textsuperscript{-12}</td>
<td>DAF-2</td>
<td>120×10\textsuperscript{-12}</td>
<td>0.5-2</td>
<td>3.55×10\textsuperscript{-12}</td>
<td>Oct 5–9, 2009</td>
<td>Olasehinde et al., 2010</td>
</tr>
<tr>
<td>Seto Inland Sea, Japan</td>
<td>1.4–9.17×10\textsuperscript{-12}</td>
<td>DAF-2</td>
<td>3-41×10\textsuperscript{-12}</td>
<td>–0.02-0.4</td>
<td>0.22×10\textsuperscript{-12}</td>
<td>Sep, 2013 and Jun, 2014</td>
<td>Anifowose and Sakugawa, 2017</td>
</tr>
</tbody>
</table>

Table 1 Photoproduction rates \( (R) \), methods, average NO concentrations, NO\textsubscript{2} concentrations and average flux densities of NO in different regions.
<table>
<thead>
<tr>
<th>Location</th>
<th>Concentration</th>
<th>Method</th>
<th>pH</th>
<th>Temperature</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kurose River, Japan</td>
<td>9.4–300×10^{-12}</td>
<td>DAF-2</td>
<td>-</td>
<td></td>
<td>Olasehinde et al., 2009</td>
</tr>
<tr>
<td>Kurose River (K1 station), Japan</td>
<td>4×10^{-12}</td>
<td>DAF-2</td>
<td>0.06</td>
<td></td>
<td>Anifowose et al., 2015</td>
</tr>
<tr>
<td>Jiaozhou Bay</td>
<td>-</td>
<td>DAN</td>
<td>7.2×10^{-12}</td>
<td></td>
<td>Tian et al., 2016</td>
</tr>
<tr>
<td>Jiaozhou Bay and its adjacent waters</td>
<td>-</td>
<td>DAN</td>
<td>10.9×10^{-12}</td>
<td></td>
<td>Xue et al., 2011</td>
</tr>
<tr>
<td>Coastal water off Qingdao</td>
<td>1.52×10^{-12}</td>
<td>DAN</td>
<td>0.75</td>
<td></td>
<td>Liu et al., 2017</td>
</tr>
<tr>
<td>Central equatorial Pacific</td>
<td>&gt; 10^{-12}</td>
<td>Chemiluminescence</td>
<td>46×10^{-12}</td>
<td>0.2</td>
<td>R/V Knorr 73/7</td>
</tr>
<tr>
<td>Northwest Pacific Ocean</td>
<td>0.5 ± 0.2×10^{-12}</td>
<td>DAF-2</td>
<td>0.06</td>
<td>1.8×10^{-12}</td>
<td>This study</td>
</tr>
</tbody>
</table>

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?

Salinity and other influencing factors were added (lines 310–315).

“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 ×10^{-12} mol L^{-1} s^{-1})” and NO_2^- (0.06 µmol L^{-1}) in our study area (lines 304–306).
“In Table 1, we can find that the average photoproduction rate of NO measured in our cruise (0.5 × 10^{-12} mol L^{-1} s^{-1}) was lower than that of the Seto Inland Sea (1.4–38.8×10^{-12} mol L^{-1} s^{-1}) and Kurose River (9.4–300×10^{-12} mol L^{-1} s^{-1}) which could be ascribed to higher background NO\textsubscript{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\textsubscript{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\textsubscript{2} concentration of upstream K1 station was similar to ours (0.06 μmol L^{-1}), the higher \( R_{NO} \) (4×10^{-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\textsubscript{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 (lines 333–352).**

“The NO flux densities were computed with (Eq 6):

\[
F = k_{sea} ([NO] - pNO_{air} \times H^{p}) \\
\text{Eq 6}
\]

\[
pNO_{air} = x'NO_{air} \times (p_{ss} - p_{w}) \\
\text{Eq 7}
\]

here \( F \) stands for the flux density (mass area\textsuperscript{-1} time\textsuperscript{-1}) across the air-sea interface, \( k_{sea} \) is the gas transfer velocity (length time\textsuperscript{-1}), [NO] is the measured concentration of NO in the surface seawater (mass volumen\textsuperscript{-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):
\[
\ln p_w = 24.4543 - 6745.09/(T + 273.15) - 4.8489\times\ln (T + 273.15)/100 - 0.000544\times S
\]  
(Eq 8)

\(H^p\) is the Henry's law constant which is calculated after Sander (2015) as:

\[
H^p(T) = H^\Theta \times \exp (-\Delta sol H/R \times (1/T - 1/T^\Theta))
\]  
(Eq 9)

where \(-\Delta sol H/R = \frac{d\ln H}{d\ln(p)}\), \(H^\Theta\), and \(-\Delta sol H/R\) are tabulated \((-\Delta sol H/R=1600\) and \(H^\Theta=1.9\times10^{-5}\) mol m\(^{-3}\) pa\(^{-1}\)) in Sander (2015). Sander (2015) reviewed several literatures about NO \(H^\Theta\) 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),

\[
k_{sea} = k_w (1 - \gamma_a)
\]  
(Eq 10)

\(\gamma_a\) 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 \(\gamma_a\) 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)

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

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 $0.5 \times 10^{-12}$ 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°C to 30°C) (lines 356–364).

"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 \(\dot{R}_{\text{NO}}\) 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):

\[
\dot{R}_{\text{NO}} \times \frac{I_{\text{ambient}}}{I_{\text{simulator}}} = [\text{NO}] \times R_s, \tag{Eq 11}
\]

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 (lines 367-373):

“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°E 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 (lines 376–386):

“Then [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 $49 \times 10^{-12}$ mol L$^{-1}$, which was consistent with previous results in the central equatorial Pacific ($46 \times 10^{-12}$ mol L$^{-1}$), while it was lower than near continent seawater like the Seto Inland Sea (up to $120 \times 10^{-12}$ mol L$^{-1}$) and the Jiaozhou Bay ($157 \times 10^{-12}$ 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).

In Table 1, The resulting flux density of NO for WTNP ranged from 0 to $13.9 \times 10^{-12}$ mol m$^{-2}$ s$^{-1}$, with an average of $1.8 \times 10^{-12}$ 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 coastal 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 (line 395).

“I$_{\text{ocean}}$ was set to 185 W m$^{-2}$, while I$_{\text{ss}}$ 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 $Ed(z, \lambda)$ 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 (lines 396-398).

“In Smyth (2011), $Kd_{340}$ to $Kd_{360}$ 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°C 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 (line 399).

“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>UV A>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) (line 396).

“As described above, \( K_{D-354} \) was applied to estimate the MLD.”

Editorial: The wording could be improved by careful editing.

We would carefully modify our manuscript and make it improved.

The following references were added.


Zellner, R., Exner, M., and Herrmann, H.: Absolute OH quantum yields in the laser photolysis of nitrate,

Response to Prof. Oliver Zafiriou.

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

This paper’s major ocean-relevant finding is that “NO photoproduction from the natural seawater samples from the WTNP did not show any correlations with pH, water temperature and salinity as well as dissolved nitrite concentrations.”

Our reply: Thank you for your advice, we have amended our manuscript according to your advice.

In artificial seawater samples of our study, NO photoproduction rates from dissolved nitrite showed increasing trends with decreasing pH, increasing temperatures and increasing salinity. This means several factors would affect NO photoproduction rates, thus it is understandable that there were no significant relationships between NO photoproduction rates with pH, water temperature and salinity as well as nitrite concentrations in natural seawater samples from WTNP since the several factors were different between sampling stations. Besides, we also estimated NO concentration in the surface water, the sea-to-air flux, and the photoproduction rates in the mixed layer in our study area.

This is consistent with ref10, which found a strong correlation of R with [NO₂⁻] at >0.3 μM (no data below that) with Y intercept R= 2 × 10^{-12} very close to the reported R here 2.1 ±1.3 × 10^{-12} (Table 1). The implication is that, despite oceanic [NO₂⁻] varying ~0.02-0.5 μM (what is [NO₂⁻] detection limit?) in this study, the major source(s) of NO are unknown, consistent with R10’s correlation and suggesting that the method unfortunately may have been applied in regions where R is outside the DAF-2 method’s range of validity.

Our reply: The [NO₂⁻] detection limit is about 0.05 μmol L⁻¹, while 1/2 of the detection limit (0.025 round-off to 0.02) was used as the concentration of the sampling stations below the detection limit (lines 188–192).

“The concentrations of dissolved inorganic nitrogen (DIN = nitrate, nitrite, and ammonium) from the cruise were analyzed using an automated nutrient analyzer (SKALAR San++ system, SKAIAR, Netherlands) onboard. The detection limits were 0.05 μmol L⁻¹ for nitrate, nitrite and ammonium.
When the concentration was below detection limit, $\frac{1}{2}$ of the detection limit (0.025 round-off to 0.02) was used.”

**Our reply:** In the study of Anifowose and Sakugawa (2017), NO$_2^-$ concentration, which varied from ~0.02-0.3 μmol L$^{-1}$, showed linear correlation with $R_{NO}$ (1.4-9.2 $\times 10^{-12}$ mol L$^{-1}$ s$^{-1}$, $R^2=0.9537$) in the surface seawater from the Seto Inland Sea in 2013 and 2014, so the average rate $2.1 \pm 1.3 \times 10^{-12}$ mol L$^{-1}$ s$^{-1}$ in our study (under simulator) was inside the DAF-2 method’s range of validity.

The method used is “DAF-2” method for NO (ref 9), previously used in seawater (ref 10, in a major journal). Thus it is not surprising that the authors utilized DAF-2. However, this review argues that the DAF-2 results are highly questionable because its response factor may vary in uncharacterized ways under varying conditions, such as T, spectral quality and intensity of light, amount and nature of CDOM that yields ROS and other radicals, [NO$_2^-$], and possibly also [O$_2$] and [NH$_4^+$] (as NH$_3$), and redox-active trace metals. Thus the central issue is: To what extent the $R_{NO}$ values found (and lack of correlation) are due to unidentified marine biogeochemical factors vs. un-assessed method variables? The authors need to clarify these aspects in detail.

**Our reply:** If we take the missing 30% of $f_{NO}$ as the experimental error, then in our study, using the $J_{NO}$ in the artificial seawater, the average $%f_{NO}$ value in natural water was calculated to be 52% (−30%), indicating that there are other unknown nitrogenous compounds. For example, NO$_2^-$ can be produced from NO$_3^-$ photolysis (NO$_3^-$ $\rightarrow$ NO$_2^-$+$\frac{1}{2}$O$_2$) or other organic matters which could further lead to NO production (Kieber et al., 1999; Goldstein and Rabani, 2007; Minero et al., 2007; Benedict et al., 2017). Thus, unidentified marine biogeochemical factors might account for the 48% (+30%) of the NO production while un-assessed method variables might account for 30% of the NO production (lines 326–333).

“In our study, the average $%f_{NO}$ value in natural water was 52% (-30%), this indicated that there are about 48% (+30%) other unknown nitrogenous compounds, for example, NO$_2^-$ produced from NO$_3^-$ photolysis (R7) or from other organic matter which could further lead to NO production (Benedict et al., 2017; Goldstein and Rabani, 2007; Kieber et al., 1999; Minero et al., 2007).”

Danger: the DAF-2 method is assumed to involve a complex series of reactions (below), terminating
in DAF-2 → DAF-2T. Yet the postulated central role of O₂ (Ref 9, fig1) was never shown, NO + O₂ kinetics follow [NO][O₂] – slow at low [NO]. DAF-2T likely can form with or without O₂ (see them, affect DAF-2T yields (only 1-18%, an 18× variation! (ref 9)), so that matrix effect evaluation requires assessing these “YD factors” in the matrix at hand.

**Our reply:** In our study, the external standard method was used with a series of NO standard as follows: an aliquot of 10 mL Milli-Q water was bubbled with N₂ gas at a flow of 10 mL min⁻¹ for 2 h to remove O₂ after 10 min of ultrasonic and heat degassing. The solution was then bubbled with high-purity NO gas (99.9 %, Dalian Date Gas Ltd., China) for 30 min. The concentration of the saturated NO stock solution was 1.4 mmol L⁻¹, which could be used within 3 h (Lantoine et al., 1995). A secondary standard of NO solution was also prepared in N₂-purged water from the NO stock solution (Xing et al., 2005; iu et al., 2017). The series samples were trapped by DAF-2 by injecting series of NO standard solution into DAF-2 solution (1.4 μmol L⁻¹ in artificial seawater) using different (micro)syringe. Then the measured product (DAF-2T) peak area was plotted against NO concentration, and the standard curve was y = 0.101 x (x: μmol L⁻¹, y: nmol L⁻¹); the intercept was removed because in our irradiation experiment, the peak area of the control samples (wrapped in aluminum foil) was subtracted from all the samples. Thus, our detection method was somewhat a little different from Ref 9 although the reaction between NO and DAF-2 in our study was the same as Ref 9.

**Method chemistry #1 (from ref 9):** “However, DAFs do not react directly with NO but rather with the oxidized form of NO. In fact, it has been proposed that the reaction mechanism of DAF with NO involves N₂O₃ according to the following scheme: NO + O₂→2NO₂ (2) 2NO₂ + 2NO→2N₂O₃ (3)” Thus the simplest case involves truly pure water + light + nitrite +DAF-2. In the presence or absence of O₂, the dominant reaction of *OH, which has not been considered, is *OH + NO₂* → NO₂, that N₂O₃ can form in the absence of O₂; the presence of O₂ adds a second pathway forming DAF- 2T. Furthermore, can other oxidants convert NO to NO⁺, which may be able react with DAF-2 to form DAF-2T.

**Our reply:** In the Supporting Information to accompany the manuscript of ref #10, Olasehinde et al (2010) studied the effect of the addition of benzene which served as *OH scavenger, and the
results showed (Supporting Information of ref #10, page 5 line 4) “no appreciable difference between the fluorescence intensity of DAF-2T formed in the presence and absence of benzene, suggesting the negligible effect of •OH radicals on the nitric oxide generated in equation S1. Further, it has been shown that 2 μM DAF-2 was sufficient to effectively scavenge all NO• formed from the irradiation of 10 μM NO2 in Milli-Q water in the presence of other in situ generated radicals (5).” Thus we think that the influence of •OH, whether existed in the water samples or photolyzed from NO2, could be neglected.

Method chemistry #2 also, (ref 9) “Since …•OH was generated along with NO upon NO2 was a possibility that the degradation of DAF-2 could be a result of the reaction of •OH with DAF-2. To study this, we carried out a 30 min irradiation of 0.2 μM DAF-2 with 100 μM H2O2 in Milli-Q water and analyzed DAF-2 before and during the illumination period, at suitable intervals. The signal intensities of DAF-2 were constant during the illumination period (Figure 5), suggesting that the degradation of DAF-2 under these conditions could not be attributed to the reaction of DAF-2 with OH radicals.” and “the mean value (±standard deviation) of YD 0.042 ± 0.003 was used in all calculations of RNO.” How was YD measured in a way relevant to seawater? Ref 9 never showed that a significant amount of OH• was formed by the irradiation of HOOH; also, another reaction, OH• + HOOH→HOH + HOO•; HOO• →O2•− + H+, might compete with OH• + DAF-2 destruction. Thus even in the simplest “pure water” matrix, the DAF-2 method calibration is in adequate. But in this paper we do not care about “pure water,” except insofar as it can validate the method. In seawater, OH• also forms other inorganic radicals (Br2•, CO3•) that have major effects on the NO2• + hv →pathways. These reactions presumably make YD factors from pure water irrelevant, yet ref 9 used a pure-water value. There seem to be no determinations of YD in this paper.

Our reply: It is agreed that YD factors in Milli-Q water is different from those in seawater medium. As mentioned above, the external standard method was used in our study. The YD value of Ref 9 was not used in our study, and we think YD was similar in our artificial seawater standards to that in our seawater samples. Although YD was lower (only 1-18% with an 18x variation), the studies by Olasehinde et al (2009; 2010), Anifowose et al (2015) and Anifowose and Sakugawa (2017) showed good results and provide a new method to evaluate NO concentration and its production and consumption in the seawater.
Oceanography: seawater samples were from 1 meter, using a CTD, greatly increasing the chances that some samples are contaminated by the ship. 1-m samples for measurements that may be sensitive to trace contaminants (such as $R_{SO}$) are best obtained using a small boat away from the ship, or taken in the mixed layer from a few meters below the ship’s hull depth.

**Our reply:** Thank you for your advice, we would improve our sampling method with a small boat in the future if the condition permits or we would take photolysis samples from the mixed layer.

The possibility that some NO forms from NH$_4^+$ (NH$_3$) via photochemical reactions is ignored. The reported [NH$_4^+$] seem high (≈0.2–1.2 μM) and do not vary spatially as expected (https://agupubs.onlinelibrary.wiley.com/doi/full/10.1029/2007GB003039): “Generally speaking, seawater NHx concentrations are lower in regions of low productivity; nutrient-limited communities being more efficient at utilizing recycled nitrogen and thus maintaining a lower ambient concentration. Thus high latitudes tend to have substantially greater NHx concentrations than low latitudes in the open ocean, with high-productivity coastal and shelf seas tending to have highest concentrations, irrespective of latitude [Johnson, 2004].” Were NH$_4^+$ data influenced by ship’s sewage-related effluents (vapor or liquids)? NH$_4^+$ in seawater forms nitrite and nitrate via singlet oxygen reactions that may involve NO intermediates, also, CO$_3^-$ + NH$_3$ → NH$_2^*$; NH$_2^*$ + O$_2$ → NH$_2$OO*, NH$_2$OO* → NO + H$_2$O.

**Our reply:** Firstly, NH$_4^+$ data was not influenced by ship’s liquid sewage, because the sewage was released after the samples were collected from CTD. Secondly, about the vapor, we think the samples might not be polluted by NH$_3$. Because during the cruise to the Yellow Sea and the East China Sea in 2017, the same vessel “Dongfanghong 2” was also used and the same sampling and analytical method were used, while the NH$_4^+$ were at lower level. However, it seems that in our study, NH$_4^+$ concentration was higher than Johnson et al. (2008). It might be the typhoon that made deep layer NH$_4^+$ mixed with surface layer in our study area in winter.

The relevant reactions were added to the manuscript and Laszlo et al. (1998) found that this CO$_3^-$ could also produce by ·OH. This potential pathway to produce NO was contained in “48% (+30%) other unknown nitrogenous compounds” (lines 45–54).
“besides, in natural sunlit seawater, photolyzed dissolved nitrate (NO$_3^-$) could be a potential source of NO through NO$_2$ (R 7); during the process of ammonium (NH$_4^+$/NH$_3$) oxidation in to NO$_2^-$ and NO$_3^-$, NO might be an intermedium (Joussotdubien and Kadiri, 1970), or NO could be produced through amino-peroxyl radicals (R 8 to R 11) (Laszlo et al., 1998; Clarke et al., 2008)

\[
\text{NO}_3^- \xrightarrow{\text{by}} \text{NO}_2^- + \frac{1}{2} \text{O}_2 \quad (R \ 15)
\]

\[
\text{OH}^+ + \text{HCO}_3^- \rightarrow \text{CO}_3^- + \text{H}_2\text{O}/\text{OH}^- \quad (R \ 16)
\]

\[
\text{OH}^+ + \text{NH}_3 \rightarrow \text{NH}_2\text{H}_2\text{O} \quad (R \ 17)
\]

\[
\text{CO}_3^- + \text{NH}_3 \rightarrow \text{NH}_2\text{HCO}_3^- \quad (R \ 18)
\]

\[
\text{NH}_2\text{O}_2 \rightarrow \text{NH}_3\text{O}_2 \quad (R \ 19)
\]

\[
\text{NH}_2\text{O}_2 \rightarrow \text{NO} + \text{H}_2\text{O} \quad (R \ 20)\n\]

The otherwise useful table 1 needs a “Method” column, and it should be noted that the method of Zafiriou and McFarland almost certainly does not remove NO fast enough to give a total NO formation rate (as the DAF-2 method is intended to do), so is not directly comparable.

Our reply: The “Method” column was added in revised manuscript.

<table>
<thead>
<tr>
<th>Regions</th>
<th>$R$ (mol L$^{-1}$ s$^{-1}$)</th>
<th>Method</th>
<th>NO (mol L$^{-1}$)</th>
<th>NO$_2^-$ (µmol L$^{-1}$)</th>
<th>Flux (mol m$^{-2}$ s$^{-1}$)</th>
<th>Sampling date</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seto Inland Sea, Japan</td>
<td>8.7–38.8×10$^{-12}$</td>
<td>DAF-2</td>
<td>120×10$^{-12}$</td>
<td>0.5–2</td>
<td>3.55×10$^{-12}$</td>
<td>Oct 5–9, 2009</td>
<td>Olasehinde et al., 2010</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Sep, 2013</td>
<td>Anifowose and Sakugawa, 2017</td>
</tr>
<tr>
<td>Seto Inland Sea, Japan</td>
<td>1.4–9.17×10$^{-12}$</td>
<td>DAF-2</td>
<td>3.41×10$^{-12}$</td>
<td>–0.02–0.4</td>
<td>0.22×10$^{-12}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kurose River, Japan</td>
<td>9.4–300×10$^{-12}$</td>
<td>DAF-2</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kurose River (K1 station), Japan</td>
<td>4×10$^{-12}$</td>
<td>DAF-2</td>
<td>1.6×10$^{-12}$</td>
<td>0.06</td>
<td>–</td>
<td>Monthly, 2013</td>
<td>Anifowose et al., 2015</td>
</tr>
</tbody>
</table>
Since almost all oceanic mixed-layer NO data are now from the DAF-2 method (Table 1), it would be useful for this Discussion to clearly establish the limits of its applicability.

**Our reply:** Seen from Table 1, Olasehinde et al. (2010) and Anifowose and Sakugawa (2017) showed that the detection limits might be about 0.02 μmol L⁻¹ of NO₂⁻ in the Seto Inland Sea, Japan. In our study, although the concentration of NO₂⁻ ranged from 0.02 to 0.33 μmol L⁻¹, the linear relationship was not found. This might because that other factors like pH, salinity were different between samples collected at different stations (lines 328–330).

“According to the photoproduction rates and the relevant NO₂⁻ in Olasehinde et al. (2010), Anifowose and Sakugawa (2017) (Table 1), the photoproduction rates under lower than 0.02 μmol L⁻¹ NO₂⁻ might not be determined in nearshore waters like the Seto Inland Sea.”

The following references are added.


Photoproduction of nitric oxide in seawater

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Abstract. 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 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 rates (average: \(0.5 \pm 0.2 \times 10^{-12}\) mol L\(^{-1}\) s\(^{-1}\)) in the natural seawater samples from the WTNP did not show any correlations with pH, water temperature and salinity as well as dissolved inorganic nitrite concentrations. The flux induced by NO photoproduction in the WTNP (average: \(13 \times 10^{-12}\) mol m\(^{-2}\) s\(^{-1}\)) were significantly larger than the NO air–sea flux densities (average: \(1.8\times10^{-12}\) mol m\(^{-2}\) s\(^{-1}\)) indicating a further NO loss process in the surface layer.

1 Introduction

Nitric oxide (NO) is a short–lived intermediate of the oceanic nitrogen cycle, see e.g. Bange (2008) and Kuypers et al. (2018). There are only a few reports about oceanic NO determination method so far because of its reactivity (Zafiriou et al., 1980; Lutterbeck and Bange, 2015; Liu et al., 2017). NO is
produced and consumed during various microbial processes such as nitrification, denitrification and anammox (Schreiber et al., 2012; Kuypers et al., 2018). Moreover, it is known that both phytoplankton and zooplankton can metabolize NO and are influenced by ambient (extracellular) NO concentrations (Singh and Lal, 2016; Wang et al., 2017; Astier et al., 2018).

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):

\[ \text{NO}_2^- + \text{H}_2\text{O} \xrightarrow{h\nu} \text{NO} + \text{OH}^- + \text{OH}^+ \]  (R 21)

Mack and Bolton (1999) had reviewed the possible subsequent reaction like the produced NO and hydroxyl radical (OH) could react to produce HNO$_2$ reversely (R2), and some reaction that consumed NO like R3 to R7

\[ \text{NO} + \text{OH} \rightarrow \text{HNO}_2 \]  (R 22)

\[ \text{NO} + \text{NO}_2 \rightarrow \text{N}_2\text{O}_3 \]  (R 3)

\[ \text{N}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{H}^+ + 2\text{NO}_2 \]  (R 23)

\[ \text{NO} + \text{NO} \rightarrow \text{N}_2\text{O}_4 \]  (R 24)

\[ 2\text{NO}_2 \rightarrow \text{N}_2\text{O}_4 \]  (R 25)

\[ \text{N}_2\text{O}_4 + \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \text{NO}_2^- + \text{NO}_3^- \]  (R 26)

besides, in natural sunlit seawater, photolyzed dissolved nitrate (NO$_3^-$) could be a potential source of NO through NO$_2^-$ (R 8); during the process of ammonium (NH$_4^+$/NH$_3$) oxidation into NO$_2^-$ and NO$_3^-$, NO might be an intermedium (Joussotdubien and Kadiri, 1970), or NO could be produced through amino–peroxyl radicals (NH$_2$O$_2$) through R 8 to R 11 (Laszlo et al., 1998; Clarke et al., 2008)

\[ \text{NO}_3^- \xrightarrow{h\nu} \text{NO}_2^- + \frac{1}{2}\text{O}_2 \]  (R 27)

\[ \text{OH}^- + \text{HCO}_3^- + \text{CO}_3^{2-} \rightarrow \text{CO}_3^- + \text{H}_2\text{O} + \text{OH}^- \]  (R 28)

\[ \text{OH}^- + \text{NH}_3 \rightarrow \text{NH}_2^- + \text{H}_2\text{O} \]  (R 29)

\[ \text{CO}_3^- + \text{NH}_3 \rightarrow \text{NH}_2^+ + \text{HCO}_3^- \]  (R 30)

\[ \text{NH}_2^- + \text{O}_2 \rightarrow \text{NH}_2\text{O}_2^- \]  (R 31)

\[ \text{NH}_2\text{O}_3^- \rightarrow \text{NO}^- + \text{H}_2\text{O} \]  (R 32)

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 (Olasehinde et al., 2009; Olasehinde et al., 2010; Anifowose and Sakugawa, 2017), 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 seemed the rates in Kurose River (average: $499 \times 10^{-12} \text{ mol L}^{-1}\text{ s}^{-1}$) 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 $1.6 \times 10^{-12} \text{ mol L}^{-1}$, at lowest level, which was because of higher scavenging rate in river water (NO 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). However, NO showed higher concentration level in coastal waters than in open sea, higher photoproduction rates might account for this. In this study, we present the results of our measurements of NO photoproduction in laboratory experiments using artificial and natural seawater samples. The major objectives of our studies were (i) to decipher the factors affecting NO photoproduction in seawater, (ii) to determine the photoproduction rates of NO from samples collected during a cruise to the western tropical North Pacific Ocean (WTNP) and (iii) to quantify the role of photoproduction as a source of NO in the surface waters of the WTNP.

2 Methods

2.1 Determination of dissolved NO in aqueous samples

For the measurements of dissolved NO we applied the method described by Olasehinde et al. (2009): In brief, NO in the aqueous samples was determined by trapping it with added 4,5–diaminofluorescein (DAF–2, chromatographic grade from Sigma–Aldrich, USA) and measuring the reaction product triazolofluorescein (DAF–2T) with a high performance liquid chromatography system (HPLC). We used an Agilent 1260 Infinity HPLC (Agilent Technologies Inc., USA) system equipped with a Venusil XBP–C18 column (5.0 μm; 4.6 mm × 250 mm i.d.). The column temperature was set to 25°C and the mobile phase was comprised of acetonitrile (HPLC grade from Merck, Darmstadt, Germany) and phosphate buffer (disodium hydrogen phosphate heptahydrate, guaranteed reagent from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) solution (10 mmol L$^{-1}$ at pH 7.4) with a ratio of 8:92 (v:v) and a flow rate of 1 mL min$^{-1}$ in the isocratic mode.
The injected sample volume was 5.0 μL. The eluate was analyzed with a fluorescence diode array detector at wavelengths of 495 and 515 nm for excitation and emission, respectively. The retention time of DAF–2T was about 5.5 min.

An aliquot of 10 mL artificial seawater was bubbled with N₂ gas at a flow of 10 mL min⁻¹ for 2 h to remove O₂ after 10 min of ultrasonic and heat degassing. The solution was then bubbled with high-purity NO gas (99.9 %, Dalian Date Gas Ltd., China) for 30 min. The concentration of the saturated NO stock solution was 1.4 mmol L⁻¹, which could be used within 3 h (Lantoine et al., 1995). A series of diluted NO solutions were prepared in N₂-purged water from the NO stock solution using a microsyringe (Xing et al., 2005; Liu et al., 2017). And the series samples were trapped by DAF-2 solution.

The detection limit of dissolved NO in Milli–Q water was 9.0×10⁻¹¹ mol L⁻¹, which was determined by S/N=3 (3×0.03) with the blank samples (n=7) and the slope (0.101) in the low concentration range (3.3 – 33×10⁻¹⁰ mol L⁻¹). And average relative standard error of the NO measurements was +/- 5.7 % at a concentration of 3.0 × 10⁻⁹ mol L⁻¹.

2.2 Set-up of irradiation experiments

We performed irradiation experiments with Milli–Q water (18.2 MΩ cm, Millipore Company, USA), artificial seawater and natural seawater samples. Artificial seawater was prepared by dissolving 23.96 g NaCl, 5.08 g MgCl₂, 3.99 g Na₂SO₄, 1.12 g CaCl₂, 0.67 g KCl, 0.20 g NaHCO₃, 0.10 g KBr, 0.03 g H₃BO₃ and 0.03 g NaF in 1 L of Milli–Q water (Bajt et al., 1997) and filtered by 0.2 μm polyethersulfone membrane (Pall, USA) before the experiments.

All irradiation experiments (except the experiments for the temperature dependence, see section below) were conducted at a constant temperature of 20°C by controlling the temperature of thermostat water bath (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 installed in the simulator and a little higher than the water bath surface.

All quartz cuvettes were treated in the same manner except the cuvettes wrapped in aluminum foil which served as dark control.

Milli–Q water and artificial seawater samples were spiked with varying amounts of NaNO₂ (puriss. p.a. ACS grade from Sigma–Aldrich, USA; for details see sections below). All other chemicals were of
analytical grade from Tianjin Kemiou Chemical Reagent Co., Ltd or Shanghai Sinopharm Chemical Reagent Co., Ltd.

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. The data from the experiments with Milli–Q and artificial seawater samples were fitted with a simple linear regression in artificial seawater samples (see below). However, a linear relationship was not found > 30 min for the natural seawater samples, therefore, we decided to choose 30 min as the total experimental time for natural seawater samples. Statistical analyses were done using SPSS v.16.0 or Origin 9.0 and results were considered significant at p ≤ 0.05.

The artificial light source was a 1.5 kW xenon lamp, which provided a light intensity of 765 W m⁻². The lamp was installed in an immersion well photochemical reactor called SUNTEST CPS+ solar simulator produced by ATLAS, Germany. The solar simulator employed in this study has been demonstrated to produce spectra which mimics that of the solar radiation and emits a radiation of wavelength from 300 to 800 nm (Wu et al., 2015).

2.3 Experimental outline

2.3.1 Optimal DAF–2 concentration and storage time

In order to find out the optimal DAF–2 concentration, 10 mL of artificial seawater containing 0.5 μmol L⁻¹ NO₂⁻ was irradiated with various concentrations of DAF–2 ranging from 0.7 μmol L⁻¹ to 4.8 μmol L⁻¹ for 2 h. To ascertain the sample storage time, 10 mL with artificial seawater samples containing 5.0 μmol L⁻¹ or 0.5 μmol L⁻¹ NO₂⁻ were irradiated with various concentrations of DAF–2 for 2 h. After irradiation, samples were kept in the dark and measured every 2 h.

2.3.2 Influence of pH, temperature, salinity and wave lengths

The influence of the pH was assessed by adjusting artificial seawater samples to pH levels of 7.1, 7.6 and 8.1 by addition of appropriate amounts of hydrochloric acid (2 mol L⁻¹) or caustic soda solution (2 mol L⁻¹).
To assess the influence of the temperature, artificial seawater samples were adjusted to temperatures of 10°C, 20°C and 30°C by controlling the temperature of the thermostat water bath.

To assess the influence of the salinity on the photoproduction of NO from dissolved NO$_2^-$, artificial seawater samples were adjusted to different salinity of 20, 30 and 35 by adding Milli-Q water or NaCl to the stock solution of artificial seawater.

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

2.4 Calculations of photoproduction rates ($R_{NO}$), photoproduction rate constant ($J_{NO}$) and reaction yield

For the artificial seawater experiments determining the generation of NO from the NO$_2^-$ photochemical degradation, the data fitted with a simple linear regression with the form $y = R_{NO} \times t + b$, where $y$ is the NO concentration which was calculated by the signal intensity of DAF–2T at time $t$ and $R_{NO}$ is the photoproduction rate.

The photoproduction rate constant of NO from nitrite ($J_{NO}$) was determined by preparing different concentrations of NO$_2^-$ (0.5, 2.0 and 5.0 μmol L$^{-1}$) in Milli–Q water and artificial seawater. The slope of the linear correlation between photoproduction rates and concentrations of NO$_2^-$ represents $J_{NO}$ (Anifowose et al., 2015).

The yield of NO formation ($%f_{NO}$) from the photodegradation via NO$_2^-$ was estimated according to Anifowose et al. (2015)

\[
%f_{NO} = 100 \times J_{NO} \times c(\text{NO}_2^-) \times R_{NO}^{-1}
\]

(Eq 12)

where $c(\text{NO}_2^-)$ is the initial concentration of NO$_2^-$. 

2.5 Seawater samples

Surface seawater samples were collected from a water depth of 1 m during a ship campaign to the western tropical North Pacific Ocean on board the R/V “Dong Fang Hong 2” from 13 November 2015 to 5 January 2016. This cruise covered two sections: 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.
Stations S0701 – S0723 were sampled between 11 and 28 November (i.e. the first part of the N/S section), followed by sampling of W/E section between 16 and 27 December and sampling of stations S0725 – S0735 between 30 December 2015 and 05 January 2016 (i.e. second part of the N/S section). In addition, relevant surface currents are indicated in Fig. 1 (Fine et al., 1994; Zhao et al., 2016; Zhang et al., 2018). The location of the Kuroshio Current on 15 November 2015 was taken from https://www1.kaiho.mlit.go.jp/.

Seawater samples were collected using 8–liter Niskin bottles equipped with silicon O–rings and Teflon–coated springs and mounted on a Sea–Bird CTD (conductivity, temperature, depth) instrument (Sea–Bird Electronics, Inc., USA). A 750 mL black glass bottle was rinsed with in situ seawater three times, and then was filled with seawater quickly through a siphon. When the overflowed sample reached the half volume of the bottle, the siphon was withdrawn rapidly, and the bottle was sealed quickly. Samples were filtered through 0.45 μm and 0.2 μm polyethersulfone membranes (Pall, USA) to minimize microbial influence (Kieber et al., 1996; Yang et al., 2011). Then the filtered seawater was transferred in the dark into acid–cleaned and pre–combusted amber glass bottles, stored in darkness at 4°C and brought back to the laboratory on land. Samples were re–filtered with 0.2 μm polyethersulfone membranes (Pall, USA) before the irradiation experiments. DAF–2 solutions were added in the dark. The irradiation experiments were conducted within two weeks after the samples arrived in the land laboratory, the maximum storage time was about two months.

2.6 Dissolved inorganic nitrogen (DIN) and pH measurements

The concentrations of dissolved inorganic nitrogen (DIN = nitrate, nitrite, and ammonium) from the cruise were analyzed using an automated nutrient analyzer (SKALAR San++ system, SKALAR, Netherlands) onboard. The detection limits were 0.05 μmol L⁻¹ for nitrate, nitrite and ammonium. When the concentration was below detection limit, 1/2 of the detection limit (0.025 round-off to 0.02) was used.

The pH values were measured just before the experiments by using a benchtop pH meter (Orion Star A211, Thermo Scientific™, USA) which was equipped with an Orion 8102 Ross combination pH electrode (Thermo Scientific™, USA). In order to ensure comparability with the temperature in the irradiation experiments, pH values of the natural seawater samples were measured at 20°C. The pH meter
was calibrated with three NIST–traceable pH buffers (pH = 4.01, 7.00 and 10.01 at 20 °C). The precision of pH measurements was +/−0.01.

3 Results and Discussion

3.1 Optimal DAF–2 concentration and storage time

NO concentrations generated from photolysis of artificial seawater samples with an initial NO$_2^−$ concentration of 0.5 µmol L$^{-1}$ increased with increasing DAF–2 concentrations and reached a maximum at a DAF–2 concentration of 1.4 µmol L$^{-1}$ (Fig. 2a). At DAF–2 concentrations >1.4 µmol L$^{-1}$ no further increase of the NO concentrations was observed. Thus, we used a DAF–2 concentration of 1.4 µmol L$^{-1}$ for all experiments.

Samples after reaction with DAF–2 and stored at 4°C in the dark were stable for at least 28 h with the measurement interval about 2 h (Fig. 2b). The relative standard deviations of the resulting NO concentrations after irradiating samples containing 0.5 µmol L$^{-1}$ and 5.0 µmol L$^{-1}$ NO$_2^−$ were +/− 13% and +/− 7%, respectively. This demonstrated that photolysis samples with NO which were allowed to react with DAF–2 could be stored for at least one day at 4°C in the dark.

3.2 Photoproduction of NO in Milli–Q water and artificial seawater

The photoproduction rates of NO in samples with NO$_2^−$ concentrations of 0.5, 2.0 and 5.0 µmol L$^{-1}$ were generally higher in artificial seawater than in Milli–Q water (Fig. 3a and 3b). The resulting $J_{NO}$ were $5.6 \pm 0.9 \times 10^{-4}$ min$^{-1}$ and $9.4 \pm 1.4 \times 10^{-4}$ min$^{-1}$ for Milli–Q water and artificial seawater, respectively. They are lower than the $J_{NO}$ of $3.4.2 \times 10^{-4}$ min$^{-1}$ for Milli–Q water reported by Anifowose et al. (2015). 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.

3.3 Influence of pH, temperature, salinity and wavelengths

All irradiation experiments were conducted in artificial seawater with two different NO$_2^−$ concentrations of 0.5 and 5.0 µmol L$^{-1}$. The resulting NO concentrations were generally higher when irradiating the samples with the initial NO$_2^−$ concentration of 5.0 µmol L$^{-1}$. NO photoproduction rates showed
increasing trends with decreasing pH, increasing temperatures and increasing salinity, the relationship between rates with salinity and temperature rates is significant (p <0.5) (Fig. 4 and 5). Reaction (1) indicates that decreasing pH which results in lower concentrations of OH\(^{-}\) which, in turn, will promote NO formation via NO\(_2^-\). This is in line with the finding of Li et al. (2011) who found that the photodegradation rate of NO\(_2^-\) in Milli-Q water was higher at pH = 6.5 than at pH = 9.5. 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\(_2\)O\(_4\) and N\(_2\)O\(_3\) hydrolysis reaction (R4 and R7) as reviewed by Mack and Bolton (1999). However in previous study 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 single wavelength light in nitrite solution. This might indicated that decreasing pH in our study mainly reduced NO consumption rather than increased NO production.

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

\[ R = A \times \exp \left( -\frac{E}{R \times T} \right) \]  \text{(Eq 13)}

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 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 \( T_1 \) and \( T_2 \):

\[ R_{T_2} = R_{T_1} \times \exp \left( \frac{E}{R} \times \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \right) \]  \text{(Eq 14)}

If we assumed that \( E \) was a constant in the temperature ranges of 10 to 30\(^\circ\)C when NO\(_2^-\) = 0.5 \( \mu \)mol L\(^{-1}\), and we plot \( \ln R \) against \( 1/T \), we would get the \( E \) value as 57.5 kJ mol\(^{-1}\) K\(^{-1}\). Using the photoproduction rate at 20\(^\circ\)C (293.15 K) as our reference point (\( T_1 \)), an expression of the \( R_T \) with the temperature was as follows:

\[ R_T = 2.7 \times 10^{-10} \times \exp \left( 6920 \times \left( \frac{1}{293.15} - \frac{1}{T} \right) \right) \]  \text{(Eq 15)}

Similarly, we could conclude expression of the \( R_T \) with the temperature when NO\(_2^-\) = 5.0 \( \mu \)mol L\(^{-1}\),

\[ R_T = 7 \times 10^{-10} \times \exp \left( 11026 \times \left( \frac{1}{293.15} - \frac{1}{T} \right) \right) \]  \text{(Eq 16)}
However, NO production rate at 0.5 μmol L⁻¹ nitrite did not increase from 20 to 30°C, the plausible explanation was that NO₂⁻ concentration here was the mainly influencing factor, NO₂⁻ might be run out at 20°C, if NO₂⁻ concentration increased, like up to 5.0 μmol L⁻¹, the temperature could make a noticeable difference.

Higher salinity obviously enhanced photoproduction rates of NO in both Milli-Q water and artificial seawater samples (with 0.5 μmol L⁻¹ or 5.0 μmol L⁻¹ initial NO₂⁻ concentrations). The regression relationship is $y = 0.37x - 4.55$ for 0.5 μmol L⁻¹ NO₂⁻ and $y = 2.3x - 39.5$ for 5.0 μmol L⁻¹ NO₂⁻, respectively, where $x$ is the salinity (‰) and $y$ is the photoproduction rate ($\times 10^{-10}$ mol L⁻¹ s⁻¹). This result indicates that with increasing ion strength NO production is enhanced, however, the exact mechanism is unknown and need further study. Zafiriou and McFarland (1981) also demonstrated that artificial seawater comprised with major and minor salts showed complex interactions. But Chu and Anastasio (2007) reported that added Na₂SO₄ (4.0–7.0 mmol L⁻¹) in solution had no effect on the quantum yield of OH.

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 band. The contribution of visible band, UVA band and UVB band were <1%, 30.7%, 85.2% and <1.0%, 34.2%, 63.1% for 0.5 and 5.0 μmol L⁻¹ NO₂⁻, 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 NO₂⁻ more rapidly than those exposed only to the 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 wild band of UVA (320–420 nm) that led to the summational higher rates under UVA than UVB (in our system 300-320). Moreover, according to the UV–visible absorption spectra of NO₂⁻, $\lambda_{max}$ was 354 nm, which is in the range of UVA (320–420 nm) (Zuo and Deng, 1998; Zafiriou and McFarland, 1981).

### 3.4 Kinetics of the NO photoproduction

The yields of NO formation from NO₂⁻ (%f₅₀) in artificial seawater samples were about 70.1% and 97.9% for the initial NO₂⁻ concentrations of 0.5 and 5.0 μmol L⁻¹, respectively. The missing NO yield (29.9% for 0.5 μmol L⁻¹ and 2.1% for 5.0 μmol L⁻¹) might result from NO production via other (unknown)
nitrogen–containing substrates (Anifowose et al., 2015). Another plausible explanation would be that during the process of NO\textsubscript{2}– photoproduction, some NO were oxidized into NO\textsubscript{2}, then NO\textsubscript{2} dimerized (R5) and the dipolymer N\textsubscript{2}O\textsubscript{4} would hydrolyze into NO\textsubscript{2}– and NO\textsubscript{3}– (R7), which actually reduce the concentration of NO\textsubscript{2}– (Mack and Bolton, 1999).

Assuming a 100% yield from NO\textsubscript{2}– degradation and a fast reaction of NO with DAF–2 the observed linear relationships during the various irradiation experiments (Fig. 6) indicate that NO photoproduction was following a pseudo zero–order reaction. However, the \( R_{NO} \) ratios (average: 4.8) listed in Table 2 were not the same for the experiments despite the fact that the ratio of the initial NO\textsubscript{2}– concentrations (= 10) was the same for all experiments. This result, however, does point to reactions which is different from a zero–order reaction.

3.5 Photoproduction rates of NO in the western tropical North Pacific Ocean

During the cruise surface temperatures and salinities were in the range from 22.15°C to 30.19°C and 34.57 to 35.05 respectively. The concentrations of NO\textsubscript{3}, NH\textsubscript{4}+ and NO\textsubscript{2}– ranged from 0.03 µmol L\textsuperscript{–1} to 1.6 µmol L\textsuperscript{–1}, 0.20 µmol L\textsuperscript{–1} to 1.2 µmol L\textsuperscript{–1} and 0.02 µmol L\textsuperscript{–1} to 0.33 µmol L\textsuperscript{–1}, respectively (Fig. 6).

The measured photoproduction rates of NO ranged from 0.3 ×10\textsuperscript{–10} mol L\textsuperscript{–1} min\textsuperscript{–1} (station S0711) to 2.9 ×10\textsuperscript{–10} mol L\textsuperscript{–1} min\textsuperscript{–1} (station S0303), with an average value of 13.0 ± 7.6 ×10\textsuperscript{–11} mol L\textsuperscript{–1} min\textsuperscript{–1}.

Photoproduction rates did not show significant correlations with NO\textsubscript{2}–, NO\textsubscript{3}–, NH\textsubscript{4}+, pH, salinity, water temperature as well as with colored dissolved organic matter (data not shown, the same method with Zhu et al. (2017)) (statistics computed with SPSS v.16.0).

The non–existing linear relationship between \( R_{NO} \) and dissolved NO\textsubscript{2}– during our cruise is in contrast to the results of Olasehinde et al. (2010), Anifowose et al. (2015) and Anifowose and Sakugawa (2017) who observed positive linear relationships between NO photoproduction rates and the NO\textsubscript{2}– concentrations in the surface waters of the Seto Inland Sea and the Kurose River. This might because that other factors like pH, salinity were different between samples collected at different stations.

In Table 1, we found that the average photoproduction rate of NO measured in our cruise is lower than that of the Seto Inland Sea and the Kurose River which could be ascribed to higher background NO\textsubscript{2}– in the inland sea waters (Olasehinde et al., 2009; 2010). Our result is slightly lower than the \( R_{NO} \) from the central equatorial Pacific Ocean (> 10\textsuperscript{–12} mol L\textsuperscript{–1} s\textsuperscript{–1}), the lower concentration of NO\textsubscript{2}– (0.06 µmol L\textsuperscript{–1}) in our study area might account for this (Zafiriou and McFarland, 1981). In Table 1, the NO\textsubscript{2}–
concentration of 0.06 µmol L\(^{-1}\) in our study was lower than most of other study area like Qingdao coastal waters (0.75 µmol L\(^{-1}\)) and the Seto Inland Sea (0.4-0.5 µmol L\(^{-1}\)). In the study of Anifowose et al. (2015), since the NO\(_2^\text{-}\) 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 the difference of the river water and the seawater, considering lower nitrite level of K1, dissolved organic matter might also account for the higher \(R_{NO}\). 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 photodegrade itself to produce NO\(_2^\text{-}\), finally to promote \(R_{NO}\). In our study, the rates were adjusted to the ambient conditions, which included nighttime samples when the rates were lower. From the T–S diagram (Fig.7), we found that higher photoproduction rates at stations S0701 and S0704 might resulted from the influence of the Kuroshio (see Fig. 1), with enhanced concentrations of NO\(_2^\text{-}\). The higher NO production rates measured for stations S0303/S0307 and S0717–S0723 might have been influenced by the South Equatorial and North Equatorial Currents, respectively, but were obviously not associated with enhanced NO\(_2^\text{-}\) concentrations.

If we take the missing 30% of \(f_{NO}\) in artificial seawater as the experimental error, then in our study, using the \(J_{NO}\) in the artificial seawater, the average \(\%f_{NO}\) value in natural water was calculated to be 52% (–30%), indicating that there are other unknown nitrogenous compounds, for example, NO\(_2^\text{-}\) produced from NO\(_3^\text{-}\) photolysis (R8) or from other organic matter which could further lead to NO production (Kieber et al., 1999; Benedict et al., 2017; Goldstein and Rabani, 2007; Minero et al., 2007).

According to the photoproduction rates and the relevant NO\(_2^\text{-}\) in Olasehinde et al. (2010), Anifowose and Sakugawa (2017) (Table 1), the photoproduction rates under lower than 0.02 µmol L\(^{-1}\) NO\(_2^\text{-}\) might not be determined in nearshore waters like the Seto Inland Sea.

### 3.6 Flux densities of NO in the surface layer of the WTNP

#### 3.6.1 Air–sea flux density of NO

The NO flux densities were computed with (Eq 6):

\[
F = k_{sea} ([NO] - p_{NO_{air}} \times H)^{p}
\]  

(Eq 17)

\[
p_{NO_{air}} = x'NO_{air} \times (p_{w} - p_{w})
\]  

(Eq 18)

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\(^{-1}\)), [NO] is the measured concentration of NO in the surface seawater (mole volume\(^{-1}\))
\[ x'_{\text{NOair}} \] is the mixing ratio of atmosphere NO (dimensionless). And \( p_\infty \) is the barometric pressure while \( p_\infty \) was calculated after Weiss and Price (1980):

\[ \ln p_\infty = 24.4543 - 6745.09/(T + 273.15) - 4.8489\ln (T + 273.15)/100 - 0.000544 \times S \]  
(Eq 19)

\( H^p \) is the Henry's law constant which is calculated after Sander (2015) as:

\[ H^p(T) = H^0 \times \exp \left( -\Delta \text{sol} H/R \times (1/T - 1/T^0) \right) \]  
(Eq 20)

where \( -\Delta \text{sol} H/R = \frac{\text{dln} H}{\text{dln}(T)} \) \( H^p \), and \( -\Delta \text{sol} H/R \) are tabulated in Sander (2015) \((-\Delta \text{sol} H/R=1600 \) and \( H^p=1.9 \times 10^{-3} \text{ mol m}^{-3} \text{ pa}^{-1} \)). The reviewed several literatures about NO, \( H^0 \) and the values in different literatures were similar (Sander, 2015). In our calculation, the value in the Warneck and Williams (2012) were used.

Then \( k_{\text{sea}} \) was calculated after (Wanninkhof, 2014) as (Eq 10),

\[ k_{\text{sea}} = k_w (1 - \gamma_a) \]  
(Eq 21)

\( \gamma_a \) 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), \( k_w \) is the air side air-sea gas transfer coefficient (length time\(^{-1}\)) according to (Mcgillis et al., 2000;Jähne et al., 1987;Sharqawy et al., 2010), for the details of the calculation of \( k_w \) and \( \gamma_a \) see Tian et al. (2018).

Since onboard wind speeds were not available, ECMWF reanalysis data sets (ERA-5 hourly data) were applied. We used a value of \( 10^{-11} \text{ (v/v)} \) for atmospheric NO (Law, 2001). The atmosphere pressure was set to 101.325 kPa.

Since the measurements \([\text{NO}]\) were not available from the cruise we estimated \([\text{NO}]\) by assuming that (1) NO production is mainly resulting from \( \text{NO}_2^- \) photodegradation and (2) the NO photoproduction \( R_{\text{NO}} \) 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):

\[ R_{\text{NO}} \times \frac{I_{\text{ambient}}}{I_{\text{simulator}}} = [\text{NO}] \times R_s, \]  
(Eq 22)

where \( R_s \) represents the sum of the rate constants for the scavenging compounds reacting with NO times the concentrations of the scavenger compounds, \( I_{\text{ambient}} \) and \( I_{\text{simulator}} \) denote the light intensity of the sampling station and the CPS+ simulator (765 W m\(^{-2}\)). \( I_{\text{ambient}} \) was ECMWF reanalysis data sets (ERA-5 hourly data, interpolation method). 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° E Equatorial regions), which showed an increasing trend from river to open sea. It seemed that NO life time 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 close to continent like New Guinea Island and Japan, average lifetime about 100 s were applied in our study, however the uncertainty was not reported in the literature, but estimated uncertainty about 30% might be appropriate. 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. Then [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 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 account for this in river water than in seawater (Anifowose and Sakugawa, 2017).

In Table 1, 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 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.

### 3.6.2 Oceanic photoproduction rates of NO

The photoproduction rates from our irradiation experiments were extrapolated to the oceanic photoproduction in the WTNP with the equation from (Bange and Uher, 2005; Uher and Andreae, 1996)

\[
R_{\text{ocean}} = R_{\text{NO}} \times \left( \frac{I_{\text{ocean}}(1-\exp(-K_D \times MLD))}{I_S \times K_D \times MLD} \right) \quad \text{(Eq 23)}
\]

where \(R_{\text{ocean}}\) and \(R_{\text{NO}}\) are the photoproduction rates for the ocean mixed layer and seawater irradiation experiments, respectively, see Section 3.5. \(I_{\text{ocean}}\) and \(I_S\) are the average global irradiance at the surface of the ocean mixed layer and the solar simulator used here, \(K_D\) is the light attenuation coefficient and MLD is the estimated mixed layer depth at the sampled station.
\( I_{\text{ocean}} \) was set to 185 W m\(^{-2}\), while \( I_{\alpha} \) was 765 W m\(^{-2}\) in our study (Bange and Uher, 2005; Wu et al., 2015). As described above, \( K_{D,354} \) was applied to estimate the MLD. In Smyth (2011), \( K_{D,340} \) to \( K_{D,380} \) derived from 10% residual light level depths ranged from 0.04 m\(^{-1}\) to 0.07 m\(^{-1}\) for our study area, we used the average value of 0.05. 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. The resulting average \( R_{\text{ocean}} \) was about 8.6 ± 4.9 × 10\(^{-12}\) mol L\(^{-1}\) min\(^{-1}\) for the WTNP at the time of our cruise. Besides, the temperature at 20°C in our laboratory experiment would induce about 10% error (Fig. 4e).

The flux induced by NO photoproduction in the WTNP (NO photoproduction rates divide by MLD, average: \( 13 \times 10^{-12} \) mol m\(^{-2}\) s\(^{-1}\)) 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.

**Conclusion**

The results of our irradiation experiments showed that NO photoproduction from NO\(_2^-\) in artificial seawater is significantly affected by changes in pH, temperature and salinity. We found increasing NO production rates from dissolved NO\(_2^-\) with decreasing pH, increasing temperatures and increasing salinity. In contrast we did not find any correlations of NO photoproduction with pH, salinity, water temperature as well as dissolved NO\(_2^-\) in natural surface seawater samples from a cruise to the western tropical North Pacific Ocean (November 2015 – January 2016). We conclude that the trends observed in our irradiation experiments with artificial seawater do not seem to be representative for WTNP because of the complex settings of open ocean environments. Moreover, we conclude that future changes of NO photoproduction due to ongoing environmental changes such as ocean warming and acidification are, therefore, difficult to predict and need to be tested by irradiation experiments of natural seawater samples under varying conditions. The flux induced by NO photoproduction in the WTNP (average: \( 13 \times 10^{-12} \) mol m\(^{-2}\) s\(^{-1}\)) 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. This indicates a further NO loss process in the surface layer of the WTNP. In order to decipher and to quantify the NO production and consumption pathways in the oceanic surface layer more comprehensive laboratory and onboard measurements are required.
Author contributions.

YT, GY, CL, HC and PL prepared the original manuscript and designed the experiments; HB made many modifications and gave a lot of suggestions on design of figures and the computing method. All authors contributed to the analysis of the data and discussed the results.

Competing interests.

The authors declare that they have no conflict of interest.

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Figure Captions

Fig. 1. Locations of the sampling stations in the western tropical North Pacific Ocean. The acronyms NGCC, SEC, NECC, NEC, and STCC stand for New Guinea Coastal Current, South Equatorial Current, North Equatorial Counter Current, North Equatorial Current, and Subtropical Counter Current, respectively.

Fig. 2. Changes of NO concentrations with initial DAF–2 concentration of 0, 0.7, 1.4, 2.1, 2.8, 3.5 and 4.2 μmol L$^{-1}$ after irradiation time of 2 h (a) and changes of different NO concentrations with storage time monitored at about 2 h time intervals (b).

Fig. 3. Photoproduction rates of NO with 0.5, 2, and 5.0 μmol L$^{-1}$ NO$_2^-$ (a) and the calculated $J_{NO}$ values in Milli–Q water and artificial seawater (b), symbols in red represented for the artificial seawater samples and in black for Milli–Q water.

Fig. 4. NO concentration changes with irradiation time at different pH, salinity, temperature and waveband conditions (a, c, e, g for 0.5 μmol L$^{-1}$ NO$_2^-$ and b, d, f, h for 5.0 μmol L$^{-1}$ NO$_2^-$).

Fig. 5. Changes of NO photoproduction rates with irradiation time at different pH, salinity, temperature and waveband conditions (a, c, e, g for 0.5 μmol L$^{-1}$ NO$_2^-$ and b, d, f, h for 5.0 μmol L$^{-1}$ NO$_2^-$).

Fig. 6. Seawater temperature, salinity, concentrations of NO$_2^-$, NO$_3^-$, NH$_4^+$, and photoproduction rates of NO ($R_{NO}$) in the western tropical North Pacific Ocean. (a: W/E transect; b: N/S transect)

Fig. 7. The potential temperature–salinity (T–S) diagram with NO photoproduction rates indicated in the color bar. Water mass characteristics of surface currents shown in Figure 1 are indicated. The acronyms NGCC, SEC, NECC, NEC, and STCC stand for New Guinea Coastal Current, South Equatorial Current, North Equatorial Counter Current, North Equatorial Current, and Subtropical Counter Current, respectively.
**Fig. 1.** Locations of the sampling stations in the western tropical North Pacific Ocean. The acronyms NGCC, SEC, NECC, NEC, and STCC stand for New Guinea Coastal Current, South Equatorial Current, North Equatorial Counter Current, North Equatorial Current, and Subtropical Counter Current, respectively.
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**Fig. 5.** Changes of NO photoproduction rates with irradiation time at different pH, salinity, temperature and waveband conditions (a, c, e, g for 0.5 μmol L\(^{-1}\) NO\(_2\)\(^-\) and b, d, f, h for 5.0 μmol L\(^{-1}\) NO\(_2\)\(^-\)).
Fig. 6. Seawater temperature, salinity, concentrations of NO$_2^-$, NO$_3^-$, NH$_4^+$, and photoproduction rates of NO (R$_{NO}$) in the western tropical North Pacific Ocean (a: W/E transect; b: N/S transect.).
Fig. 7. The potential temperature–salinity (T–S) diagram with NO photoproduction rates indicated in the color bar. Water mass characteristics of the surface currents shown in Figure 1 are indicated. The acronyms NGCC, SEC, NECC, NEC, and STCC stand for New Guinea Coastal Current, South Equatorial Current, North Equatorial Counter Current, North Equatorial Current, and Subtropical Counter Current, respectively.
Table Captions

**Table 1** Photoproduction rates ($R$), average NO concentrations and average flux densities of NO in different regions.

**Table 2** The ratios of photoproduction rates ($R5.0/R0.5$) in the different irradiation experiments.
Table 1 Photoproduction rates ($R$), average NO concentrations, NO$_2^-$ concentrations and average flux densities of NO in different regions.

<table>
<thead>
<tr>
<th>Regions</th>
<th>$R$ (mol L$^{-1}$ s$^{-1}$)</th>
<th>NO (mol L$^{-1}$)</th>
<th>NO$_2^-$ (µmol L$^{-1}$)</th>
<th>Flux (mol m$^{-2}$ s$^{-1}$)</th>
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Table 2 The ratios of photoproduction rates ($R_{5.0}/R_{0.5}$) in the different irradiation experiments.

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