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# The Aqueous Phase Yield Of Alkyl Nitrates From Roo+No: Implications For Photochemical Production In Seawater

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## Comments

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# The aqueous phase yield of alkyl nitrates from ROO + NO: Implications for photochemical production in seawater

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[1] Alkyl nitrates have been observed in remote oceanic regions of the troposphere and in the surface ocean. The mechanism for their production in the oceans is not known. A likely source is the reaction of ROO + NO (where R is an alkyl group). Steady-state laboratory experiments show that alkyl nitrates are produced in the aqueous phase via this reaction, with branching ratios of 0.23 ± 0.04, 0.67 ± 0.03, and 0.71 ± 0.04 for methyl, ethyl, and propyl nitrate respectively. The branching ratios in aqueous solution are significantly higher than in the gas phase. Irradiation of surface seawaters yield rates of alkyl nitrate production on the order of $10^{-18}$ mol $cm^{-3}$ $s^{-1}$, suggesting that the reaction of ROO and NO is an important source of alkyl nitrates in seawater. *INDEX TERMS:* 4852 Oceanography: Biological and Chemical: Photochemistry; 4820 Oceanography: Biological and Chemical: Gases; 4850 Oceanography: Biological and Chemical: Organic marine chemistry; 0312 Atmospheric Composition and Structure: Air/sea constituent fluxes (3339, 4504); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry. **Citation:** Dahl, E. E., E. S. Saltzman, and W. J. de Bruyn, The aqueous phase yield of alkyl nitrates from ROO + NO: Implications for photochemical production in seawater, *Geophys. Res. Lett.*, *30*(6), 1271, doi:10.1029/2002GL016811, 2003.

## 1. Introduction

[2] Tropospheric ozone is an important greenhouse gas and hydroxyl radical (OH) precursor. Ozone formation and the distribution of ozone in remote areas are controlled by the distribution and speciation of reactive nitrogen (NOy) in the troposphere. Alkyl nitrates, which can make up a significant fraction of reactive nitrogen in remote areas, are believed to have a natural oceanic source.

[3] The SAGA-3 expedition in the equatorial Pacific produced the first evidence that alkyl nitrates have an oceanic source [*Atlas et al.*, 1993]. Maxima in ethyl and isopropyl nitrate, correlated with bromoform and clearly associated with the pattern of equatorial upwelling, were observed over the equatorial Pacific Ocean [*Atlas et al.*, 1993; *Thompson et al.*, 1993]. These maxima could neither be attributed to long-range transport nor to in situ atmospheric production suggesting that the alkyl nitrates are produced in the oceans [*Atlas et al.*, 1993; *Thompson et al.*, 1993]. *Blake et al.* [1999] and *Fischer et al.* [2002] have made similar atmospheric observations. *Chuck et al.* [2002] measured alkyl nitrates in Atlantic Ocean surface waters and suggest a possible biogenic source.

[4] The formation of alkyl nitrates in the polluted atmosphere is initiated by the oxidation of alkanes via:

$$RH + OH \rightarrow R + \mathrm{H_2O} \tag{1}$$

$$R + O_2 \rightarrow ROO \tag{2}$$

Where RH is an alkane. The resultant peroxy radical can react with nitric oxide to produce an alkyl nitrate or nitrogen dioxide [*Darnell et al.*, 1976].

$$ROO + NO \rightarrow RONO_2 \tag{3a}$$

$$\rightarrow RO + NO_2 \tag{3b}$$

The branching ratio for the formation of alkyl nitrate [$k_{3a}/(k_{3a} + k_{3b})$] is dependent on the carbon number of the alkane, with high molecular weight favoring alkyl nitrate formation [*Atkinson et al.*, 1983]. The branching ratio is also temperature dependent, with low temperatures favoring alkyl nitrate formation [*Atkinson et al.*, 1983]. Yields of $C_1-C_3$ alkyl nitrates under atmospheric conditions are low (<3%) [*Atkinson et al.*, 1982].

[5] Similar chemistry may occur in seawater where there are natural sources of both NO and ROO. The photolysis of nitrite produces NO and OH as the primary products [*Zafiriou and True*, 1979].

$$NO_2^- \xrightarrow{h\upsilon, H_2O} NO + OH + OH^- \tag{4}$$

Alkyl peroxy radicals are produced photochemically from CDOM (colored dissolved organic matter) by intramolecular H-atom abstractions, electron transfer reactions, and homolytic bond cleavages [*Blough*, 1997; *Zhou and Mopper*, 1990; *Mill et al.*, 1980; *Faust and Hoignè*, 1987]. *Moore and Blough* [2002] recently observed the photochemical production of methyl nitrate in seawater during laboratory irradiation experiments. In their experiments, adding nitrite to seawater increased the production of methyl nitrate.

[6] In this study, laboratory experiments on synthetic solutions were carried out to determine the yield of methyl, ethyl and propyl nitrates from the aqueous phase reaction of ROO + NO. Several natural waters were also irradiated with

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**Table 1.** Reactions and Rates Used in a Model of the Nitrogen Chemistry in the Experiment

| Reaction | Rate Constant |
|---|---|
| $NO_2^- + h\upsilon + H_2O \rightarrow NO + OH + OH^-$ | $7 \times 10^{-5}\ s^{-1}$ |
| $RH + OH + O_2 \rightarrow ROO + H_2O$ | $1.4 \times 10^{9}\ M^{-1}\ s^{-1}$[a] |
| $ROO + NO \rightarrow RONO_2$ or $RO + NO_2$ | $2.8 \times 10^{9}\ M^{-1}\ s^{-1}$[b] |
| $2NO_2 + H_2O \rightarrow 2H^+ + NO_2^- + NO_3^-$ | $7 \times 10^{7}\ M^{-1}\ s^{-1}$[c] |
| $2H^+ + NO_2^- + NO_3^- \rightarrow 2NO_2 + H_2O$ | $29\ M^{-3}\ s^{-1}$ |
| $NO + NO_2 + H_2O \rightarrow 2NO_2^- + 2H +$ | $3 \times 10^{-7}\ M^{-1}\ s^{-1}$[c] |
| $2NO_2^- + 2H + \rightarrow NO + NO_2 + H_2O$ | $1.8 \times 10^{-7}\ M^{-3}\ s^{-1}$ |
| $NO_3^- + h\upsilon + H_2O \rightarrow NO_2 + OH + OH^-$ | $7 \times 10^{-5}\ s^{-1}$ |
| $NO + OH \rightarrow NO_2^- + H^+$ | $2 \times 10^{10}\ M^{-1}\ s^{-1}$[d] |
| $NO_2 + h\upsilon \rightarrow NO$ | $7 \times 10^{-4}\ s^{-1}$ |
| $NO_2 + OH \rightarrow H^+ + NO_3^-$ | $4.5 \times 10^{9}\ M^{-1}\ s^{-1}$[e] |
| $2NO + 1/2O_2 + H_2O \rightarrow 2NO_2^- + 2H^+$ | $9 \times 10^{6}\ M^{-2}\ s^{-1}$[f] |

Photolysis rate constants were calculated based on the intensity of the source.

[a] *Getoff* [1989].

[b] *Padmaja and Huie* [1993].

[c] *Schwartz* [1984].

[d] *Strehlow and Wagner* [1982].

[e] *Loegager and Sehested* [1993].

[f] *Zafiriou and True* [1979].

and without nitrite additions to determine the production rate of alkyl nitrates.

## 2. Experimental

### 2.1. Yield Experiments

[7] Steady-state irradiation experiments were carried out on solutions of nitrite and alkane to determine the yield of alkyl nitrate from the aqueous phase reaction of ROO and NO. NO and OH were produced via reaction 4 and alkyl peroxy radicals were produced by H atom abstraction from the alkane by OH followed by $O_2$ oxidation as in reactions 1 and 2.

[8] In these experiments, alkane was provided in excess, relative to nitrite, and essentially all of the OH produced reacted with the alkane to yield the peroxy radical. The steady-state yield of alkyl nitrate was determined from the amount of alkyl nitrate produced relative to the loss of nitrite.

$$Percent\ Yield = \frac{\Delta[RONO_2]}{\Delta\left[NO_2^-\right]} \times 100\%$$

[9] A kinetic model was used to simulate the experimental conditions and to evaluate the results. The model included the reactions listed in Table 1. Model simulations suggest that $NO_2$ generated by reaction pathway 3b is rapidly converted to nitrate and nitrite via $NO_2$ + $NO_2$ in the presence of water. Thus approximately half of the nitrite lost via pathway 3b is regenerated, and the measured yields therefore underestimate the true branching ratio. The branching ratio $[k_{3a}/(k_{3a} + k_{3b})]$ is obtained experimentally using the expression:

$$Branching\ Ratio = \frac{\Delta[RONO_2]}{\Delta[RONO_2] + 2{*}\Delta\left[NO_3^-\right]}$$

This interpretation assumes that alkyl nitrates are not formed from the reaction $NO_2$ + RO (i.e. the reverse reaction of 3b). *Atkinson et al.* [1983] argued on energetic grounds that in the gas phase this reaction channel is not important. However, this has not been studied in the aqueous phase.

[10] The reported branching ratios include an estimate of all known sources of random error involved in the experimental and analytical procedures, reported as $1\sigma$. Possible systematic errors may include unaccounted for losses of NO (such as on the cell walls) that do not result in nitrite reformation. Such errors are believed to be minor because a mass balance was obtained between the nitrite concentration prior to irradiation, and the sum of nitrite, nitrate, and alkyl nitrates after irradiation.

### 2.2. Experimental Apparatus and Procedures

[11] Irradiations were carried out using a 1000-Watt xenon arc lamp, with a copper sulfate solution IR filter, and a 300–400 nm bandpass interference filter ($T_{max}$ = 70% at 360 nm; $\lambda_{max\ abs}$ $NO_2^-$ = 350 nm). The experimental solution was irradiated in a thermostatted, water-jacketed quartz cell for 1–2 hours. The intensity of the light entering the cell was approximately 4.5 times that of natural sunlight at the same wavelengths. The oxygen concentration in the experimental solutions was reduced to below 1% air saturation to minimize the rate of reaction of NO + $O_2$.

[12] Solutions were analyzed for nitrite and alkyl nitrates both prior to and after irradiation. Nitrite and nitrate were analyzed using a spectrophotometric method [*Grasshoff*, 1976]. Alkyl nitrates were detected using purge and trap gas chromatography with mass spectrometric detection. Ethyl, isopropyl, and n-propyl nitrate standards were prepared from serial dilution of the pure liquids. Methyl nitrate was standardized relative to isopropyl nitrate by serial dilution of a methyl/isopropyl nitrate mixture. NMR was used to determine the methyl/isopropyl nitrate ratio in the mixture.

### 2.3. Natural Water Irradiations

[13] Several Pacific coastal surface water samples were collected near the University of California at Irvine and one oligotrophic surface ocean water sample was collected aboard ship at 35°N 123°W (Station M) [*Smith and Druffel*, 1998]. The samples were analyzed for nitrite, nitrate, and alkyl nitrates prior to irradiation. The fluorescence (excitation 350 nm, emission 360–600 nm) of each sample was determined as a measured of the relative CDOM levels [*Smart et al.*, 1976]. Irradiations were carried out in the laboratory on unfiltered and filtered aliquots of the seawater samples. If the nitrite concentration of the water was less than 1 $\mu$M, unfiltered and filtered aliquots were also irradiated with addition of nitrite. Following irradiation, the solutions were reanalyzed for alkyl nitrates, and the alkyl nitrate production rate was calculated. Methyl nitrate was not determined in these experiments because of co-elution with unknown peaks in seawater under the chromatographic conditions used. A sunlight-normalized formation rate was obtained by dividing the measured rates by the intensity of the light source relative to sunlight at solar noon at the equator.

## 3. Results and Discussion

### 3.1. Experimental Results-Yield Experiments

[14] The branching ratios were calculated from the observed yields, with correction for recycling of nitrate to nitrite, as described above. The mean branching ratio determined for methyl nitrate was 0.23 ± 0.04. This is significantly lower than those of ethyl and propyl nitrate, which are 0.67 ± 0.03 and 0.71 ± 0.04, respectively. The

**Table 2.** The Rates of Formation of Ethyl (EtNO3), Isopropyl (i-PrNO3), and N-Propyl (n-PrNO3) Nitrate Normalized to Sunlight Intensity for Water Samples Irradiated in the Laboratory

| | | | Production Rate ($10^{-18}$ mol cm$^{-3}$ s$^{-1}$) | | |
|---|---|---|---|---|---|
| Water | Filtered (Yes/No) | Nitrite ($10^{-6}$ M) | EtNO3 | i-PrNO3 | n-PrNO3 |
| Sheriff's Station | No | 1.5 | 8.4 | 5.1 | 1.5 |
| | Yes | 1.5 | 12.0 | 7.1 | 2.1 |
| Newport Pier | No | 0.1 | 0.4 | 0.2 | 0.6 |
| | No | 1.0 | 6.5 | 2.8 | 1.3 |
| | Yes | 0.1 | 0.4 | 0.2 | 0.6 |
| | Yes | 1.0 | 5.8 | 2.6 | 1.5 |
| Laguna Beach | No | 0.2 | 1.0 | 0.5 | 0.1 |
| | No | 1.2 | 8.2 | 4.0 | 1.0 |
| | Yes | 0.2 | 1.1 | 0.7 | 0.2 |
| | Yes | 1.1 | 5.1 | 1.9 | 0.5 |
| Open Ocean | Yes | 0.0 | 0.2 | 0.2 | 0.1 |
| | Yes | 1.2 | 6.8 | 3.8 | 1.0 |

Samples collected at Newport Pier, Laguna Beach, and the open ocean were irradiated with and without the addition of nitrite. The standard deviations (1s) of the production rates were 10%.

mean branching ratios of ethyl and propyl nitrate are not different from one another, within the uncertainty of the measurements. The branching ratios for all three alkyl nitrates exhibit no temperature-dependence over the measured range of 5–30°C.

[15] The ratio of formation of n-propyl to isopropyl nitrate in the propane experiments was 0.52 ± 0.06. The interpretation of this ratio is complicated by the fact that it reflects both the relative rates of H abstraction at the primary and secondary carbons of propane, and the branching ratio for alkyl nitrate formation at the resulting n-propyl and isopropyl peroxy radicals. *Kwok and Atkinson* [1995] used kinetic gas phase data to estimate the relative reactivity of various H-atoms on alkanes toward abstraction by OH. If this relative reactivity applies to the aqueous phase, the ratio of n-propyl and isopropyl peroxy radicals in these experiments should be 0.36. This would imply that that branching ratio for isopropyl nitrate formation is 0.63, lower than that of the n-propyl nitrate (0.94). This result is quite different from those of *Atkinson et al.* [1982] in the gas phase, which suggested that n-propyl nitrate has a lower branching ratio than isopropyl nitrate. Experimental work is needed in order to determine the relative reactivity of OH toward various H-atoms on alkanes in the aqueous phase.

[16] For the analogous gas phase reactions the ethyl and propyl nitrate yields are 1% and 2% respectively, significantly lower than the aqueous phase yields measured here. As shown by *Atkinson et al.* [1982, 1983, 1987] alkyl nitrates are produced in the gas phase (at least partly) via a chemical activation unimolecular isomerization mechanism, with the yield increasing at higher pressures as expected from standard Lindemann-Hinshelwood unimolecular reaction theory. The low yields measured by *Atkinson et al.* [1982, 1983, 1987] are not in the high-pressure limit and are expected to be higher at higher pressures and in the condensed phase.

### 3.2. Experimental Results-Natural Water Irradiations

[17] Table 2 lists the production rates of alkyl nitrate production for surface water samples, normalized to solar noon at the equator. The rates ranged from 0.2–12.0 × $10^{-18}$ mol cm$^{-3}$ s$^{-1}$ for ethyl nitrate, 0.2–7.1 × $10^{-18}$ mol cm$^{-3}$ s$^{-1}$ for isopropyl nitrate, and 0.1–2.0 × $10^{-18}$ mol cm$^{-3}$ s$^{-1}$ for n-propyl nitrate.

[18] The ratios of the production rates of the alkyl nitrates formed relative to one another were relatively constant among the waters studied, with ethyl nitrate formation rates significantly larger than those of the propyl nitrates. Isopropyl nitrate formed at a rate approximately 3–4 times that of n-propyl nitrate. This is significantly different from the relative amounts of propyl nitrates formed in the yield experiments. This indicates that the OH-initiated oxidation of alkanes dissolved in seawater is probably not the principle source of alkyl peroxy radicals, and suggests that other pathways involving photolysis of CDOM are responsible. The formation of alkyl nitrates can potentially serve as a tracer for the formation rate and speciation of carbon-centered radicals in seawater.

[19] The formation rate of alkyl nitrates is related to nitrite concentration, as might be expected since nitrite photolysis is the primary source of NO in seawater. The alkyl nitrate production rate in the Newport Pier and Laguna Beach waters was increased significantly by addition of nitrite prior to irradiation (Table 2). A more detailed study of the nitrite dependence of alkyl nitrate formation was carried out using the filtered open ocean water sample. This water sample originally had a nitrite level of 4 × $10^{-8}$ M and production rates of 2.0 ± 0.1 × $10^{-19}$, 1.5 ± 0.5 × $10^{-19}$, and 0.5 ± 0.2 × $10^{-19}$ mol cm$^{-3}$ s$^{-1}$ for ethyl, isopropyl, and n-propyl nitrate respectively. Increasing the nitrite concentration to 1.2 × $10^{-6}$ M increased the production rate of ethyl, isopropyl, and n-propyl nitrate to 6.8 ± 1.5 × $10^{-18}$, 3.8 ± 0.2 × $10^{-18}$, and 1.0 ± 0.2 × $10^{-18}$ mol cm$^{-3}$ s$^{-1}$. Alkyl nitrate production appears to have a logarithmic dependence on nitrite concentration (Figure 1). This suggests alkyl nitrate production may be nitrite (NO) limited at low nitrite levels. At higher nitrite concentrations,

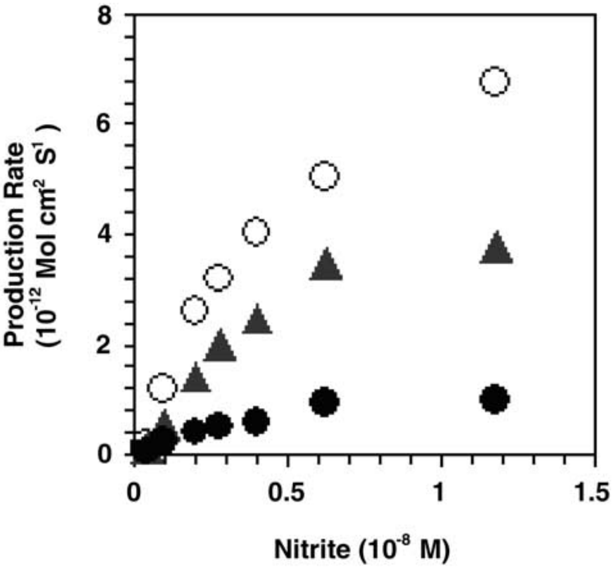

**Figure 1.** The formation rates of ethyl, isopropyl, and n-propyl nitrate as a function of nitrite in open ocean water. This sample was collected from the surface ocean at 35°N 123°W and represents oligotrophic ocean waters. ○ ethyl nitrate, ▲ isopropyl nitrate, ● n-propyl nitrate.

the production of alkyl peroxy radicals may become rate limiting.

[20] The alkyl nitrate production rate in natural waters should also reflect the production rate of the precursor peroxy radicals, and should therefore also be related to CDOM concentrations and/or reactivity. In these experiments, fluorescence was measured to determine the relative abundance of CDOM. However, in these waters (as in many natural waters) nitrite and CDOM levels strongly co-vary. Differentiating between the effects of nitrite and CDOM requires a detailed understanding of the nitrite dependence of alkyl nitrate production. Further studies to examine these relationships are in progress.

### 3.3. Discussion

[21] The aqueous reaction of ROO + NO appears to be an efficient source of alkyl nitrates in the aqueous phase, suggesting that this mechanism is a likely source of alkyl nitrates in seawater. As stated earlier, there are natural sources of alkyl peroxy radicals and NO in seawater. The results of this study do not exclude the possibility of other production mechanisms for alkyl nitrates in seawater.

[22] The rates observed in the natural water experiments suggest that photochemical production is environmentally significant. *Chuck* [2002] reported mixed layer alkyl nitrate concentrations in the Atlantic Ocean ranging from $1.7-7.7 \times 10^{-15}$ mol cm$^{-3}$ for ethyl nitrate. For a station just north of the equator, *Chuck* [2002] reported a mixed layer concentration for ethyl nitrate of $\sim 3.3 \times 10^{-15}$ mol cm$^{-3}$. The ethyl nitrate production rate in our open ocean seawater sample, normalized to equatorial sunlight intensity, was $2 \times 10^{-19}$ mol cm$^{-3}$ s$^{-1}$ (Table 2). Assuming that alkyl nitrate is produced photochemically in the upper 10 meters of the ocean and is vertically mixed to an average mixed layer depth of 75 m, this production rate would generate the observed mixed layer concentrations in approximately 5 hours of solar noon conditions.

[23] Based on the observations made in these experiments, alkyl nitrates can be expected to be readily formed anywhere ROO and NO radicals occur in solution. This includes fresh water bodies such as rivers and lakes and atmospheric solutions such as aerosols and cloud droplets. One would also expect alkyl nitrates to form in intracellular fluids where both alkyl peroxy and NO radicals occur [*Stamler et al.*, 1992; *Halliwell and Gutteridge*, 1989]. These studies suggest that alkyl nitrates may be useful probes for understanding the radical chemistry of natural waters and biological solutions.

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## References

Atkinson, R., S. M. Ashmann, W. P. L. Carter, and A. M. Winer, Kinetics of the gas-phase reactions of OH radicals with alkyl nitrates at 299 ± 2K, *Int. J. Chem. Kinet.*, *14*, 919–926, 1982.

Atkinson, R., W. P. L. Carter, and A. M. Winer, Effects of temperature and pressure of alkyl nitrate yields in the photo oxidations of n-pentane and n-heptane, *J. Phys. Chem.*, *87*, 2012–2018, 1983.

Atkinson, R., S. M. Ashmann, and A. M. Winer, Alkyl Nitrate formation from the reaction of a series of branched $RO_2$ radicals with NO as a function of temperature and pressure, *J. Atmos. Chem.*, *5*, 91–102, 1987.

Atlas, E., W. Pollock, J. Greenberg, and L. Heidt, Alkyl nitrates, nonmethane hydrocarbons and halocarbon gases over the equatorial Pacific Ocean during Saga 3, *J. Geophys. Res.*, *98*, 16,933–16,947, 1993.

Blake, N. J., et al., Aircraft measurements of the latitudinal, vertical, and seasonal variations of NMHCs, methyl nitrate, methyl halides, and DMS during the First Aerosol Characterization Experiment (ACE 1), *J. Geophys. Res.*, *104*, 21,803–21,817, 1999.

Blough, N. V., Photochemistry in the sea-surface micro layer, in *The Sea-Surface and Global Change*, edited by P. S. Liss and R. Duce, pp. 383–424, Cambridge Univ. Press, New York, 1997.

Chuck, A. L., Biogenic halocarbons and light alkyl nitrates in the marine environment, Ph.D. diss., Univ. of East Anglia, Norfolk, UK, 2002.

Chuck, A. L., S. M. Turner, and P. S. Liss, Direct evidence for a marine source of alkyl nitrates, *Science*, *297*, 1151–1154, 2002.

Darnell, K. R., W. P. L. Carter, A. M. Winer, A. C. Lloyd, and J. N. Pitts Jr., Importance of $RO_2$ + NO in alkyl nitrate formation from C4–C6 alkane photooxidations under simulated atmospheric condition, *J. Phys. Chem.*, *80*, 1948–1950, 1976.

Faust, B. C., and J. Hoignè, Sensitized photo oxidation of phenols by fulvic acid and in natural waters, *Environ. Sci. Technol.*, *21*, 10,957–10,964, 1987.

Fischer, R., R. Weller, H. W. Jacobi, and K. Ballschmiter, Levels and pattern of volatile organic nitrates and halocarbons in the air at Neumayer Station (70°S), Antarctic, *Chemosphere*, *48*, 981–992, 2002.

Getoff, N., Advancements of radiation induced degradation of pollutants in drinking and wastewater, *Appl. Radiat. Isot.*, *40*, 585–594, 1989.

Grasshoff, K., *Methods of Seawater Analysis*, Verlag Chemie, Weinheim, Germany, 1976.

Halliwell, B., and J. M. C. Gutteridge, *Free Radicals in Biology and Medicine*, 2nd ed., Oxford Univ. Press, New York, 1989.

Kwok, E. S. C., and R. Atkinson, Estimation of hydroxyl radical reaction rate constants for gas-phase organic compounds using a structure-reactivity relationship: An update, *Atmos. Environ.*, *29*, 1685–1695, 1995.

Loegager, T., and K. Sehested, Formations and decay of peroxynitric acid: A pulse radiolysis study, *J. Phys. Chem.*, *97*, 6664–6669, 1993.

Mill, T., D. G. Hendry, and H. Richardson, Free radical oxidants in natural waters, *Science*, *207*, 886–887, 1980.

Moore, R. M., and N. V. Blough, A marine source of methyl nitrate, *Geophys. Res. Lett.*, *29*(15), 1737, doi:10.1029/2002GL014989, 2002.

Padmaja, S., and R. E. Huie, The reaction of nitric oxide with organic peroxyl radicals, *Biochem. Biophys. Res. Commun.*, *195*, 539–544, 1993.

Schwartz, S., Gas-aqueous reactions of sulfur and nitrogen oxides in liquid-water clouds, in *$SO_2$, NO and $NO_2$ Oxidation Mechanisms: Atmospheric Considerations*, *Acid Precip. Ser.*, *3*, edited by J. G. Calvert, pp. 173–208, Butterworth-Heinemann, Woburn, Mass., 1984.

Smart, P. L., B. L. Finlayson, W. D. Rylands, and C. M. Ball, The relation of fluorescence to dissolved organic carbon in surface waters, *Water Res.*, *10*, 805–811, 1976.

Smith, K. L., and E. R. M. Druffel, Long time-series monitoring of an abyssal site in the NE Pacific: An introduction, *Deep Sea Res., Part II,45*, 573–586, 1998.

Stamler, J. S., D. J. Singel, and J. Loscalzo, Biochemistry of nitric oxide and its redox-activated forms, *Science*, *258*, 1898–1902, 1992.

Strehlow, H., and I. Wagner, Flash photolysis in aqueous nitrite solutions, *Z. Phys. Chem. Munich*, *132*, 151–160, 1982.

Thompson, A. M., et al., Ozone observations and a model of marine boundary layer photochemistry during SAGA-3, *J. Geophys. Res.*, *98*, 16,955–16,968, 1993.

Zafiriou, O. C., and M. B. True, Nitrite photolysis in seawater by sunlight, *Mar. Chem.*, *8*, 9–32, 1979.

Zhou, X., and K. Mopper, Determination of photochemically produced hydroxyl radicals in seawater and freshwater, *Mar. Chem.*, *30*, 71–88, 1990.

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