

Dear Mario Hoppema,

We would like to thank you and the anonymous reviewer for your comments and suggestions which helped us to improve our manuscript. Please find a point-by-point responses (in red) to all comments (in black) and the changes in our manuscript (in blue) 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.

Reply to Mario Hoppema.

Please be consistent with all equation numbers. So do not use R1, R2 etc, but start with (1), (2) etc and do so for the whole manuscript.

Response: The numbers all have been corrected.

L28 “because of its reactivity” This should be something like “high reactivity with other substances”

Response: Thank you for your advice, this sentence has been changed into “because of its high reactivity with other substances”.

There are only a few reports about oceanic NO determination method so far because of its high reactivity with other substances (Zafiriou et al., 1980; Lutterbeck and Bange, 2015; Liu et al., 2017).

L35 Shouldn't one write 2 OH[·] instead of OH[·] + OH[·] ?

Response: They are different, one OH[·] represents for hydroxyl radical (OH[·]), and the superscript is point, while the other is OH⁻, and the superscript is hyphen.

L36-38 “Mack and Bolton (1999) had reviewed the possible subsequent reaction like the produced NO and hydroxyl radical (OH) could react to produce HNO₂ reversely (R2), and some reaction that consumed NO like R3 to R7” This sentence is not clear. Please modify.

Response: The sentence has been modified.

Mack and Bolton (1999) reviewed the possible subsequent reaction of Eqn. (1), for example, the produced NO and hydroxyl radical (OH[·]) of Eqn. (1) could react to produce HNO₂ reversely Eqn. (2), and some reaction that consumed NO or its oxides like Eqn. (3) to Eqn. (8)

L42 The way this reaction is given is not correct. Actually, these are two reactions. Please correct.

Response: This reaction has been corrected into two reactions.



L45 Besides (with capital, start new sentence here)

Response: This word has been corrected.

Besides, in natural sunlit seawater, photolyzed dissolved nitrate (NO₃⁻) could be a source of NO through NO₂⁻ Eqn. (9);

L45 “could be a potential source” This is double and a style error. Either “could be” or “is a potential source”

Response: The word “potential” has been removed.

photolyzed dissolved nitrate (NO₃⁻) could be a source of NO through NO₂⁻ Eqn. (9);

L46 R8 is given but this does not contain the reaction that is mentioned.

Response: R8 was a wrong number, we have changed it into “Eqn. (9)”

L48 R8 to R12 (not R11)

Response: R11 was corrected.

or NO could be produced through amino-peroxyl radicals (NH₂O₂[·]) through Eqn. (10) to (14)

(Laszlo et al., 1998; Clarke et al., 2008)

L55 summarizes

Response: The word “summarized” has been revised into “summarizes”.

Table 1 summarizes studies about photochemical production of NO measured in the surface waters of the equatorial Pacific Ocean (Zafiriou et al., 1980; Zafiriou and McFarland, 1981).

L119 “with a simple linear regression in artificial seawater samples” This is not clear. Please modify.

Response: The sentence has been modified.

The results showed that both in Milli-Q and artificial seawater samples, the photoproduct NO showed linear relationship against time (see below).

L120 “a linear relationship was not found > 30 min for the natural seawater samples” This is not clear, in particular the “>30 min”. Please modify text.

Response: The sentence has been modified.

However, a linear relationship was only found in the irradiation time range of 30 min for the natural seawater samples, while the relationship was not found after 30 min.

L152 the data were fitted

Response: The word “were” has been added.

the data were fitted with a simple linear regression

L226 delete the first which

Response: The first which was deleted.

Reaction (1) indicates that decreasing pH results in lower concentrations of OH⁻ which, in turn, will promote NO formation via NO₂⁻.

L260-261 “Zafiriou and McFarland (1981) also demonstrated that artificial seawater comprised with major and minor salts showed complex interactions.” This is very general and thus does not contain any useful info. Please modify.

Response: Some results have been added into our manuscript.

Zafiriou and McFarland (1980) demonstrated that artificial seawater comprised with major and minor salts showed complex interactions and the addition of EDTA could diminished NO concentration, which meant trace metals could keep NO concentration at a higher level, which is similar to our results.

L299 “The non-existing linear relationship” This is not correct wording. Change to something like: There was no linear relationship found between RNO and dissolved NO₂⁻ during our cruise, which is in contrast to the results of ...

Response: The sentence has been corrected.

There was no linear relationship found between R_{NO} and dissolved NO₂⁻ during our cruise, which 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 NO₂⁻ concentrations in the surface waters of the Seto Inland Sea and the Kurose River.

L324-325 “to be 52% (– 30%)” Is the minus correct, or should it be plus-minus (\pm)?

Response: In our study, the yields of NO formation from NO_2^- ($\%f_{\text{NO}}$) in artificial seawater samples were about 70.1% and 97.9% for the initial NO_2^- concentrations of 0.5 and 5.0 $\mu\text{mol L}^{-1}$, respectively. The missing NO yield (29.9% for 0.5 $\mu\text{mol L}^{-1}$ and 2.1% for 5.0 $\mu\text{mol L}^{-1}$) might result from NO production via other (unknown) nitrogen-containing substrates (Anifowose et al., 2015). Thus, as the experimental error, we think the missing 30% of f_{NO} in artificial seawater showed be minus. The sentence “the average $\%f_{\text{NO}}$ value in natural water was calculated to be 52% (–30%)” means that “the average $\%f_{\text{NO}}$ value in natural water might be calculated to be 22% to 52%”.

L329 delete lower

Response: The word “lower” has been deleted.

the photoproduction rates under 0.02 $\mu\text{mol L}^{-1}$ NO_2^- might not be determined in nearshore waters like the Seto Inland Sea.

L419-420 “indicating a further NO loss process in the surface layer. This indicates a further NO loss process in 419 the surface layer of the WTNP.” Double info. Delete one.

Response: “This indicates a further NO loss process in 419 the surface layer of the WTNP.” has been deleted.

The flux induced by NO photoproduction in the WTNP (average: $13 \times 10^{-12} \text{ mol m}^{-2} \text{ s}^{-1}$) were significantly larger than the NO air–sea flux densities (average: $1.8 \times 10^{-12} \text{ mol m}^{-2} \text{ s}^{-1}$) indicating a further NO loss process in the surface layer.

L459 ... 129, 10597-10601, 2007 (add page numbers)

Response: The page numbers have been added.

Goldstein, S., and Rabani, J.: Mechanism of nitrite formation by nitrate photolysis in aqueous solutions: The role of peroxyxynitrite, nitrogen dioxide, and hydroxyl radical, J. Am. Chem. Soc., 129, 10597-10601, <https://doi.org/10.1021/ja073609+>, 2007.

L493 J. Geophys. Res., 109, C12003, doi:10.1029/2004JC002378. (complete ref)

Response: The error has been corrected.

Montégut, C. D. B.: Mixed layer depth over the global ocean: An examination of profile data and a profile-based climatology, J. Geophys. Res.: Oceans, 109, <https://doi.org/10.1029/2004JC002378>, 2004.

L509-511 Please provide update (no discussion paper), if available)

Response: The discussion paper has been replaced by its updated version.

Tian, Y., Xue, C., Liu, C. Y., Yang, G. P., Li, P. F., Feng, W. H., and Bange, H. W.: Nitric oxide (NO) in the Bohai Sea and the Yellow Sea, Biogeosciences, 16, 4485-4496, <https://doi.org/10.5194/bg-16-4485-2019>, 2019.

L540 H 2 O 2 (change format)

Response: “H 2 O 2” has been revised into “ H_2O_2 ”

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

nitrate, nitrite and dissolved H₂O₂ at 308 and 351 nm in the temperature range 278–353 K, J. Atmos. Chem., 10, 411-425, <https://doi.org/10.1007/BF00115783>, 1990.

Table 1 Please use date format like 5 October 2009

Response: The date format has been revised.

Table 1 According to your answer to referee #2, this table should contain a column Method. The table shown here does not contain such a column

Response: The column Method has been added into the revised Table 1.

Regions	<i>R</i> (mol L ⁻¹ s ⁻¹)	Method	NO (mol L ⁻¹)	NO ₂ ⁻ (μmol L ⁻¹)	Flux (mol m ⁻² s ⁻¹)	Sampling date	References
Seto Inland Sea, Japan	8.7-38.8×10 ⁻¹²	DAF-2	120×10 ⁻¹²	0.5-2	3.55×10 ⁻¹²	5-9 October, 2009	Olasehinde et al., 2010
Seto Inland Sea, Japan	1.4-9.17×10 ⁻¹²	DAF-2	3-41×10 ⁻¹²	0-0.4	0.22×10 ⁻¹²	September, 2013 and June, 2014	Anifowose and Sakugawa, 2017
Kurose River, Japan	9.4-300×10 ⁻¹²	DAF-2	—	—	—	—	Olasehinde et al., 2009
Kurose River (K1 station), Japan	4×10 ⁻¹²	DAF-2	1.6×10 ⁻¹²	0.06	—	Monthly, 2013	Anifowose et al., 2015
Jiaozhou Bay	—	DAN	157×10 ⁻¹²	—	7.2×10 ⁻¹²	June, July, and August, 2010	Tian et al., 2016
Jiaozhou Bay and its adjacent waters	—	DAN	(160 ± 130) ×10 ⁻¹²	—	10.9×10 ⁻¹²	8-9 March, 2011	Xue et al., 2011
Coastal water off Qingdao	1.52×10 ⁻¹²	DAN	260×10 ⁻¹²	0.75	—	November, 2009	Liu et al., 2017
Central equatorial Pacific	> 10 ⁻¹²	Chemilumi nescence	46×10 ⁻¹²	0.2	2.2×10 ⁻¹²	R/V Knorr 73/7 15 November,	Zafiriou and Mcfarland., 1981
The northwest Pacific Ocean	(0.5 ± 0.2) ×10 ⁻¹²	DAF-2	49×10 ⁻¹²	0.06	1.8×10 ⁻¹²	2015 to 26 January, 2016	This study

Reply to reviewer.

1. General comments

This manuscript is a revised version of an earlier submission that suffered from a range of shortcomings concerning presentational aspects, scientific evaluation and wider interpretation. However, the authors' revisions significantly improved this submission. Most of my recommendations have been implemented to a satisfactory standard. However, some minor issues remain and should be addressed before publication. These are highlighted in the enclosed annotated manuscript.

Response: Thank you for your advice and the minor issues have been corrected according to your advice.

In my review of the original submission I noted that the manuscript could be improved by careful English language editing. Unfortunately, this has not been done satisfactorily so far. Consequently, wording and grammar errors in the submission at times noticeably distract from its scientific contents. While I don't expect standards corresponding to native speakers, I feel that this issue should be addressed alongside the minor revisions requested in my annotations.

Response: The wording and grammar errors as well as the language editing have been corrected and improved.

Page 2 Line 37: Only R3a and R4 consume NO directly. Other reactions do not. Please revise accordingly.

Response: Thank you for your advice. Because consumption of NO's oxides like N_2O_3 , N_2O_2 , NO_2 , and N_2O_4 could also promote the consumption of NO, thus "NO and its oxides" instead "NO" was added into the manuscript.

some reactions that consumed NO or its oxides like Eqn. (3) to Eqn. (8)

Page 2 Line 41: Numbering error - please correct

Response: The numbering error has been corrected.

Page 3 Line 63: NO lifetime in river water: please add supporting reference. Define 'lifetime': is this half life with respect to a first order scavenging rate constant?

Response: We have added (Anifowose et al., 2015) into the manuscript.

Lifetime was defined as the reciprocal of overall scavenging rate constant (first order) of NO (Olasehinde et al., 2010).

Anifowose et al. (2015) found that in Kurose River, NO lifetime, which was defined as the reciprocal of first order scavenging rate constant of NO (Olasehinde et al., 2010), was only 0.25 s.

Page 3 Line 65: NO concentrations are determined by the balance of production and removal, not only by photoproduction. You should mention this in your statement, and note that changes in scavenging rates may also affect NO.

Response: The relevant description has been added into the manuscript.

Table 1 summarizes 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

Sea and Yellow Sea (Liu et al., 2017; Tian et al., 2019) and the Kurose River (Japan) (Olasehinde et al., 2009; Anifowose et al., 2015). NO concentration was determined by the balance of the production and the removal process, thus changes of NO production and removal rates could influence NO concentration in the seawater. In the surface seawater, photochemical was regarded as the main production process (Zafiriou and McFarland, 1981; Olasehinde et al., 2010; Anifowose et al., 2015). In Table 1, NO photoproduction rates varied among different seawater samples, the photoproduction rates in Kurose River (average: $499 \times 10^{-12} \text{ mol L}^{-1} \text{ s}^{-1}$) was the biggest, which might be 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 the lowest level, which was because of higher scavenging rate in river water. Anifowose et al. (2015) found that in Kurose River, NO lifetime, which was defined as the reciprocal of first order scavenging rate constant of NO (Olasehinde et al., 2010), was only 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 levels in coastal waters than in open sea, higher photoproduction rates in coastal waters than open sea or other production process in coastal waters might account for this.

Page 4 Line 107: about? what was the error margin then?

Response: "about 70 mm" were corrected into " $70 \pm 1 \text{ mm}$ ".

The optical pathlength was $70 \pm 1 \text{ mm}$.

Page 8 Line 216: This statement is incomplete. To compare experimental settings you would need to calculate self shading factors from optical pathlength and CDOM absorption coefficients at the wavelength of interest (355 nm?). For open ocean waters this self shading factor f should be close to 1, but high CDOM levels may cause $f = 0.2$ to 0.3 , but this is unlikely for Milli-Q or artificial seawater. I recommend comparing irradiance levels.

Response: During their study, the rates were adjusted into the natural sunlight, which was determined at noon under clear sky conditions in Higashi-Hiroshima ($34^{\circ} 25' \text{ N}$, $132^{\circ} 0' \text{ E}$) on May 1st, 1998 (Arakaki et al., 1998). Thus, the average solar radiation flux of May was about 1055 W m^{-2} (NOAA), higher than that in our study.

The resulting J_{NO} were $5.6 \pm 0.9 \times 10^{-4} \text{ min}^{-1}$ and $9.4 \pm 1.4 \times 10^{-4} \text{ min}^{-1}$ for Milli-Q water and artificial seawater, respectively. They are lower than the J_{NO} of $34.2 \times 10^{-4} \text{ min}^{-1}$ for Milli-Q water reported by Anifowose et al. (2015). The difference might be explained by higher solar radiation flux in their study, which was about 1055 W m^{-2} .

Page 10 Line 255: Why "obviously"? It might be better to refer to your results instead.

Response: We have described our results instead.

At $0.5 \mu\text{mol L}^{-1}$ and $5.0 \mu\text{mol L}^{-1}$ initial NO_2^- concentrations of Milli-Q water and artificial seawater samples, higher salinity showed higher photoproduction rates of NO.

Page 10 Line 260: Too vague: What did Zafiriou and McFarland (1981) report, and how does this compare to your results?

Response: Some results have been added into revised manuscript.

Zafiriou and McFarland (1980) demonstrated that artificial seawater comprised with major and minor salts showed complex interactions and the addition of EDTA could diminished NO

concentration, which meant trace metals could keep NO concentration at higher level, which is similar to our results.

Page 10 Line 263: Missing concluding statement at the end of this paragraph.

Response: Some concluding statements have been added at the end of this paragraph.

Overall, in artificial seawater samples, photoproduction rates showed an increasing trend with salinity.

Page 10 Line 272: Grammar error: Fragment.

Response: The error was corrected.

In the study of Chu and Anastasio (2007), under single wavelength light, quantum yield of OH decreased with the wavelength (280 nm to 360 nm and plateau until 390 nm) which meant that single wavelength light of UVB had higher photoproduction rate than UVA. Compared with the results in our study, it might be that the wild band of UVA (320–420 nm) led to the summational higher rates under UVA than UVB (in our system 300-320).

Page 10 Line 275: again no conclusions

Response: The conclusions have been added at the end of this paragraph.

Thus, it seems reasonable that in our study, the photoproduction rate under UVA was higher than UVB, with full wave length, the highest photoproduction rates are highest, and in the visible band, the NO photoproduction rates approached zero.

Page 11 Line 296: You need to specify the CDOM variable used e.g. absorption coefficient at wavelength 355 nm? You also need to spell out what statistical test was used, e.g. Spearman's rank correlation?

Response: The description “adsorption coefficient wavelength” and the “statistical test method” have been added into the revised manuscript.

Photoproduction rates did not show significant correlations with NO_2^- , NO_3^- , NH_4^+ , pH, salinity, water temperature as well as with colored dissolved organic matter (data not shown, the same method with Zhu et al. (2017), absorption coefficients at 355 nm) (SPSS v.16.0, Pearson correlation test).

Page 13 Line 362: The text below gives the data source for " I_{ambient} ". However, you should also indicate the range of I_{ambient} values and the resulting correction factors = ($I_{\text{ambient}}/I_{\text{simulator}}$)

Response: According to reviewer's suggestion, the ranges of I_{ambient} and the resulting correction factors have been added into the manuscript.

I_{ambient} was ECMWF reanalysis data sets (ERA-5 hourly data, interpolation method, Table S1), which ranged from 0 to 762.9 W m⁻² and the resulting $\frac{I_{\text{ambient}}}{I_{\text{simulator}}}$ ranged from 0 to 1.01 with an average of 0.35.

Page 13 Line 367: Again: How did you define 'lifetime' (see my earlier comment)

Response: The reference has been added into the revised manuscript.

Lifetime was defined as the reciprocal of overall scavenging rate constant (first order) of NO

(Olasehinde et al., 2010).

Anifowose et al. (2015) found that in Kurose River, NO lifetime, which was defined as the reciprocal of first order scavenging rate constant of NO (Olasehinde et al., 2010), was only 0.25 s.

Page 14 Line 373: how do you justify this percentage uncertainty? The lifetimes in lines 367-8 suggest a larger uncertainty.

Response: 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 (28–216 s, 170 °E Equatorial regions) varied a lot, however in the following statement we explained that NO lifetime in our study area might be similar to that in the central Equatorial Pacific. Besides, in the study of Zafiriou et al. (1980), NO lifetime was 28–144 s in the equatorial Pacific seawater samples, but the uncertainty was not reported, thus it is difficult to determine the uncertainty. However, in Zafiriou et al. (1980), they estimated NO concentration in seawater with an uncertainty factor of 2.5, thus to be more cautious, we revised our uncertainty 30% into an rigorous description as “with an uncertainty factor of 2.5”

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 (with an uncertainty factor of 2.5) was applied in our study.

Page 14 Line 395: refer to data source (ERA5?)

Response: I_{ocean} and I_{ss} were separately referenced from Bange and Uher (2005) and Wu et al. (2015). I_{ocean} was set to 185 W m^{-2} (Bange and Uher, 2005) while I_{ss} was 765 W m^{-2} in our study (Wu et al., 2015).

Page 15 Line 398: add missing units

Response: The missing unit has been added.

As described above, $K_{\text{D}-354}$ was applied to estimate the MLD. In Smyth (2011), $K_{\text{D}-340}$ to $K_{\text{D}-380}$ 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 m^{-1} .

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 several 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 temperature, and increasing salinity. In contrast, NO photoproduction rates (average: $0.5 \pm 0.2 \times 10^{-12} \text{ mol L}^{-1} \text{ s}^{-1}$) 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: $13 \times 10^{-12} \text{ mol m}^{-2} \text{ s}^{-1}$) were significantly larger than the NO air-sea flux densities (average: $1.8 \times 10^{-12} \text{ mol m}^{-2} \text{ s}^{-1}$) 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 high reactivity with other substances (Zafiriou et al., 1980; Lutterbeck and Bange, 2015; Liu et al., 2017). NO is produced and consumed during various microbial processes such as nitrification,

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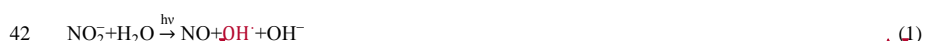
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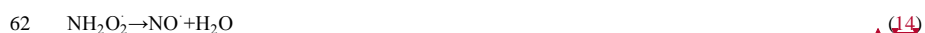
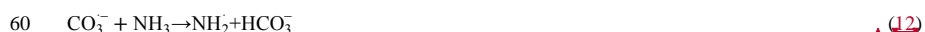
37 denitrification₂ and anammox (Schreiber et al., 2012; Kuypers et al., 2018). Moreover, it is known that
 38 both phytoplankton and zooplankton can metabolize NO and are influenced by ambient (extracellular)
 39 NO concentrations (Singh and Lal, 2017; Wang et al., 2017; Astier et al., 2018).
 40 Apart from (micro)biological processes, NO can be produced photochemically from dissolved nitrite
 41 (NO₂⁻) in the sunlit surface ocean (Zafiriou and True, 1979; Zafiriou and McFarland, 1981):



43 Mack and Bolton (1999) reviewed the possible subsequent reaction of Eqn. (1), for example, the
 44 produced NO and hydroxyl radical (OH[·]) of Eqn. (1) could react to produce HNO₂ reversely Eqn. (2),
 45 and some reactions that consumed NO or its oxides like Eqn. (3) to Eqn. (8).



53 Besides, in natural sunlit seawater, photolyzed dissolved nitrate (NO₃⁻) could be a source of NO through
 54 NO₂⁻ Eqn. (9); during the process of ammonium (NH₄⁺/NH₃) oxidation into NO₂⁻ and NO₃⁻, NO might
 55 be an intermedium (Joussotdubien and Kadiri, 1970), or NO could be produced through amino-peroxyl
 56 radicals (NH₂O₂) through Eqn. (10) to (14) (Laszlo et al., 1998; Clarke et al., 2008)



63 Table 1 summarizes studies about photochemical production of NO measured in the surface waters of
 64 the equatorial Pacific Ocean (Zafiriou et al., 1980; Zafiriou and McFarland, 1981), the Seto Inland Sea
 65 (Olasehinde et al., 2009; Olasehinde et al., 2010; Anifowose and Sakugawa, 2017), the Bohai Sea and

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138 Yellow Sea (Liu et al., 2017; Tian et al., 2019) and the Kurose River (Japan) (Olasehinde et al., 2009;
 139 Anifowose et al., 2015). NO concentration was determined by the balance of the production and the
 140 removal process, thus changes of NO production and removal rates could influence NO concentration in
 141 the seawater. In the surface seawater, photochemical was regarded as the main production process
 142 (Zafiriou and McFarland, 1981; Olasehinde et al., 2010; Anifowose et al., 2015). In Table 1, NO
 143 photoproduction rates varied among different seawater samples, the photoproduction rates in Kurose
 144 River (average: $499 \times 10^{-12} \text{ mol L}^{-1} \text{ s}^{-1}$) was the biggest, which might be due to an increase of nitrite
 145 being released into the river in agricultural activity during the study time. However, NO concentration
 146 was about $1.6 \times 10^{-12} \text{ mol L}^{-1}$, at the lowest level, which was because of higher scavenging rate in river
 147 water. Anifowose et al. (2015) found that in Kurose River, NO lifetime, which was defined as the
 148 reciprocal of first order scavenging rate constant of NO (Olasehinde et al., 2010), was only 0.25 s. The
 149 lifetime of NO showed an increasing trend from river (several seconds) to inland sea (dozens of seconds)
 150 to open sea (dozens to hundreds of seconds), reviewed in Anifowose and Sakugawa (2017). However,
 151 NO showed higher concentration levels in coastal waters than in open sea, higher photoproduction rates
 152 in coastal waters than open sea or other production process in coastal waters might account for this.

153 In this study, we present the results of our measurements of NO photoproduction in laboratory
 154 experiments using artificial and natural seawater samples. The major objectives of our studies were (i)
 155 to decipher the factors affecting NO photoproduction in seawater, (ii) to determine the photoproduction
 156 rates of NO from samples collected during a cruise to the western tropical North Pacific Ocean (WTNP)
 157 and (iii) to quantify the role of photoproduction as a source of NO in the surface waters of the WTNP.

158 2 Methods

159 2.1 Determination of dissolved NO in aqueous samples

160 For the measurements of dissolved NO we applied the method described by Olasehinde et al. (2009). In
 161 brief, NO in the aqueous samples was determined by trapping it with added 4,5-diaminofluorescein
 162 (DAF-2, chromatographic grade from Sigma-Aldrich, USA) and measuring the reaction product
 163 triazolofluorescein (DAF-2T) with a high performance liquid chromatography system (HPLC). We used
 164 an Agilent 1260 Infinity HPLC (Agilent Technologies Inc., USA) system equipped with a Venusil XBP-
 165 C18 column (5.0 μm ; 4.6 mm \times 250 mm i.d.). The column temperature was set to 25 $^{\circ}\text{C}$ and the mobile

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phase was comprised of acetonitrile (HPLC grade from Merck, Germany) and phosphate buffer (disodium hydrogen phosphate heptahydrate, guaranteed reagent from Sinopharm Chemical Reagent Co., Ltd, 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.

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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.

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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 (3.3×10^{-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.

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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 70 ± 1 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.

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

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

212 Triplicate samples from each treatment were collected every 0.5 h with an entire irradiation time of 2 h.
 213 At the sampling time, the SUNTEST CPS+ was turned off and triplicate subsamples were collected from
 214 each sample in the dark with microsyringe (50 µL), and then the cuvettes were quickly put back into the
 215 water bath to continue the experiment until two hours. The results showed that both in Milli-Q and
 216 artificial seawater samples, the photoproduct NO₂⁻ showed linear relationship against time (see below).
 217 However for the natural seawater samples, a linear relationship was only found in the irradiation time
 218 range of 30 min, while the relationship was not found after 30 min. Therefore, we decided to choose 30
 219 min as the total experimental time for natural seawater samples. Statistical analyses were done using
 220 SPSS v.16.0 or Origin 9.0 and results were considered significant at $p \leq 0.05$.

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

226 2.3 Experimental outline

227 2.3.1 Optimal DAF-2 concentration and storage time

228 In order to find out the optimal DAF-2 concentration, 10 mL of artificial seawater containing 0.5 µmol
 229 L⁻¹ NO₂⁻ was irradiated with various concentrations of DAF-2 ranging from 0.7 µmol L⁻¹ to 4.8 µmol
 230 L⁻¹ for 2 h.

231 To ascertain the sample storage time, 10 mL with artificial seawater samples containing 5.0 µmol L⁻¹ or
 232 0.5 µmol L⁻¹ NO₂⁻ were irradiated with various concentrations of DAF-2 for 2 h. After irradiation,
 233 samples were kept in the dark and measured every 2 h.

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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 NO₂⁻, 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 NO₂⁻ photochemical degradation, the data were 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 NO₂⁻ (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 NO₂⁻ represents J_{NO} (Anifowose et al., 2015).

The yield of NO formation (% f_{NO}) from the photodegradation via NO₂⁻ was estimated according to Anifowose et al. (2015)

$$\%f_{NO} = 100 \times J_{NO} \times c(NO_2^-) \times R_{NO}^{-1}$$

where $c(NO_2^-)$ is the initial concentration of NO₂⁻.

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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°N to 2°N along 146°E with 6 and 12 stations, respectively, and a W/E section from 137°E to 161°E along the equator with 13 stations (Fig. 1). 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 referenced from <https://www1.kaiho.mlit.go.jp/>.

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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

299 the concentration was below detection limit, $\frac{1}{2}$ of the detection limit (0.025 round-off to 0.02) was
300 used.

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

307 3 Results and Discussion

308 3.1 Optimal DAF-2 concentration and storage time

309 NO concentrations generated from photolysis of artificial seawater samples with an initial NO_2^-
310 concentration of $0.5 \mu\text{mol L}^{-1}$ increased with increasing DAF-2 concentrations and reached a maximum
311 at a DAF-2 concentration of $1.4 \mu\text{mol L}^{-1}$ (Fig. 2a). At DAF-2 concentrations $>1.4 \mu\text{mol L}^{-1}$ no further
312 increase of the NO concentrations was observed. Thus, we used a DAF-2 concentration of $1.4 \mu\text{mol L}^{-1}$
313 for all experiments.

314 Samples after reaction with DAF-2 and stored at 4 °C in the dark were stable for at least 28 h with the
315 measurement interval about 2 h (Fig. 2b). The relative standard deviations of the resulting NO
316 concentrations after irradiating samples containing $0.5 \mu\text{mol L}^{-1}$ and $5.0 \mu\text{mol L}^{-1}$ NO_2^- were $\pm 13\%$
317 and $\pm 7\%$, respectively. This demonstrated that photolysis samples with NO which were allowed to
318 react with DAF-2 could be stored for at least one day at 4 °C in the dark.

319 3.2 Photoproduction of NO in Milli-Q water and artificial seawater

320 The photoproduction rates of NO in samples with NO_2^- concentrations of 0.5, 2.0 and $5.0 \mu\text{mol L}^{-1}$ were
321 generally higher in artificial seawater than in Milli-Q water (Fig. 3a and 3b).

322 The resulting J_{NO} were $5.6 \pm 0.9 \times 10^{-4} \text{ min}^{-1}$ and $9.4 \pm 1.4 \times 10^{-4} \text{ min}^{-1}$ for Milli-Q water and artificial
323 seawater, respectively. They are lower than the J_{NO} of $34.2 \times 10^{-4} \text{ min}^{-1}$ for Milli-Q water reported by
324 Anifowose et al. (2015). The difference might be explained by higher solar radiation flux in their study,
325 which was about 1055 W m^{-2} .

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删除的内容: 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.

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3.3 Influence of pH, temperature, salinity and wavelengths

All irradiation experiments conducted in artificial seawater were added with two different NO_2^- concentrations of 0.5 and 5.0 $\mu\text{mol L}^{-1}$. The resulting NO concentrations were generally higher when irradiating the samples with the initial NO_2^- concentration of 5.0 $\mu\text{mol L}^{-1}$. NO photoproduction rates showed increasing trends with decreasing pH, increasing temperature, and increasing salinity, the relationships between rates with salinity and temperature were significant ($p < 0.5$) (Fig. 4 and 5). Reaction (1) indicates that decreasing pH 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_2O_4 and N_2O_3 hydrolysis reaction (Eqn. (4) and Eqn. (8)) 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:

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

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 :

$$R_{T_2} = R_{T_1} \times \exp\left(\frac{E}{R} \times \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right)$$

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

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372 $R_T = 2.7 \times 10^{-10} \times \exp(6920 \times (\frac{1}{293.15} - \frac{1}{T}))$

(18)

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

374 $R_T = 7 \times 10^{-10} \times \exp(11026 \times (\frac{1}{293.15} - \frac{1}{T}))$

(19)

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375 However, NO production rate at $0.5 \mu\text{mol L}^{-1}$ nitrite did not increase from 20 to 30°C , the plausible
376 explanation was that NO_2^- concentration here was the mainly influencing factor, NO_2^- might be run out
377 at 30°C , if NO_2^- concentration increased to $5.0 \mu\text{mol L}^{-1}$, the temperature could make a noticeable
378 difference.

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379 At $0.5 \mu\text{mol L}^{-1}$ and $5.0 \mu\text{mol L}^{-1}$ initial NO_2^- concentrations of Milli-Q water and artificial seawater
380 samples, higher salinity showed higher photoproduction rates of NO. The regression relationship is $y =$
381 $0.37x - 4.55$ for $0.5 \mu\text{mol L}^{-1} \text{NO}_2^-$ and $y = 2.3x - 39.5$ for $5.0 \mu\text{mol L}^{-1} \text{NO}_2^-$, respectively, where x is
382 the salinity (‰) and y is the photoproduction rate ($\times 10^{-10} \text{mol L}^{-1} \text{s}^{-1}$). This result indicates that with
383 increasing ion strength NO production is enhanced, however, the exact mechanism is unknown and need
384 further study. Zafiriou and McFarland (1980) demonstrated that artificial seawater comprised with major
385 and minor salts showed complex interactions and the addition of EDTA could diminished NO
386 concentration, which meant trace metals could keep NO concentration at a higher level, which is similar
387 to our results. But Chu and Anastasio (2007) reported that addition Na_2SO_4 ($4.0\text{--}7.0 \text{mmol L}^{-1}$) in solution
388 had no effect on the quantum yield of OH which might because of the complex of the natural seawater
389 samples. Overall, in artificial seawater samples, photoproduction rates showed an increasing trend with
390 salinity.

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(with $0.5 \mu\text{mol L}^{-1}$ or $5.0 \mu\text{mol L}^{-1}$ initial NO_2^- concentrations)

391 The highest NO photoproduction rates were observed with full wave length band whereas the lowest NO
392 rates were observed with UVB. The NO photoproduction rates approached zero at wave lengths in the
393 visible band. The contribution of visible band, UVA band and UVB band were $<1\%$, 30.7% , 85.2% and
394 $<1.0\%$, 34.2% , 63.1% for 0.5 and $5.0 \mu\text{mol L}^{-1} \text{NO}_2^-$, respectively. Our results are in line with the
395 findings of Zafiriou and McFarland (1981) who found that samples exposed to (UV+visible) wave
396 lengths lost NO_2^- more rapidly than those exposed only to the visible wave lengths alone. In the study of
397 Chu and Anastasio (2007), under single wavelength light, quantum yield of OH decreased with the
398 wavelength (280 nm to 360 nm and plateau until 390 nm) which meant that single wavelength light of
399 UVB had higher photoproduction rate than UVA. Compared with the results in our study, it might be the
400 wild band of UVA (320-420 nm) that led to the summational higher rates under UVA than UVB (in our

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that artificial seawater comprised with major and minor salts showed
complex interactions

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system 300–320 nm). Moreover, according to the UV–visible absorption spectra of NO_2^- , λ_{max} was 354 nm, which is in the range of UVA (320–420 nm) (Zuo and Deng, 1998; Zafiriou and McFarland, 1981). Thus, it seems reasonable that in our study, the photoproduction rate under UVA was higher than UVB; with full wave length, the photoproduction rates are the highest; and in the visible band, the NO photoproduction rates approached zero.

3.4 Kinetics of the NO photoproduction

The yields of NO formation from NO_2^- ($\%f_{\text{NO}}$) in artificial seawater samples were about 70.1% and 97.9% for the initial NO_2^- concentrations of 0.5 and 5.0 $\mu\text{mol L}^{-1}$, respectively. The missing NO yield (29.9% for 0.5 $\mu\text{mol L}^{-1}$ and 2.1% for 5.0 $\mu\text{mol L}^{-1}$) 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_2^- photoproduction, some NO were oxidized into NO_2 , then NO_2 dimerized (Eqn. (6)) and the dipolymer N_2O_4 would hydrolyze into NO_2^- and NO_3^- (Eqn. (7)), which actually reduce the concentration of NO_2^- (Mack and Bolton, 1999).

Assuming a 100% yield from NO_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_2^- concentrations (= 10) was the same for all experiments. This result, however, does point to reaction 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_3^- , NH_4^+ and NO_2^- ranged from 0.03 $\mu\text{mol L}^{-1}$ to 1.6 $\mu\text{mol L}^{-1}$, 0.20 $\mu\text{mol L}^{-1}$ to 1.2 $\mu\text{mol L}^{-1}$ and 0.02 $\mu\text{mol L}^{-1}$ to 0.33 $\mu\text{mol L}^{-1}$, respectively (Fig. 6). The measured photoproduction rates of NO ranged from $0.3 \times 10^{-10} \text{ mol L}^{-1} \text{ min}^{-1}$ (station S0711) to $2.9 \times 10^{-10} \text{ mol L}^{-1} \text{ min}^{-1}$ (station S0303), with an average value of $13.0 \pm 7.6 \times 10^{-11} \text{ mol L}^{-1} \text{ min}^{-1}$. Photoproduction rates did not show significant correlations with NO_2^- , NO_3^- , NH_4^+ , pH, salinity, water temperature as well as with colored dissolved organic matter (data not shown, the same method with Zhu et al. (2017), absorption coefficients at 355 nm) (SPSS v.16.0, Pearson correlation test).

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454 ~~There was no linear relationship found between~~ R_{NO} and dissolved NO_2^- during our cruise, ~~which~~ is in
 455 contrast to the results of Olasehinde et al. (2010), Anifowose et al. (2015), and Anifowose and Sakugawa
 456 (2017) who observed positive linear relationships between NO photoproduction rates and the NO_2^-
 457 concentrations in the surface waters of the Seto Inland Sea and the Kurose River. This might because
 458 that other factors like pH, salinity were different between samples collected at different stations.
 459 In Table 1, we found that the average photoproduction rate of NO measured in our cruise is lower than
 460 that of the Seto Inland Sea and the Kurose River which could be ascribed to higher background NO_2^- in
 461 the inland sea waters (Olasehinde et al., 2009; 2010). Our result is slightly lower than the R_{NO} from the
 462 central equatorial Pacific Ocean ($> 10^{-12} \text{ mol L}^{-1} \text{ s}^{-1}$), the lower concentration of NO_2^- ($0.06 \mu\text{mol L}^{-1}$)
 463 in our study area might account for this (Zafiriou and McFarland, 1981). In Table 1, the NO_2^-
 464 concentration of $0.06 \mu\text{mol L}^{-1}$ in our study was lower than most of other study area like Qingdao coastal
 465 waters ($0.75 \mu\text{mol L}^{-1}$) and the Seto Inland Sea ($0.4 \mu\text{mol L}^{-1}$ or $0.5-2 \mu\text{mol L}^{-1}$). In the study of
 466 Anifowose et al. (2015), since the NO_2^- concentration of upstream K1 station was similar to ours (0.06
 467 $\mu\text{mol L}^{-1}$), the higher R_{NO} might attributed to lower pH (7.36) as mentioned above. Or it might be because
 468 the difference of the river water and the seawater, considering lower nitrite levels of K1, dissolved
 469 organic matter might also account for the higher R_{NO} . Because of its conservative mixing behavior with
 470 salinity, dissolved organic matter always showed a higher level in river than open sea (Zhu et al., 2017),
 471 which could photodegrade itself to produce NO_2^- , finally to promote R_{NO} . In our study, the rates were
 472 adjusted to the ambient conditions, which included nighttime samples when the rates were lower. From
 473 the T-S diagram (Fig. 7), we found that higher photoproduction rates at stations S0701 and S0704 might
 474 resulted from the influence of the Kuroshio (see Fig. 1), with enhanced concentrations of NO_2^- . The
 475 higher NO production rates measured for stations S0303/S0307 and S0717, S0723 might have been
 476 influenced by the South Equatorial and North Equatorial Currents, respectively, but were obviously not
 477 associated with enhanced NO_2^- concentrations.
 478 If we take the missing 30% of f_{NO} in artificial seawater as the experimental error, then in our study, using
 479 the J_{NO} in the artificial seawater, the average % f_{NO} value in natural water was calculated to be 52% ($-$
 480 30%), indicating that there are other unknown nitrogenous compounds, for example, NO_2^- produced from
 481 NO_3^- photolysis (Eqn. 9) or from other organic matter which could further lead to NO production
 482 (Kieber et al., 1999; Benedict et al., 2017; Goldstein and Rabani, 2007; Minero et al., 2007).

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

492 3.6 Flux densities of NO in the surface layer of the WTNP

493 3.6.1 Air-sea flux density of NO

494 The NO flux densities were computed with (Eqn. (20)):

$$495 F = k_{sea} ([NO] - pNO_{air} \times H^p)$$

$$496 pNO_{air} = x'NO_{air} \times (p_{ss} - p_w)$$

497 here F stands for the flux density (mass area⁻¹ time⁻¹) across the air-sea interface, k_{sea} is the gas transfer
 498 velocity (length time⁻¹), $[NO]$ is the measured concentration of NO in the surface seawater (mol volume⁻¹),
 499 $x'NO_{air}$ is the mixing ratio of atmosphere NO (dimensionless). And p_{ss} is the barometric pressure
 500 while p_w was calculated after Weiss and Price (1980):

$$501 \ln p_w = 24.4543 - 6745.09/(T + 273.15) - 4.8489 \times \ln(T + 273.15)/100 - 0.000544 \times S$$

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

$$503 H^p(T) = H^\theta \times \exp(-\Delta sol H/R \times (1/T - 1/T^\theta))$$

504 where $-\Delta sol \frac{H}{R} = \frac{d \ln H}{d \ln(\frac{1}{T})}$, H^θ , and $-\Delta sol H/R$ are tabulated in Sander (2015) ($-\Delta sol H/R = 1600$ and H^θ
 505 $= 1.9 \times 10^{-5}$ mol m⁻³ pa⁻¹). The reviewed several literatures about NO, H^θ and the values in different
 506 literatures were similar (Sander, 2015). In our calculation, the value in the Warneck and Williams (2012)
 507 were used.

508 Then k_{sea} was calculated after Wanninkhof (2014) as Eqn. (24):

$$509 k_{sea} = k_w (1 - \gamma_a)$$

510 γ_a is the fraction of the entire gas concentration gradient across the airside boundary layer as a fraction
 511 of the entire gradient from the bulk water to the bulk air (dimensionless), k_a is the air side air-sea gas
 512 transfer coefficient (length time⁻¹) according to (Jähne et al., 1987; McGillis et al., 2000; Sharqawy et al.,
 513 2010), for the details of the calculation of k_w and γ_a see Tian et al. (2019).

514 Since onboard wind speeds were not available, ECMWF reanalysis data sets (ERA-5 hourly data) were
 515 applied (Fig. 6). We used a value of 10⁻¹¹ (v/v) for atmospheric NO (Law, 2001). The atmosphere
 516 pressure was set to 101.325 kPa.

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534 Since the measurements [NO] were not available from the cruise we estimated [NO] by assuming that
 535 (1) NO production is mainly resulting from NO_2^- photodegradation and (2) the NO photoproduction R_{NO}
 536 as measured in our irradiation experiment is balanced by the NO scavenging rate R_s (3) rates of nitrite
 537 photoproduction into NO was proportional to the irradiance flux in order to adjust the rates under
 538 simulator light into ambient light at the sampling time (Zafiriou and McFarland, 1981; Olasehinde et al.,
 539 2010):

$$540 R_{\text{NO}} \times \frac{I_{\text{ambient}}}{I_{\text{simulator}}} = [\text{NO}] \times R_s, \quad (25)$$

541 where R_s represents the sum of the rate constants for the scavenging compounds reacting with NO times
 542 the concentrations of the scavenger compounds, I_{ambient} and $I_{\text{simulator}}$ denote the light intensity of
 543 the sampling station and the CPS+ simulator (765 W m^{-2}). I_{ambient} was ECMWF reanalysis data sets
 544 (ERA-5 hourly data, Fig. 6), which ranged from 0 to 762.9 W m^{-2} and the resulting $\frac{I_{\text{ambient}}}{I_{\text{simulator}}}$ ranged
 545 from 0 to 1.01 with an average of 0.35. In the study of Zafiriou et al., (1980) and Anifowose and
 546 Sakugawa, (2017), they reviewed the NO lifetime in the different area for the Kurose River (0.05–1.3 s),
 547 the Seto Inland sea (1.8–20 s), and the central Equatorial Pacific (28–216 s, 170°E Equatorial regions),
 548 which showed an increasing trend from river to open sea. It seemed that NO life time in our study area
 549 should be most similar to the central Equatorial Pacific. Considering part of our sampling stations were
 550 in open sea while some stations were close to continent like New Guinea Island and Japan, average
 551 lifetime about 100 s (with an uncertainty factor of 2.5) was applied in our study. Tian et al (2019) found
 552 that NO concentration in the surface water showed no significant difference with that in the bottom water
 553 (average depth: 43 m), so it seems reasonable to estimate the steady state NO concentration with the NO
 554 concentration in the mixed layer. Then [NO] was estimated to range from 0 to $292 \times 10^{-12} \text{ mol L}^{-1}$ (0
 555 means that sampling time during nighttime), with an average of $49 \times 10^{-12} \text{ mol L}^{-1}$, which was consistent
 556 with previous results in central equatorial Pacific ($46 \times 10^{-12} \text{ mol L}^{-1}$), while it was lower than near
 557 continent seawater like the Seto Inland Sea (up to $120 \times 10^{-12} \text{ mol L}^{-1}$) and the Jiaozhou Bay (157×10^{-12}
 558 mol L^{-1}), which might be because of higher nitrite concentration. NO showed the lowest concentration
 559 in Kurose River, the shortest life time might account for this in river water than in seawater (Anifowose
 560 and Sakugawa, 2017).

561 In Table 1, the resulting flux density of NO for WTNP ranged from 0 to $13.9 \times 10^{-12} \text{ mol m}^{-2} \text{ s}^{-1}$, with
 562 an average of $1.8 \times 10^{-12} \text{ mol m}^{-2} \text{ s}^{-1}$, which is in good agreement with that in central equatorial Pacific

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(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 (Uher and Andreae, 1996; Bange and Uher, 2005)

$$R_{ocean} = R_{NO} \times \left(\frac{I_{ocean}(1 - \exp(-K_D \times MLD))}{I_{ss} \times K_D \times MLD} \right) \quad (26)$$

where R_{ocean} and R_{NO} are the photoproduction rates for the ocean mixed layer and seawater irradiation experiments, respectively, see Section 3.5. I_{ocean} and I_{ss} 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_{ocean} was set to 185 W m^{-2} (Bange and Uher, 2005) while I_{ss} was 765 W m^{-2} in our study (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 m^{-1} . 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_{ocean} was about $8.6 \pm 4.9 \times 10^{-12} \text{ mol L}^{-1} \text{ min}^{-1}$ 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: $13 \times 10^{-12} \text{ mol m}^{-2} \text{ s}^{-1}$) were significantly larger than the NO air-sea flux densities (average: $1.8 \times 10^{-12} \text{ mol m}^{-2} \text{ s}^{-1}$) 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 temperature, 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

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606 Pacific Ocean (November 2015–January 2016). We conclude that the trends observed in our irradiation
607 experiments with artificial seawater do not seem to be representative for WTNP because of the complex
608 settings of open ocean environments. Moreover, we conclude that future changes of NO photoproduction
609 due to ongoing environmental changes such as ocean warming and acidification are, therefore, difficult
610 to predict and need to be tested by irradiation experiments of natural seawater samples under varying
611 conditions. The flux induced by NO photoproduction in the WTNP (average: $13 \times 10^{-12} \text{ mol m}^{-2} \text{ s}^{-1}$)
612 were significantly larger than the NO air–sea flux densities (average: $1.8 \times 10^{-12} \text{ mol m}^{-2} \text{ s}^{-1}$) indicating
613 a further NO loss process in the surface layer. In order to decipher and to quantify the NO production
614 and consumption pathways in the oceanic surface layer more comprehensive laboratory and onboard
615 measurements are required.

616 Author contributions.

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

620 Competing interests.

621 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 $\mu\text{mol L}^{-1}$ 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 $\mu\text{mol L}^{-1}$ 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 $\mu\text{mol L}^{-1}$ NO_2^- and b, d, f, h for 5.0 $\mu\text{mol L}^{-1}$ 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 $\mu\text{mol L}^{-1}$ NO_2^- and b, d, f, h for 5.0 $\mu\text{mol L}^{-1}$ NO_2^-).

Fig. 6. Seawater temperature, salinity, concentrations of NO_2^- , NO_3^- , NH_4^+ , wind speed, light intensity, 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,

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删除的内容: 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) -

804 North Equatorial Counter Current, North Equatorial Current, and Subtropical Counter Current,
805 respectively.
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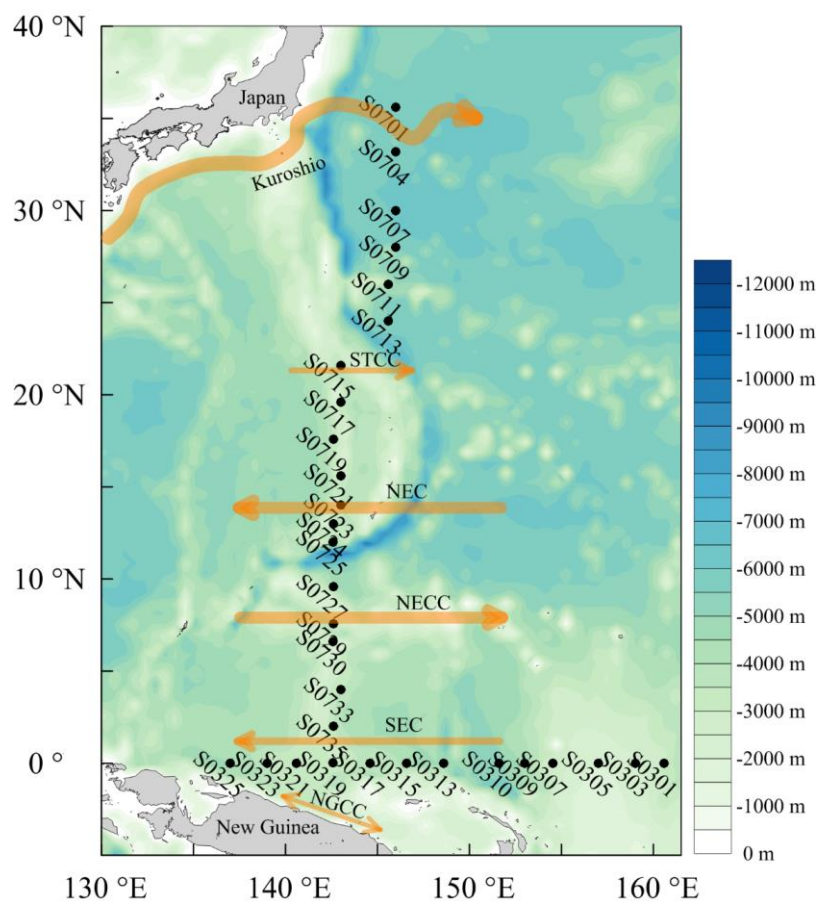


Fig. 1. Locations of the sampling stations in the western tropical North Pacific Ocean. The acronyms NGCC, SEC, NECC, NEC, and STCC stand for New Guinea Coastal Current, South Equatorial Current, North Equatorial Counter Current, North Equatorial Current, and Subtropical Counter Current, respectively.

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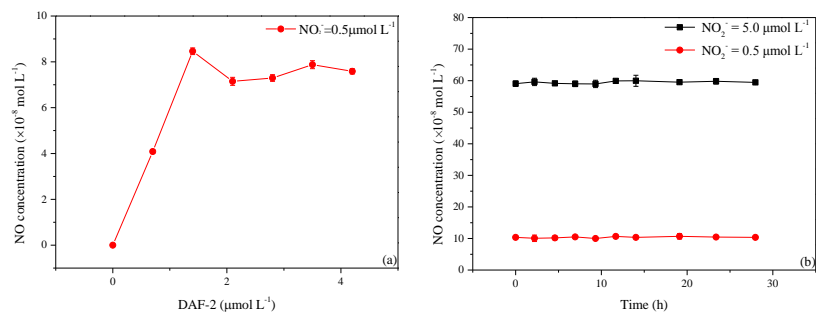


Fig. 2. Changes of NO concentrations with initial DAF-2 concentration of 0, 0.7, 1.4, 2.1, 2.8, 3.5 and 4.2 $\mu\text{mol L}^{-1}$ after irradiation time of 2 h (a) and changes of different NO concentrations with storage time monitored at about 2 h time intervals (b).

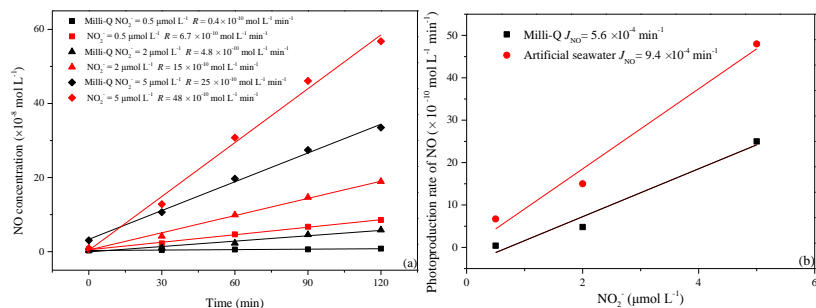


Fig. 3. Photoproduction rates of NO with 0.5, 2, and 5.0 $\mu\text{mol L}^{-1}$ NO_2^- (a) and the calculated J_{NO} values in Milli-Q water and artificial seawater (b), symbols in red represented for the artificial seawater samples and in black for Milli-Q water.

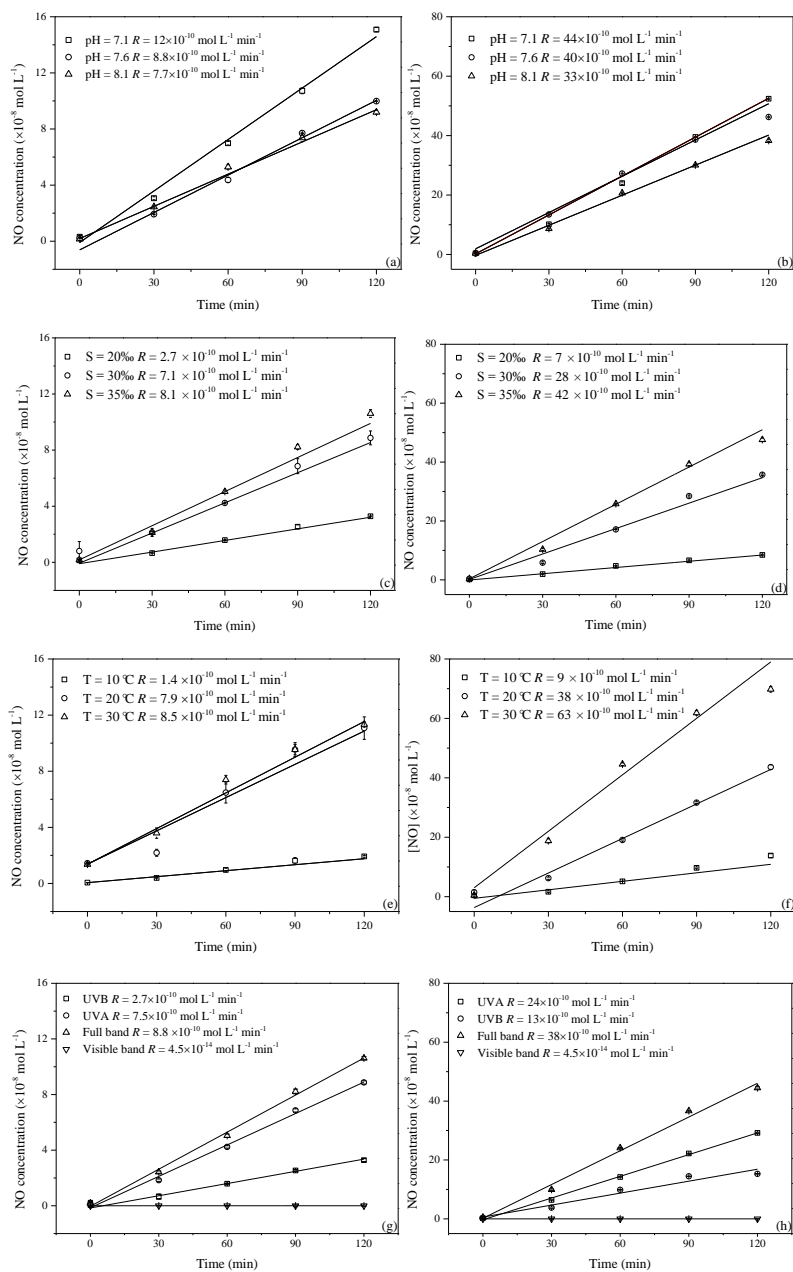
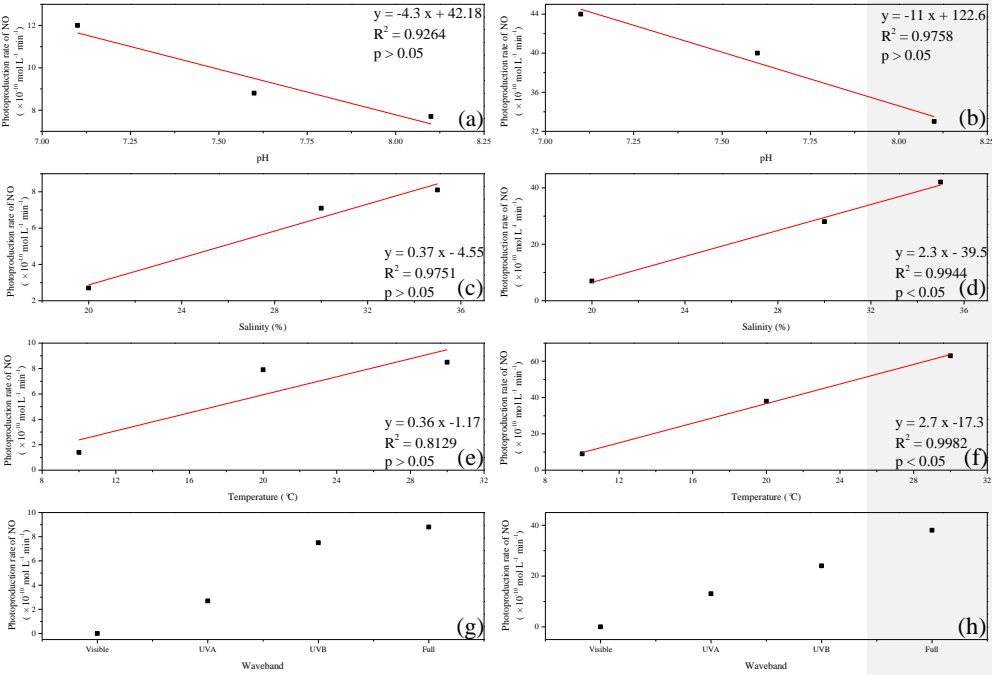


Fig. 4. NO concentration changes with irradiation time at different pH, salinity, temperature and waveband conditions (a, c, e, g for $0.5 \mu\text{mol L}^{-1} \text{NO}_2^-$ and b, d, f, h for $5.0 \mu\text{mol L}^{-1} \text{NO}_2^-$).

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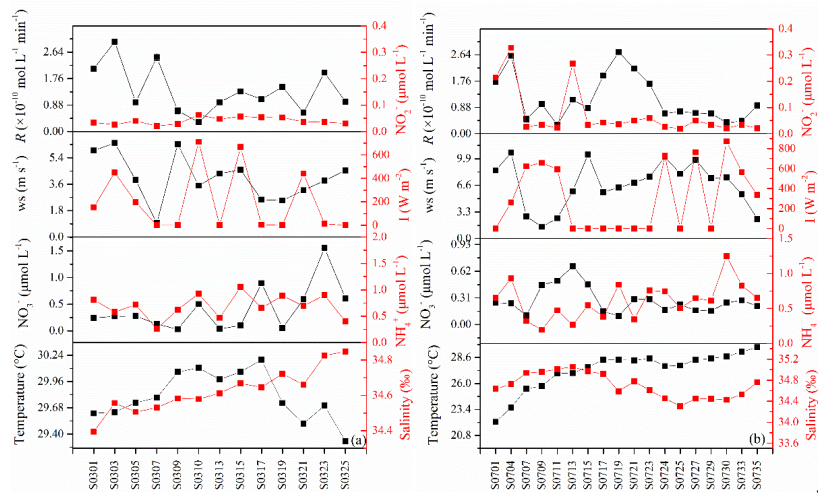


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834 **Fig. 5.** Changes of NO photoproduction rates with irradiation time at different pH, salinity, temperature
835 and waveband conditions (a, c, e, g for 0.5 $\mu\text{mol L}^{-1}$ NO_2^- and b, d, f, h for 5.0 $\mu\text{mol L}^{-1}$ NO_2^-).

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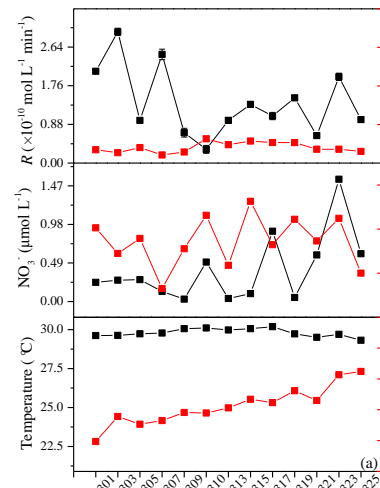
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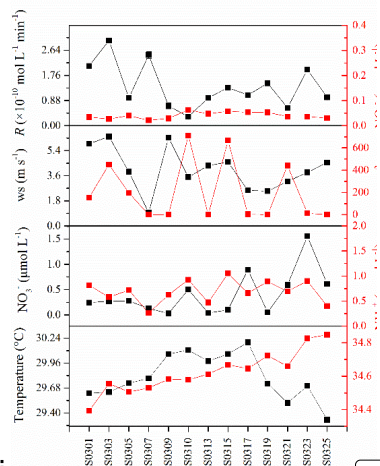
838

839 **Fig. 6.** Seawater temperature, salinity, concentrations of NO_2^- , NO_3^- , NH_4^+ , wind speed, light
840 intensity, and photoproduction rates of NO (R_{NO}) in the western tropical North Pacific Ocean (a:
841 W/E transect; b: N/S transect).

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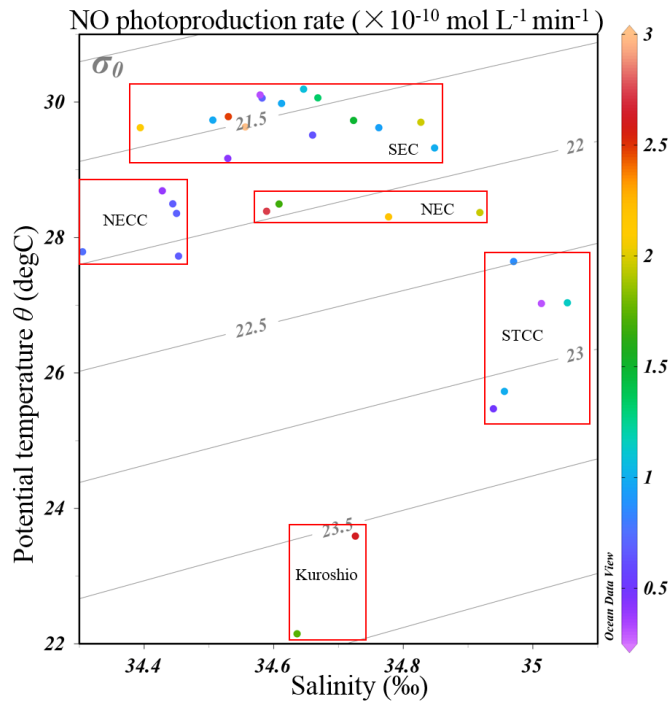


Fig. 7. The potential temperature–salinity (T–S) diagram with NO photoproduction rates indicated in the color bar. Water mass characteristics of the surface currents shown in Figure 1 are indicated. The acronyms NGCC, SEC, NECC, NEC, and STCC stand for New Guinea Coastal Current, South Equatorial Current, 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 ($R_{5.0}/R_{0.5}$) in the different irradiation experiments.

862 **Table 1** Photoproduction rates (*R*), method, average NO concentrations, NO₂⁻ concentrations and
863 average flux densities of NO in different regions.

<u>Regions</u>	<u><i>R</i></u> (mol L ⁻¹ s ⁻¹)	<u>Method</u>	<u>NO</u> (mol L ⁻¹)	<u>NO₂⁻</u> (μmol L ⁻¹)	<u>Flux</u> (mol m ⁻² s ⁻¹)	<u>Sampling date</u>	<u>References</u>
<u>Seto Inland Sea,</u> <u>Japan</u>	<u>8.7-38.8×10⁻¹²</u>	<u>DAF-2</u>	<u>120×10⁻¹²</u>	<u>0.5-2</u>	<u>3.55×10⁻¹²</u>	<u>5-9 October, 2009</u>	<u>Olasehinde et al.,</u> <u>2010</u>
<u>Seto Inland Sea,</u> <u>Japan</u>	<u>1.4-9.17×10⁻¹²</u>	<u>DAF-2</u>	<u>3-41×10⁻¹²</u>	<u>0-0.4</u>	<u>0.22×10⁻¹²</u>	<u>September, 2013</u> <u>and June, 2014</u>	<u>Anifowose and</u> <u>Sakugawa, 2017</u>
<u>Kurose River,</u> <u>Japan</u>	<u>9.4-300×10⁻¹²</u>	<u>DAF-2</u>	<u>=</u>	<u>=</u>	<u>=</u>	<u>=</u>	<u>Olasehinde et al.,</u> <u>2009</u>
<u>Kurose River</u> <u>(K1 station), Japan</u>	<u>4×10⁻¹²</u>	<u>DAF-2</u>	<u>1.6×10⁻¹²</u>	<u>0.06</u>	<u>=</u>	<u>Monthly, 2013</u>	<u>Anifowose et al.,</u> <u>2015</u>
<u>Jiaozhou Bay</u>	<u>=</u>	<u>DAN</u>	<u>157×10⁻¹²</u>	<u>=</u>	<u>7.2×10⁻¹²</u>	<u>June, July, and</u> <u>August, 2010</u>	<u>Tian et al., 2016</u>
<u>Jiaozhou Bay and</u> <u>its adjacent waters</u>	<u>=</u>	<u>DAN</u>	<u>(160 ± 130)</u> <u>×10⁻¹²</u>	<u>=</u>	<u>10.9×10⁻¹²</u>	<u>8-9 March, 2011</u>	<u>Xue et al., 2011</u>
<u>Coastal water off</u> <u>Qingdao</u>	<u>1.52×10⁻¹²</u>	<u>DAN</u>	<u>260×10⁻¹²</u>	<u>0.75</u>	<u>=</u>	<u>November, 2009</u>	<u>Liu et al., 2017</u>
<u>Central equatorial</u> <u>Pacific</u>	<u>≥ 10⁻¹²</u>	<u>Chemilum</u> <u>inescence</u>	<u>46×10⁻¹²</u>	<u>0.2</u>	<u>2.2×10⁻¹²</u>	<u>R/V Knorr 73/7</u> <u>15 November,</u>	<u>Zafiriou and</u> <u>Mcfarland., 1981</u>
<u>The north west</u> <u>Pacific Ocean</u>	<u>(0.5 ± 0.2)</u> <u>×10⁻¹²</u>	<u>DAF-2</u>	<u>49×10⁻¹²</u>	<u>0.06</u>	<u>1.8×10⁻¹²</u>	<u>2015 to 26 January,</u> <u>2016</u>	<u>This study</u>

带格式表格

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867 **Table 2** The ratios of photoproduction rates ($R_{5.0}/R_{0.5}$) in the different irradiation experiments.

	$R (\times 10^{-10} \text{ mol L}^{-1} \text{ min}^{-1})$		Ratio
	0.5 μM	5.0 μM	
pH=7.1	12	44	3.7
pH=7.6	8.8	40	4.5
pH=8.1	7.7	33	4.3
T=10 °C	1.4	9.0	6.4
T=20 °C	7.9	38	4.8
T=30 °C	8.5	63	7.4
S=20	2.7	7.0	2.6
S=30	7.1	28	3.9
S=35	8.1	42	5.2

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