

## Determination of Daytime Flux of Nitric Oxide Radical (NO<sup>•</sup>) at an Inland Sea-Atmospheric Boundary in Japan

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### Abstract

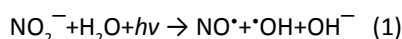
The flux of nitric oxide radical (NO<sup>•</sup>) during the daytime at the Seto Inland Sea-atmosphere boundary was measured during the sea cruises embarked upon in September, 2013 and June, 2014. Atmospheric concentration of NO<sup>•</sup> over the Seto Inland Sea and that present in the sea surface were measured. Results showed that average atmospheric NO<sup>•</sup> concentrations measured over the Inland Sea in 2013 and 2014 were  $4.4 \times 10^{-10}$  and  $5.2 \times 10^{-10}$  atm, respectively. Also during the cruises, average wind speed of 2.0 and 3.2 m s<sup>-1</sup> were measured in 2013 and 2014, respectively. In the surface seawater, the average NO<sup>•</sup> concentrations measured were  $2.1 \times 10^{-11}$  and  $1.9 \times 10^{-11}$  mol NO<sup>•</sup> L<sup>-1</sup> in 2013 and 2014, respectively. Using appropriate formula, a daytime efflux of 0.22 pmol NO<sup>•</sup> m<sup>-2</sup> s<sup>-1</sup> from the sea to the atmosphere was estimated for the two year-study. Assuming 8 h of solar intensity per day, about  $1.54 \times 10^6$  g NO<sup>•</sup> y<sup>-1</sup> efflux from the 23,000 km<sup>2</sup> Seto inland Sea surface was determined. The study confirmed that, during the day, sea could be an additional source of NO<sup>•</sup> to the atmosphere.

**Keywords:** Nitric oxide; Radical; Photo formation; Seawater; Atmosphere

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### Introduction

Many photochemical processes take place on sunlit seawater surface. Notable among them are photo formation of reactive oxygen species like nitric oxide radical (NO<sup>•</sup>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), hydroxyl radical (•OH) and superoxide radical (O<sub>2</sub><sup>•-</sup>). Absorption of solar radiation at ~300-410 nm ( $\lambda_{\max}$ , 356 nm) by nitrite leads to NO<sup>•</sup> formation, thus showing nitrite as a major photochemical source of NO<sup>•</sup> as shown in equation 1 [1].



Other previous studies have confirmed nitrite as a major NO<sup>•</sup> source in sunlit seawater [2-4]. During biogenic processes such as nitrification (oxidation of NH<sub>4</sub><sup>+</sup> to NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>) and denitrification (anaerobic reduction of NO<sub>3</sub><sup>-</sup> to N<sub>2</sub>O or N<sub>2</sub>) in the soil, NO<sup>•</sup> is also produced as an intermediate [5,6]. In the atmosphere, NO<sup>•</sup> could be produced by the reaction of atomic oxygen with the atmospheric N<sub>2</sub>O (N<sub>2</sub>O + O → 2NO<sup>•</sup>), lightning and photo-dissociation of NO<sub>2</sub> (NO<sub>2</sub> + hν → 2NO<sup>•</sup>). Other atmospheric NO<sup>•</sup> sources of anthropogenic origin include emission from agricultural soils/fields, fossil fuel combustion/vehicular emission and biomass burning [7-12]. Of the entire atmospheric NO<sup>•</sup> sources, surface-air exchange has become increasingly important

due to its immense contribution to the atmospheric NO<sup>•</sup>. For instance, a range of 4-21 Tg N yr<sup>-1</sup> has been estimated on the global scale as the total NO<sup>•</sup> emissions from soils [13]. However, there are only a few studies on the NO<sup>•</sup> emission from the surface of natural waters [1,14].

Reaction of NO<sup>•</sup> with oxygen in solution to yield NO<sub>2</sub> has been mentioned as a route for the consumption of the radical in aqueous solution [15]. Also, NO<sup>•</sup> reaction with proteins containing transition metals has been reported [16]. However, the major sink(s) of NO<sup>•</sup> in seawater is elusive up till now. While most of the reactive oxygen species (ROS) are water-soluble, NO<sup>•</sup> has low solubility and stability to self-reaction. Hence, NO<sup>•</sup> can diffuse through nitrite rich-seawater surface. Therefore, Zafiriou et al. suggested seawater as a source of atmospheric NO<sup>•</sup> in the daytime [2]. This makes the study of NO<sup>•</sup> at the marine-atmosphere layer of immense environmental significance since the presence of NO<sup>•</sup> (a member of the NO<sub>x</sub>, NO<sub>x</sub> = NO<sup>•</sup> + NO<sub>2</sub>) in the atmosphere could contribute to photochemical smog, acid rain, green-house effect, etc. For the first time, the measurement of NO<sup>•</sup> efflux from the central equatorial Pacific surface was reported [1]. Similarly, Xue et al. measured the efflux of NO<sup>•</sup> from the surface seawater of Jiaozhou Bay and adjacent waters [14]. Air-sea exchange of

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gases is a primary link between the chemistry of the ocean and atmosphere and this could influence their chemical compositions [17]. Studies by Ridley et al. showed that NO<sup>\*</sup> concentration typical of marine boundary layer and mid-troposphere could induce ozone depletion as follows [18]:



Olasehinde et al. in the pioneer study of photochemical production of NO<sup>\*</sup> in the Seto Inland Sea of Japan and reported the possibility of NO<sup>\*</sup> efflux from the sea to the atmosphere [4]. In this study, a further scientific research was undertaken to confirm this hypothesis. Hence, measurement of photochemical production of NO<sup>\*</sup> and its steady-state concentration in the surface of Seto Inland seawater, and the atmospheric NO<sup>\*</sup> concentration over the sea during the daytime were carried out during the sea cruises in September, 2013 and June, 2014. By appropriate calculations, the direction and amount of daytime NO<sup>\*</sup> flux at the sea-atmosphere boundary were determined.

## Materials and Methods

### Seawater sampling

Seawater samples were collected in September, 2013 and June, 2014 during the Hiroshima University's Toyoshio-maru sea cruises with the aid of Niskin sampling bottles and a Sea-Bird CTD carousel multi-sampling system (SBE-9Pplus, General Oceanic Inc., USA). Figure shows detailed sampling points on the sea. The samples were filtered with pre-combusted glass fiber (Advantec, 0.45 μm) and stored in amber glass bottles at 4°C in the dark (Figure 1).

### Photochemical analysis of NO<sup>\*</sup> in the seawater

The photoformation rate, total scavenging rate constant and the steady-state concentrations of the NO<sup>\*</sup> produced in the seawater under solar irradiation were measured in the laboratory according to the method by [3]. Detailed descriptions of the solar simulator and HPLC used have been described elsewhere [3,19]. All NO<sup>\*</sup> photochemical data were normalized to a 2-nitrobenzaldehyde (2-NB) degradation rate of 0.0093 s<sup>-1</sup> as determined at noon under clear sky conditions in Higashi-Hiroshima in May, 1998 [20].

### Air sampling and atmospheric NO<sup>\*</sup> measurement

The atmospheric NO<sup>\*</sup> concentration in the air samples over the Seto Inland Sea were measured during daytime at about 10 m above the sea surface as shown in Figure 1. The air samples were collected through a Teflon tubing connected to a chemiluminescence NO<sup>\*</sup>-NO<sub>2</sub>-NO<sub>x</sub> Analyzer (Model 4S, Thermo Environment Instrument, Inc., USA), which measured the atmospheric NO<sup>\*</sup> concentration. The sampling tubing was mounted to the body of the research ship such that its opening (outlet) for the air sampling was placed far away from the ship chimney and against the direction of the ship movement. Only the atmospheric NO<sup>\*</sup> data obtained when the ship was in motion were used in this study. This would ensure that interference due to NO<sup>\*</sup> pollutant from the ship chimney was excluded from the atmospheric NO<sup>\*</sup> data as much as possible. The air samples were

filtered by PTFE 47 mm size filters (Advantec, Japan) attached to both ends of the tubing. The atmospheric NO<sup>\*</sup> concentrations (ppbv) above the seawater were measured at 5 min intervals.

### Other measurements in the seawater

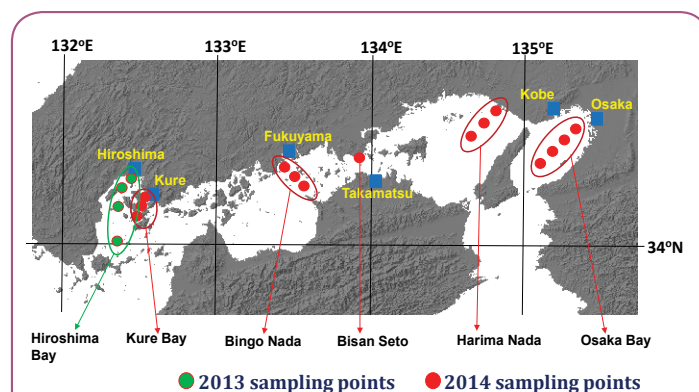
Nitrite concentrations in the seawater samples were analysed by diazotization measured at 540 nm using a spectrophotometer, while nitrate concentrations were measured according to the method developed by Zhang et al. [21]. Dissolved organic carbon (DOC) concentration was determined using a TOC-VCSH Analyzer.

## Results and Discussion

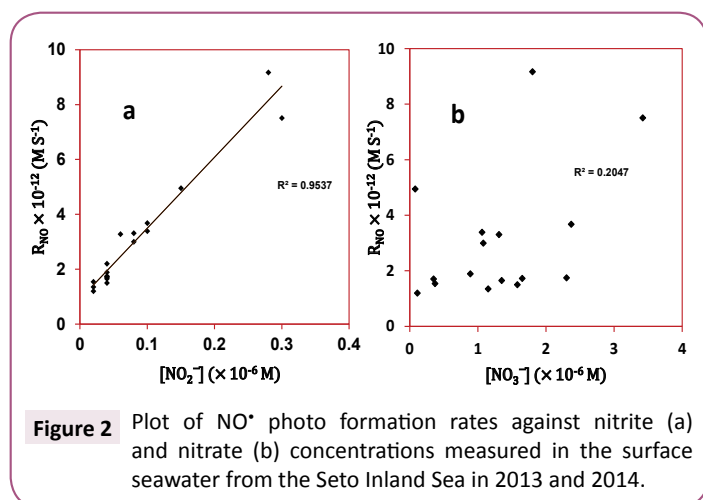
### NO<sup>\*</sup> measurement in the seawater

There were photo formation of NO<sup>\*</sup> in all the locations in the surface seawater from the Seto Inland Sea. The rates of NO<sup>\*</sup> photo formation ranged from 1.4 to 9.17 pM s<sup>-1</sup> as measured in Bingo Nada and Osaka Bay, respectively. The photo formation rates increased as the measured nitrite concentration increased, indicating nitrite as the major NO<sup>\*</sup> source according to previous studies [2-4]. This explains the variations in the measured photo formation rates of NO<sup>\*</sup> between Bingo Nada (the lowest, [NO<sub>2</sub><sup>-</sup>]=0.02 μM) and Osaka Bay (the highest, [NO<sub>2</sub><sup>-</sup>]=0.28 μM) as shown in Tables 1 and 2. Though a little lower, these results are consistent with the previous measurements in the sea surface. In the previous study, the highest nitrite concentration of ~2 μM was measured at Osaka Bay, while the lowest (~0.4 μM) was measured in Bingo Nada [4]. This, almost certainly, was responsible for the higher NO<sup>\*</sup> photo formation rates (8.7-38.8 pM s<sup>-1</sup>) in the previous study. The relatively higher nitrite concentration in Osaka Bay than all other locations in both the current and previous studies showed the vulnerability of this location to pollutions due to higher anthropogenic activities in the highly populated Osaka city (Tables 1 and 2 and Figure 2).

The total scavenging rate constants of NO<sup>\*</sup> were not considerably different, ranging 0.08-0.56 s<sup>-1</sup> across the sea surface. This gave calculated range of 3.2-41 pM NO<sup>\*</sup> steady-state concentrations with lifetime of 1.8-12.5 s during photochemical processes in the sea. The comparison of NO<sup>\*</sup> data in this study with those reported in literatures for surface waters showed good consistency (Tables 1 and 3).



**Figure 1** Sea water sampling stations in the Seto Inland Sea during the sea cruises of 2013 and 2014.



### Atmospheric NO\* measurement and flux calculation

The atmospheric NO\* concentrations measured over the Seto Inland Sea are presented in table. Zafiriou and McFarland first showed the transport of NO\* from the central equatorial Pacific, while Zacharia and Deen published the solubility of NO\* in water at 25°C to be 1.94 mM atm<sup>-1</sup> [1]. The average atmospheric NO\* concentrations measured in the six locations were in the range of 0.4-0.75 ppbv (16 ≥ n ≤ 85 in each location, n=number of measurements). These values were used in the NO\* flux calculations. To determine the flux of NO\* at the sea-air boundary (F<sub>NO\*</sub>), equations 3-5 were applied [21,22] (**Table 4**):

$$F_{NO^*} (\text{mol m}^{-2} \text{s}^{-1}) = K_L (C_{\text{sea}} - K_H p_{NO^*}) \times 1000 \quad (3)$$

Where  $K_L$  = liquid phase transfer velocity (m s<sup>-1</sup>),  $C_{\text{sea}}$  = NO\* steady-state concentration in the sea surface (mol L<sup>-1</sup>),  $K_H$  = Henry's constant for NO\* (1.9 × 10<sup>-3</sup> mol L<sup>-1</sup> atm<sup>-1</sup>) and  $p_{NO^*}$  = Partial pressure of NO\* (atm).  $K_L$  has been defined by Wanninkhof as follows [23]:

$$K_L = (2.778 \times 10^{-6}) \times (0.31 U^2 (Sc/660)^{-1/2}) \quad (4)$$

$$Sc = \mu/D \quad (5)$$

Where  $U$  and  $Sc$  are the wind speed and the Schmidt number, respectively. The  $\mu$  and  $D$  are kinematic viscosity of seawater (0.994 × 10<sup>-6</sup> m<sup>2</sup> s<sup>-1</sup>) [24] and diffusion coefficient of NO\* in seawater (3.07 × 10<sup>-9</sup> m<sup>2</sup> s<sup>-1</sup>) [25], respectively.

The average wind speeds in each location measured by the automatic weather observation instrument (Nippon Electric Instrument, Inc., Japan) attached to the ship during the cruise, were in the range of 2.0-3.5 m s<sup>-1</sup>. The average wind speed over the six locations was ~3.2 m s<sup>-1</sup>. In the six locations studied in the years 2013 and 2014, the average NO\* concentration measured in the Seto Inland Sea surface was 1.9 × 10<sup>-11</sup> mol L<sup>-1</sup>, corresponding to  $p_{NO^*}$  (sea) of 9.87 × 10<sup>-9</sup> atm. Also, the average atmospheric NO\* ( $p_{NO^*}$ ) over the sea during the daytime was 5.2 × 10<sup>-10</sup> atm. Therefore, the average NO\* efflux from the sea to the atmosphere estimated in this study was 0.22 pmol m<sup>-2</sup> s<sup>-1</sup>. This is consistent with 2.16 and 10.9 pmol m<sup>-2</sup> s<sup>-1</sup> reported as the daytime NO\* flux at the central equatorial Pacific-atmosphere and Jiaozhou Bay-atmosphere, respectively [1,14]. It should be noted that the NO\* concentration measured in the sea surface was about 19 times higher than the atmospheric NO\* concentration over the sea. This

is a little different from the study by Zafiriou and MacFarland, who reported a ~10<sup>4</sup> fold lower atmospheric NO\* concentration than that measured in the surface of equatorial Pacific [1]. This explains the difference in the rates of NO\* flux in the two studies, since the NO\* concentrations in the central equatorial Pacific (4.6 × 10<sup>-11</sup> mol L<sup>-1</sup>) was similar to that measured in the Seto Inland Sea (1.9 × 10<sup>-11</sup> mol L<sup>-1</sup>) in this study. The exceptionally high NO\* efflux (~2 order of magnitude higher) from the Jiaozhou Bay-atmosphere would be due to the relatively higher NO<sub>2</sub><sup>-</sup> concentrations (2.9-4.1 μM) in the sea surface [14] (**Table 4**).

Owing to the role of solar intensity in NO\* photochemical formation, the steady-state concentrations of NO\* in the surface seawater would exhibit diurnal variations as confirmed in a previous study [14]. Assuming 0.33 as the fraction of sunlight intensity per day (i.e., ~8 h intense solar radiation per day), an average of 2.24 × 10<sup>-6</sup> mol m<sup>-2</sup> yr<sup>-1</sup> daytime efflux of NO\* from the Seto Inland Sea was determined. Thus, the annual NO\* efflux from the Seto Inland Sea with 23,000 km<sup>2</sup> surface area to the atmosphere would be 1.54 × 10<sup>6</sup> g NO\* yr<sup>-1</sup>, corresponding to 7.2 × 10<sup>5</sup> g N yr<sup>-1</sup>. This result is about 2 orders of magnitude lower than 7.6 × 10<sup>7</sup> g N yr<sup>-1</sup> predicted by Olasehinde et al. [4]. This difference was particularly due to the correction factor for the duration of solar irradiation per day (8 h d<sup>-1</sup>) used and also due to the lower nitrite concentration in the sea surface in this study. In addition, the average wind speed in this study was ~3.2 m s<sup>-1</sup> as against 5 m s<sup>-1</sup> in the previous study [4]. The study shows that a higher mass transport of NO\* per year could be recorded in open ocean with larger surface area and other natural sea bodies with elevated nitrite concentrations. This is significant, particularly in some Asian countries surrounded by and/or divided by seawater. The higher the photochemical NO\* efflux from the surface seawater, the more plausible depletion of atmospheric ozone in the region. Consequently, this would contribute to global warming. More environmental concern will this become in countries or regions with higher natural surface water contamination.

### Contribution of \*OH towards NO\* sink in the Seto Inland Sea

The other pathway for NO\* sink in natural seawater could be its reaction(s) with other chemical species. As reported earlier by Smith and Yoshinari, NO\* concentrations in aquatic environments are likely to be controlled by both chemical and biological species [26]. One of such principal chemical species suspected during the NO\* photochemical study in the seawater was the hydroxyl radical (\*OH). This is due to the published high \*OH reaction rate constant with NO\*,  $k_{\text{OH}} \text{ NO}^* = 1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  [27]. To establish the veracity of this possibility, the \*OH photochemically produced in the seawater samples were measured as reported by Nakatani et al. [28]. The results are presented in **Table 1**. The percentage NO\* sink by the \*OH in the seawater was calculated by applying equation 6:

$$\% \text{ NO}^* \text{ sink} = (k[\text{*OH}]_{\text{ss}} / \Sigma Ks[S]) \times 100 \quad (6)$$

Where  $k$  and  $[\text{*OH}]_{\text{ss}}$  are the \*OH reaction rate constant with NO\* and \*OH steady-state concentration in the seawater, respectively,  $\Sigma Ks[S]$  is the total scavenging rate constant of NO\* in the seawater. The average \*OH steady-state concentrations and total NO\*

**Table 1** NO<sup>\*</sup> and <sup>\*</sup>OH measurements in surface seawater from the Seto Inland Sea.

Measurements	Location						
	Hiroshima Bay (n=4)	Kure Bay (n=3)	Bingo Nada (n=3)	Bisan Seto (n=1)	Harima Nada (n=3)	Osaka Bay (n=4)	
NO <sup>*</sup>	R <sub>x</sub> (pM/s)	4.5 (2.2-7.0)	1.7 (1.4-1.9)	1.6 (1.4-1.8)	3.7	1.8 (1.8-1.9)	4.8 (3.2-9.2)
	Σk <sub>s</sub> [S] (s <sup>-1</sup> )	0.3 (0.1-0.5)	0.2 (0.1-0.3)	0.2 (0.1-0.5)	0.1	0.4 (0.2-0.6)	0.2 (0.1-0.3)
	Lifetime (s)	4.6 (2.0-8.3)	4.9 (3.5-7.1)	7.4 (2.0-13)	9.7	3.2 (1.8-4.8)	7.4 (3.6-11)
	[X] <sub>ss</sub> (pM)	21 (4.4-33)	8.5 (4.9-13)	11 (3.5-18)	36	5.9 (3.2-8.8)	30 (16-41)
<sup>*</sup> OH	R <sub>x</sub> (pM/s)	21 (15-34)	12 (9.9-14)	8.8 (6.3-10)	13	9.1 (7.7-11)	16 (12-20)
	Σk <sub>s</sub> [S] (× 10 <sup>6</sup> s <sup>-1</sup> )	4.2 (1.3-6.1)	3.7 (1.8-5.8)	3.3 (1.4-5.4)	9.0	2.6 (0.9-5.0)	5.4 (3.6-7.9)
	Lifetime (μs)	0.4 (0.2-0.8)	0.3 (0.2-0.6)	0.4 (0.7-1.8)	0.1	0.6 (0.2-1.1)	0.2 (0.1-0.3)
	[X] <sub>ss</sub> (× 10 <sup>-18</sup> M)	9.4 (2.5-27)	3.9 (2.2-5.6)	3.7 (1.9-7.2)	1.4	5.1 (1.8-8.2)	3.9 (1.5-6.4)

X=NO<sup>\*</sup> or <sup>\*</sup>OH, R<sub>x</sub>=photo formation rate, Σk<sub>s</sub>[S]=total scavenging rate constant of each radical, [X]<sub>ss</sub>=steady-state concentration of each radical

**Table 2** Concentrations of NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> and dissolved organic carbon (DOC) in the Seto Inland Sea surface.

Station	Number of samples	NO <sub>2</sub> <sup>-</sup> (μM)	NO <sub>3</sub> <sup>-</sup> (μM)	DOC (μM C)
Hiroshima Bay	4	0.14 (0.04-0.3)	1.75 (nd-3.42)	107 (103-111)
Kure Bay	3	0.03 (0.02-0.04)	1.27 (0.35-2.3)	86 (79-91)
Bingo Nada	3	0.03 (0.02-0.04)	0.71 (0.11-2.3)	91 (85-97)
Bisan-Seto	1	0.10	2.37	85
Harima Nada	3	0.04 (0.04-0.04)	1.27 (0.89-1.58)	94 (86-102)
Osaka Bay	4	0.14 (0.08-0.28)	1.31 (1.06-1.8)	94 (84-106)

**Table 3** Comparative results of NO<sup>\*</sup> measurements in surface waters.

Location	Photoformation rate (pM s <sup>-1</sup> )	Steady-state concentration (× 10 <sup>-11</sup> M)	Lifetime (s)	References
Seto Inland Sea	1.4-9.17	0.3-4.1	1.8-12.5	This Study
Seto Inland Sea	8.7-38.8	2.4-32	3-20	Olasehinde et al. [4]
Central Equatorial Pacific	≥ 0.4-1.2	2.3-7.3	28-216	Zafiriou and McFarland [1]
Kurose River	1-3540	0.02-68.5	0.05-1.3	Anifowose et al. [19]

**Table 4** Atmospheric NO<sup>\*</sup> concentration, wind speed, calculated liquid phase transfer velocity and flux of NO<sup>\*</sup> at the Seto Inland sea-atmosphere boundary.

Measurement	Hiroshima Bay	Kure Bay	Bingo nada	Bisan Seto	Harima nada	Osaka Bay
[NO <sup>*</sup> ] <sub>atm</sub> (ppbv)	0.44 (0.1-0.9)	0.48 (0.1-1.4)	0.40 (nd-1.5)	0.40 (nd-1.5)	0.75 (0.2-1.3)	0.66 (0.1-1.4)
Average [NO <sup>*</sup> ] <sub>atm</sub> (× 10 <sup>-10</sup> mol m <sup>-3</sup> )	8.4	9.1	7.6	7.6	14.3	12.5
Wind speed (m s <sup>-1</sup> )	2.0 (1.1-2.9)	3.2 (0.7-5.9)	3.5 (2.2-4.3)	3.5 (2.2-4.3)	3.4 (2.0-5.8)	3.1 (1.7-4.4)
Average K <sub>L</sub> (× 10 <sup>-5</sup> m s <sup>-1</sup> )	0.5	1.3	1.5	1.5	1.5	1.2
NO <sup>*</sup> flux (× 10 <sup>-12</sup> mol m <sup>-2</sup> s <sup>-1</sup> )	0.10	0.10	0.15	0.53	0.07	0.34

[NO<sup>\*</sup>]<sub>atm</sub>=Atmospheric NO<sup>\*</sup> concentration, 16 ≥ n ≤ 85 in each location (n=number of measurements), K<sub>L</sub>=liquid phase transfer velocity of NO<sup>\*</sup> as defined in the text

scavenging rate constant measured in the surface seawater from Hiroshima Bay in 2013 were 9.4 × 10<sup>-18</sup> M and 0.28 s<sup>-1</sup>, respectively. Similarly, 3.9 × 10<sup>-18</sup> M and 0.23 s<sup>-1</sup> were the average <sup>\*</sup>OH steady-state concentration and total NO<sup>\*</sup> scavenging rate constant measured in the Seto Inland surface seawater in 2014. Using these values, the average calculated sink of NO<sup>\*</sup> by its reaction with the photo formed <sup>\*</sup>OH were 0.00003% and 0.00002% for the 2013 and 2014 samples, respectively. These consumptions are quite low and negligible, indicating that <sup>\*</sup>OH is not a major NO<sup>\*</sup> sink in the sunlit seawater. This is majorly due to the low <sup>\*</sup>OH

concentrations, notwithstanding its high reaction rate constant with NO<sup>\*</sup>. Hence, one of the pathways to NO<sup>\*</sup> loss on the sea surface could be its efflux to the atmosphere as experimentally established in the previous section.

## Conclusion

This study confirmed nitrite as the major source of NO<sup>\*</sup> generated by photochemical reaction in the sea. There was transport of NO<sup>\*</sup> from the Seto Inland sea to the atmosphere during the daytime. Nitrite concentration at the sea surface, wind speed and ambient

atmospheric  $\text{NO}^*$  concentration are important factors that control  $\text{NO}^*$  flux at the sea-atmosphere boundary. And since  $\text{NO}^*$  steady-state concentrations in the sea were low (even during the daytime), it is therefore expected that air-sea  $\text{NO}^*$  transport would prevail during the night as photolysis of seawater nitrite would be practically impossible. Contribution to the atmospheric  $\text{NO}^*$  via sea-to-air efflux would increase the production of nitrogen (IV) oxide in the air following  $\text{NO}^*$  reactions with  $\text{O}_3$  or  $\text{RO}_2^*$ . The consequent atmospheric chain reactions involve interconversion of  $\text{NO}^*$  and  $\text{NO}_2$ , oxidation of hydrocarbons and formations of reactive intermediates, especially  $^*\text{OH}$ . Similarly, the reaction of  $\text{NO}_2$  with atmospheric hydrocarbon free radicals produces

peroxyacetyl nitrates (PAN) and aldehydes. PAN is powerful respiratory and eye irritants present in smoggy atmosphere. Hence, smog formation in the air at the sea-air boundary could have part of its direct source from  $\text{NO}^*$  efflux from the sea and the consequent chain reactions involving atmospheric  $\text{NO}^*$ .

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