



HAL
open science

Superoxide and Nitrous Acid Production from Nitrate Photolysis Is Enhanced by Dissolved Aliphatic Organic Matter

Xinke Wang, Evan Dalton, Zachary Payne, Sébastien Perrier, M. Riva,
Jonathan Raff, C. George

► **To cite this version:**

Xinke Wang, Evan Dalton, Zachary Payne, Sébastien Perrier, M. Riva, et al.. Superoxide and Nitrous Acid Production from Nitrate Photolysis Is Enhanced by Dissolved Aliphatic Organic Matter. *Environmental Science and Technology Letters*, 2021, 8 (1), pp.53-58. 10.1021/acs.estlett.0c00806 . hal-03159673

HAL Id: hal-03159673

<https://hal.science/hal-03159673v1>

Submitted on 13 Oct 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

1 **Superoxide and nitrous acid production from nitrate photolysis is enhanced by**
2 **dissolved aliphatic organic matter**

3 Xinke Wang,^{†,#} Evan Z. Dalton,^{‡,#} Zachary C. Payne,[‡] Sebastien Perrier,[†] Matthieu Riva,[†]
4 Jonathan D. Raff,^{‡,§,*} and Christian George^{†,*}

5 [†]Univ Lyon, Université Claude Bernard Lyon 1, CNRS, IRCELYON, F-69626, Villeurbanne,
6 France.

7 [‡]Department of Chemistry, Indiana University, 800 East Kirkwood Avenue, Bloomington,
8 Indiana 47405, United States.

9 [§]O'Neill School of Public and Environmental Affairs, Indiana University, 1315 East 10th Street,
10 Bloomington, Indiana 47405, United States

11 *To whom correspondence should be addressed. Email: christian.george@ircelyon.univ-lyon1.fr,
12 jdraff@indiana.edu

13 [#]These authors contributed equally to this work

14

15 **ABSTRACT:** Nitrate anion (NO_3^-) is ubiquitous in the environment and its photochemistry
16 produces nitrous acid (HONO), a major source of tropospheric hydroxyl radical (OH). Enhanced
17 $\text{HONO}_{(g)}$ emissions have been observed from $\text{NO}_3^-_{(aq)}$ photolysis in field studies, although the
18 underlying reasons for this enhancement are debated. Here, we show that the enhancement is
19 induced by changes in secondary nitrate anion photochemistry due to dissolved aliphatic organic
20 matter (DAOM). Increased yields of superoxide radical (O_2^-) and HONO were observed when
21 NO_3^- solutions (pH 6) were photolyzed in the presence of DAOM surrogates of varying solubility.
22 An additional experiment titrated with additional DAOM showed a further increase in $\text{O}_2^-_{(aq)}$ and
23 $\text{HONO}_{(g)}$ simultaneously with decreased yields of gaseous nitric oxide (NO) and nitrogen dioxide
24 (NO_2). To our knowledge, this is the first time that superoxide was directly observed as an
25 intermediate in nitrate photolysis experiments, produced through DOAM oxidation by $\text{OH}_{(aq)}$.
26 Herein, we suggest that enhanced $\text{HONO}_{(g)}$ emissions from $\text{NO}_3^-_{(aq)}$ photolysis result from the
27 reaction of $\text{O}_2^-_{(aq)}$ with $\text{NO}_{2(aq)}$ and $\text{NO}_{(aq)}$ to respectively form peroxyxynitrate (OONO_2^-) and
28 peroxyxynitrite (OONO^-), which are precursors to nitrite (NO_2^-). Overall, this points to an important
29 role of O_2^- in aqueous aerosol chemistry, which is currently under-appreciated.

30

31 INTRODUCTION

32 Nitrate anion (NO_3^-) is a ubiquitous, photochemically-active compound in the atmospheric
33 condensed phase, surface water, and on boundary layer surfaces. The photochemistry of nitrate
34 anions has been extensively studied over the last decades due to its importance as a major source
35 of aqueous hydroxyl radical (OH).^{1,2} Several studies have shown that pH, nitrate concentration and
36 the presence of organic OH scavengers play important roles in the nitrite yield, which lead to the
37 large variations in the measured values of the quantum yield $\Phi(\text{NO}_2^-)$ from 0.2% to 4%.³⁻⁶ Benedict

38 et al.⁵ showed that $\Phi(\text{NO}_2^-)$ is constant at high pH, but decreases with decreasing pH in more acidic
39 solutions ($\text{pH} < 5$) due to $\text{HONO}_{(\text{aq})}$ loss to the gas phase⁴ or less effective scavenging of $\text{OH}_{(\text{aq})}$ by
40 bicarbonate/carbonate. Therefore, nitrite and NO_2 quantum yields must be assessed in the presence
41 of organic OH scavengers, which prevent conversion of aqueous NO_2^- and NO_2 back into NO_3^- by
42 OH radicals.^{4,7} While the influence of OH scavengers on the primary products of nitrate photolysis
43 is well established, the impact of organic matter on secondary nitrate photoproducts is poorly
44 understood.

45 Factors that affect $\text{NO}_2^-_{(\text{aq})}$ yields influence daytime $\text{HONO}_{(\text{g})}$ concentrations in the lower
46 troposphere. Photolysis of $\text{HONO}_{(\text{g})}$ is a major daytime source of $\text{OH}_{(\text{g})}$ radicals that accelerates
47 photochemical transformations leading to pollutant degradation and the formation of aerosols and
48 tropospheric ozone.⁸⁻¹⁰ Various $\text{HONO}_{(\text{g})}$ sources have now been identified, including soil bacteria
49 and fuel combustion,^{11,12} gas phase reaction between OH and NO,^{13,14} photosensitized conversion
50 of NO_2 on surfaces,^{15,16} and heterogeneous conversion of NO_2 on wet surfaces¹⁰ or soot
51 particles.^{17,18} Recent studies suggest that $\text{HONO}_{(\text{g})}$ was the major product of surface adsorbed and
52 particulate NO_3^- photolysis,¹⁹⁻²¹ which is surprising since the known aqueous phase
53 photochemistry predicts nitrite formation to be a relatively minor photolysis channel. However,
54 there is still a significant missing daytime source of $\text{HONO}_{(\text{g})}$,^{13,22} which limits the accuracy of
55 models used to predict and study air pollution and changes to the global climate system.

56 Superoxide radical (and its conjugate base HO_2) has recently been hypothesized to play a
57 role in $\text{HONO}_{(\text{g})}$ emission enhancement from nitrate photolysis in environmental systems. Scharko
58 et al. postulated the reaction between $\text{HO}_2/\text{O}_2^-_{(\text{aq})}$, formed from organic compound oxidation, and
59 $\text{NO}_{2(\text{aq})}$ is a significant pathway, up to 20%, for aqueous NO_2 to NO_2^- conversion via the
60 intermediate production and decomposition of aqueous peroxyxynitrate (OONO_2^-).⁴ However, to our

61 knowledge no studies have attempted to prove this mechanism by direct measurement of
62 HO_2/O_2^- (aq) concentrations in combination with nitrogen photoproducts during nitrate photolysis in
63 solutions with dissolved organic matter.

64 We investigate herein the yields of NO_2 (g), HONO (g) from nitrate photolysis, and provide
65 the first direct measurements of O_2^- (aq) from nitrate photochemistry in the presence and absence
66 of carboxylic acids and alcohols used to represent dissolved aliphatic organic matter (DAOM)
67 found in environmental aqueous systems. These results articulate a critical secondary mechanism
68 to explain enhanced HONO (g) emission from nitrate photolysis and suggest a key role of O_2^- (aq) and
69 DAOM in atmospheric multiphase chemistry.

70 **EXPERIMENTAL**

71 Photochemical experiments were conducted with batch reactors containing phosphate buffered
72 solutions (pH ~6) of nitrate in the presence and absence of aliphatic carboxylic acids or alcohols.
73 Static solutions were irradiated using optically filtered Hg-Xe arc lamps ($\lambda > 295$ nm). Zero air
74 was flowed through the headspace to detect HONO (g) and NO_x (g) using a long path absorption
75 photometer (QUMA, Model LOPAP-03) and chemiluminescence analyzer (CLD 88CYp),
76 respectively. Reported NO_y concentrations have not been corrected for secondary photolysis,
77 which amounted to 0.7–2% and 2–7% for HONO (g) and NO_2 (g), respectively. Potential gaseous
78 reaction interferences are listed in Table S3, although their influence is expected to be negligible.
79 In separate experiments, superoxide was quantitated *in situ* with a flow injection
80 chemiluminescence (FIC) analyzer (FeLume, Waterville Analytical; Figure S1B).²³ These samples
81 were stirred to reproducibility measure aqueous superoxide. The chemiluminescence probe, methyl
82 cypridina luciferin analog (MCLA), was used to selectively trap dissolved O_2^-/HO_2 .²⁴⁻²⁷ Additional

83 experimental details are provided in the Supplementary Information and described in detail
84 elsewhere.²⁸

85 **RESULTS AND DISCUSSION**

86 **NO₂ and HONO Production.** Experiments were conducted with 1 mM of surface-active DAOM
87 surrogates that form an organic film at the air-water interface under static conditions. Irradiation of
88 phosphate-buffered NO₃⁻ solutions with or without nonanoic acid (NNA, 1 mM, pH=5.8) or 1-
89 octanol (1 mM, pH=6.0) produced statistically similar concentrations of gaseous NO₂ (Figures 1A
90 and S3A). Integration of these data, after baseline subtraction of average pre-photolysis
91 concentrations, reveals a 9% enhancement in NO_{2(g)} emission rate in the presence of NNA, whereas
92 1-octanol caused an 8% decrease in NO_{2(g)} emission rate (Table S1). This supports observations by
93 Reeser et al²⁹ who showed that the NO_{2(g)} yield from static nitrate photolysis experiments is
94 sensitive to organic matter: 1-octanol lowered NO₂ emission relative to pure nitrate solutions, while
95 octanoic acid increased NO_{2(g)} emission. Reeser and coworkers suggest this is due to organic
96 surface films affecting NO_{2(g)} partitioning, although our results indicate that secondary
97 photochemistry also plays a role. Specifically, while 1-octanol and nonanoic acid are both effective
98 OH scavengers, 1-octanol leads to two times more O₂⁻(aq) production than does nonanoic acid
99 (Figure S4). Both HO_{x(aq)} species react quickly with NO_{2(aq)}, although in the case of the 1-octanol
100 system, higher O₂⁻(aq) concentrations result in a lower steady-state NO_{2(g)} concentration.

101 As shown in Figure 1B, photochemical HONO_(g) production from nitrate solutions
102 containing surface-active organics is enhanced relative to pure nitrate solutions. Nitrous acid
103 formed in pure NO₃⁻ solutions reaches a steady-state, in contrast to the faster rate of HONO
104 accumulation in the presence of the OH scavengers. For example, between 20–75 min, the HONO_(g)

105 emission rate for solutions containing NNA and 1-octanol is a factor of 2.4 and 3.2 higher,
106 respectively, relative to the pure NO_3^- solution (Table S1). This is consistent with the view that
107 $\text{OH}_{(\text{aq})}$ reacts with $\text{HONO}_{(\text{aq})}$ to limit its accumulation.³⁻⁶

108 To elucidate the role of DAOM solubility on product yields, we carried out similar
109 experiments on homogeneous solutions containing one of several highly water-soluble organics:
110 acetic (pH=5.7), propionic (pH=5.7), and valeric acids (pH=5.7), and ethanol (pH=6.0). Relative
111 to the pure nitrate solution, emission of $\text{NO}_{2(\text{g})}$ and $\text{HONO}_{(\text{g})}$ were changed by a factor of between
112 0.58–1.01 for $\text{NO}_{2(\text{g})}$ and 1.96–4.10 for $\text{HONO}_{(\text{g})}$. Concentration ranges for $\text{NO}_{2(\text{g})}$ and $\text{HONO}_{(\text{g})}$
113 were comparable to experiments with surface-active organics, although different temporal trends
114 for $\text{NO}_{2(\text{g})}$ were observed (Figures 1C and D). At $t=20$ min, the amount of $\text{NO}_{2(\text{g})}$ generated in the
115 presence of soluble organics was only half of what was generated in the presence of surface-active
116 organic molecules; subsequently, $\text{NO}_{2(\text{g})}$ concentration increased at a constant rate, reaching
117 concentrations between 4–8 ppb by $t=75$ min. Differences in DAOM mixing, HO_x accumulation
118 rates, and consumption of DAOM over time are likely responsible for observed differences in
119 $\text{NO}_{2(\text{g})}$ trends in Figure 1A, C, as discussed further in Section S7. The increasing trend in $\text{HONO}_{(\text{g})}$
120 emission observed over the course of all experiments is due to the accumulation of $\text{NO}_2^-_{(\text{aq})}$ and the
121 slow diffusion of $\text{HONO}_{(\text{g})}$ out of the solution under static conditions.

122 On average, secondary chemistry throughout the bulk solution leads to ~27% increase ($p <$
123 0.05) in the $\text{HONO}:\text{NO}_2$ ratio (R_{enhance} , Table S1) for homogenous DAOM solutions. Compared to
124 DAOM solutions with surface active organics (1-octanol and NNA), solutions of water soluble
125 DAOM species produced on average $19\pm 4\%$ ($p < 0.001$) less $\text{NO}_{2(\text{g})}$ and $6.0\pm 2.1\%$ ($p < 0.5$) more
126 $\text{HONO}_{(\text{g})}$. Note that differences in HONO emissions between DAOM types were not statistically
127 significant, which was due to the large standard deviation between the $\text{HONO}_{(\text{g})}$ data from

128 different homogenous DAOM species. Ethanol and propionic acid solutions yield a faster HONO(g)
129 emission and therefore better NO₂-to-HONO conversion rates than surface-active DAOM solutions,
130 whereas acetic and valeric acid solutions emit HONO(g) more slowly (Figure 1D, Table S1).
131 Regardless of DAOM type, our data agrees with a study by Scharko et al. which exhibited a
132 suppression of NO_{2(g)} yields from nitrate photolysis in the presence of water-soluble organic
133 molecules due to secondary chemistry converting NO_{2(aq)} to HONO(aq).^{4,16} Notably, this is a static
134 multiphase system; other possible factors impacting NO_{2(g)} and HONO(g) levels are discussed in
135 section S7.

136 **O₂⁻ Production.** Production of HONO(g) from nitrate photolysis in the presence of DAOM is
137 hypothesized to involve HO₂/O₂⁻(aq) as an intermediate.^{4,5} We tested this hypothesis by measuring
138 the concentration profiles for O₂⁻(aq) formed when nitrate solutions were photolyzed with UV-
139 visible radiation (Figure S4). Irradiation of each phosphate buffered solution (pH=6) yielded a burst
140 in O₂⁻(aq) concentration that quickly reached a maximum, followed by slight decline to quasi-
141 steady-state levels. Photolysis of aqueous nitrate alone produces superoxide (~10 nM). This likely
142 originates from production^{5,7} and subsequent photolysis of peroxyxynitrous acid (HOONO) to form
143 NO(aq) and HO₂(aq) (Scheme 1a).³⁰⁻³³ The addition of NNA (pH=6.0) or 1-octanol (pH=6.0) to
144 nitrate solutions enhances O₂⁻(aq) production 3- and 5-fold, respectively, relative to pure nitrate
145 solutions, whereas blanks experiments do not produce significant amounts of superoxide (Figure
146 S5). This O₂⁻(aq) enhancement agrees well with the 2- to 5-fold enhancement (*R*_{enhance}) in
147 HONO:NO₂ ratios observed for nitrate solutions containing organic solutes (see Table S1),
148 indicating a potential link between HONO(g) formation and HO₂/O₂⁻(aq) chemistry.

149 We therefore measured the response of NO_{y(g)} species to increases in HO₂/O₂⁻(aq) that occur
150 when ethanol is added to photolyzed solutions of nitrate and NNA. As shown in Figure 2,

151 photolysis of nitrate and NNA forms $O_2^-(aq)$, $NO_2(g)$, $HONO(g)$, and $NO(g)$. Production of $NO(g)$
 152 is accounted for by the photolysis of $NO_2^-/HONO$ [$j(HONO)=5.0\times 10^{-3} s^{-1}$] and NO_2
 153 [$j(NO_2)=1.6\times 10^{-2} s^{-1}$] in the photochemical cell, as described in Section S8. Titration with ethanol
 154 simultaneously increases $HONO(g)$ and $O_2^-(aq)$ while decreasing $NO_2(g)$ and $NO(g)$ concentrations.
 155 Furthermore, the total amount of excess $HONO(g)$ accumulated (+45 ppb) is roughly equal to the
 156 total loss of $NO_{x(g)}$ (-56 ppb) observed. Plotting the total amount of $HONO(g)$ produced vs. total
 157 $NO_{x(g)}$ consumed (Figure S6) shows that ~80% of the $NO_{x(g)}$ formed during the titrations is
 158 converted to $HONO(g)$; the missing 20% is likely retained in solution as $NO_2^-(aq)$. Sharp increases
 159 in superoxide occur immediately before significant jumps in the $HONO:NO_x$ ratio (Figure S7),
 160 supporting the hypothesis that reaction of $HO_2/O_2^-(aq)$ and $NO_{x(aq)}$ are responsible for the observed
 161 $HONO(g)$ emission enhancement.

162 **O_2^- and HONO Production Mechanism.** It is well known that organic matter scavenges $OH_{(aq)}$
 163 produced from the photolysis of NO_3^- .^{4,5} Lower $OH_{(aq)}$ concentrations impede reactions (1)–(3)
 164 and consequently increase the amount of $NO_{2(aq)}$ and $HONO/NO_2^-(aq)$ formed.



165 The lowest $NO_{2(g)}$ yield is indeed observed for acetic acid which has the slowest reaction with
 166 $OH_{(aq)}$ (Table S2), while $NO_{2(g)}$ yield is higher for ethanol or valeric acid, which are the most
 167 reactive DAOM species (Figure 1C). However, our results show that homogenous organics lead to
 168 a lower initial concentration of $NO_{2(g)}$ compared to pure nitrate solution photolysis (Figure 1A and
 169 C, $t=20$ min), indicating that secondary chemistry involving species such as $HO_2/O_2^-(aq)$
 170 significantly affect the dissolved concentration of $NO_{2(aq)}$.

171 The data support that reactions of $\text{NO}_{x(\text{aq})}$ with O_2^- (aq) are significant pathways by which
172 $\text{HONO}_{(\text{aq})}$ production is enhanced by DAOM. Superoxide reacts rapidly with $\text{NO}_{2(\text{aq})}$ ($k=4.5\times 10^9$
173 $\text{M}^{-1} \text{s}^{-1}$),^{1,7,34} to form peroxyxynitrate (OONO_2^-), which thermally decomposes to form NO_2^- (aq) and
174 $\text{O}_{2(\text{aq})}$ (1.4 s^{-1} , Scheme 1c).^{35,36} Rapid reaction between O_2^- (aq) and $\text{NO}_{(\text{aq})}$ ($4.3\times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, Scheme
175 1d)³⁷ is expected to be an additional pathway to NO_2^- (aq) formation. The product, peroxyxynitrite
176 (OONO^-), may either undergo internal rearrangement to form NO_3^- (1.0 s^{-1}),⁷ or disproportionate
177 to form NO_2^- (aq) and $\text{HOONO}_{2(\text{aq})}$ ($3.0\times 10^4 \text{ M}^{-1} \text{ s}^{-1}$).³⁸ Therefore, the enhanced levels of O_2^- (aq)
178 would react with $\text{NO}_{x(\text{aq})}$ and lead to higher $\text{HONO}_{(\text{g})}$ emissions from DAOM solutions relative to
179 what is seen for pure nitrate solutions. Notably, the combined production rate of $\text{HONO}_{(\text{g})}$ and
180 $\text{NO}_{2(\text{g})}$ [$P(\text{NO}_2 + \text{HONO})$, Table S1] is similar for all nitrate solutions, regardless of whether
181 organics are present. This indicates that the $\text{HONO}_{(\text{g})}$ enhancement in solutions containing organic
182 compounds is due to a shift in the product distribution from $\text{NO}_{2(\text{g})}$ to $\text{HONO}_{(\text{g})}$ rather than a change
183 in the rate of product formation from NO_3^- photolysis.

184 **Influence of RO_2 on measured species.** Differences in NO_x -to-HONO conversion between
185 different DAOM surrogates in Figure 1 are likely due to secondary reactions impacting O_2^- (aq)
186 levels. Reactions between $\text{OH}_{(\text{aq})}$ with DAOM leads to alkylperoxy radicals (RO_2), which form
187 $\text{O}_2^-/\text{HO}_{2(\text{aq})}$ via mechanisms that depend on $\text{RO}_{2(\text{aq})}$ structure. Alcohols react with $\text{OH}_{(\text{aq})}$ to
188 preferentially form α -hydroperoxyl radicals (Scheme 1b), which decompose unimolecularly to
189 $\text{HO}_{2(\text{aq})}$, with rate constants that increase with degree of methyl substitution.³⁹ This unimolecular
190 decomposition could explain the higher $\text{HONO}_{(\text{aq})}$ concentrations in the presence of ethanol (Figure
191 1D). Carboxylic acid peroxy radicals form less $\text{HO}_{2(\text{aq})}$ due to their stability and propensity to
192 dimerize; the dimers eventually decompose to release HO_2/O_2^- (aq) (Scheme 1b).^{40,41} However, the
193 system is more complicated since peroxy radicals may further act as O_2^- (aq) and $\text{NO}_{x(\text{aq})}$ sinks that

194 yield alkyl hydroperoxyl radicals and organic nitrates/nitrites.^{40,42,43} This may explain the trends
195 observed for acetic, propionic, and valeric acids. Carboxylic acids with shorter alkyl chains have
196 slower OH_(aq) reaction rates (Table S2), which seems to correspond to lower NO_{2(g)} emissions since
197 more OH_(aq) is available to oxidize NO_{2(aq)}. Differences in HONO_(g) production do not follow the
198 same trend, likely due to unknown differences in RO_{2(aq)} stability and reactivity towards NO_{2(aq)},
199 NO_(aq), and O₂⁻_(aq). All considerations point toward the central role of RO_{2(aq)} decomposition and
200 reactivity toward HO₂/O₂⁻_(aq), or NO_{x(aq)}, which are insufficiently defined and warrant future
201 investigations.

202 **Environmental Implications.** The presented work illustrates that nitrate photolysis in the actinic
203 range ($\lambda > 290$ nm) produces HO₂/O₂⁻_(aq) and HONO_(g) in the presence of DAOM, with an
204 enhancement stemming from secondary photochemistry between O₂⁻/HO_{2(aq)} and photoproduced
205 NO_{x(aq)}. Using production rate of NO₂ and HONO as proxies for the nitrate photolysis rate, the
206 observed $j(\text{NO}_3^-)$ are not significantly different from one another (Table S4), regardless whether
207 organics are present, indicating the role of DAOM is to increase the HONO/NO₂⁻_(aq) yield at the
208 expense of NO_{x(aq)}. Previous studies focused on the importance of HONO production from aerosol
209 nitrate and nitric acid use enhancement factors (EF) [i.e., the ratio of $j(\text{NO}_3^-)$ in the aerosol phase
210 to $j(\text{HNO}_3)$ in the gas phase] to describe release of HONO and NO_x from aerosol nitrate photolysis.
211 As shown in Table S4, the EF calculated for pure nitrate and nitrate in the presence of organic
212 molecules indicates an overall slower rate of NO₃⁻_(aq) photolysis relative to HNO_{3(g)}. This reflects
213 the factor of 10 lower quantum yield of nitrate photolysis in bulk solution compared to that of
214 HNO_{3(g)}, which is due to rapid recombination of NO₃⁻_(aq) products in the solvent cage. Nitrate
215 adsorbed to surfaces will have an incomplete solvent cage, leading to enhanced quantum yields.^{44,45}
216 Enhancement factors of 10–50 have been reported for HONO measurements in field

217 campaigns^{21,46,47} which are likely due to surface nitrate photolysis occurring in the presence of
218 organics. Importantly, reactions between NO_x and HO_2/O_2^- in the aerosol phase explain how
219 collocation of nitrate with organic matter can translate the rate enhancement factor into the
220 additional HONO production observed in the field. This chemistry is applicable to many aqueous
221 environments (e.g., cloud droplets, aqueous aerosols, surface water) and may represent a significant
222 source of HONO(g) in areas where surface waters or aqueous microlayers contain high
223 concentration of nitrate and DAOM. This chemistry should therefore be considered in models for
224 nitrate photochemistry and air quality.

225 **SUPPORTING INFORMATION.** Additional experimental details, discussion, 4 tables and 8
226 figures are provided. These include: materials; NO_x and HONO measurements; quantitation of O_2^- ;
227 factors impacting NO_2 and HONO; additional experiment involving titration of ethanol to
228 irradiated NO_3^- solution; tabulated analysis of NO_2 -to-HONO conversion for experiments;
229 schematics of the experimental setup including lamp spectrum.

230 **Notes**

231 The authors declare no competing financial interest.

232 **ACKNOWLEDEMENTS**

233 Work at IRCELYON project was supported by the ANR-RGC programme (project ANR-16-
234 CE01-0013, A-PolyU502/16). Work at Indiana University was supported by grants from the U.S.
235 National Science Foundation (NSF) (AGS-1352375 and CHE-1609752). E.Z.D. was supported by
236 a U.S. NSF Graduate Research Fellowship (2019286041). We are grateful to Prof. Whitney King
237 (Colby College) for helpful discussions regarding the FIC analyzer.

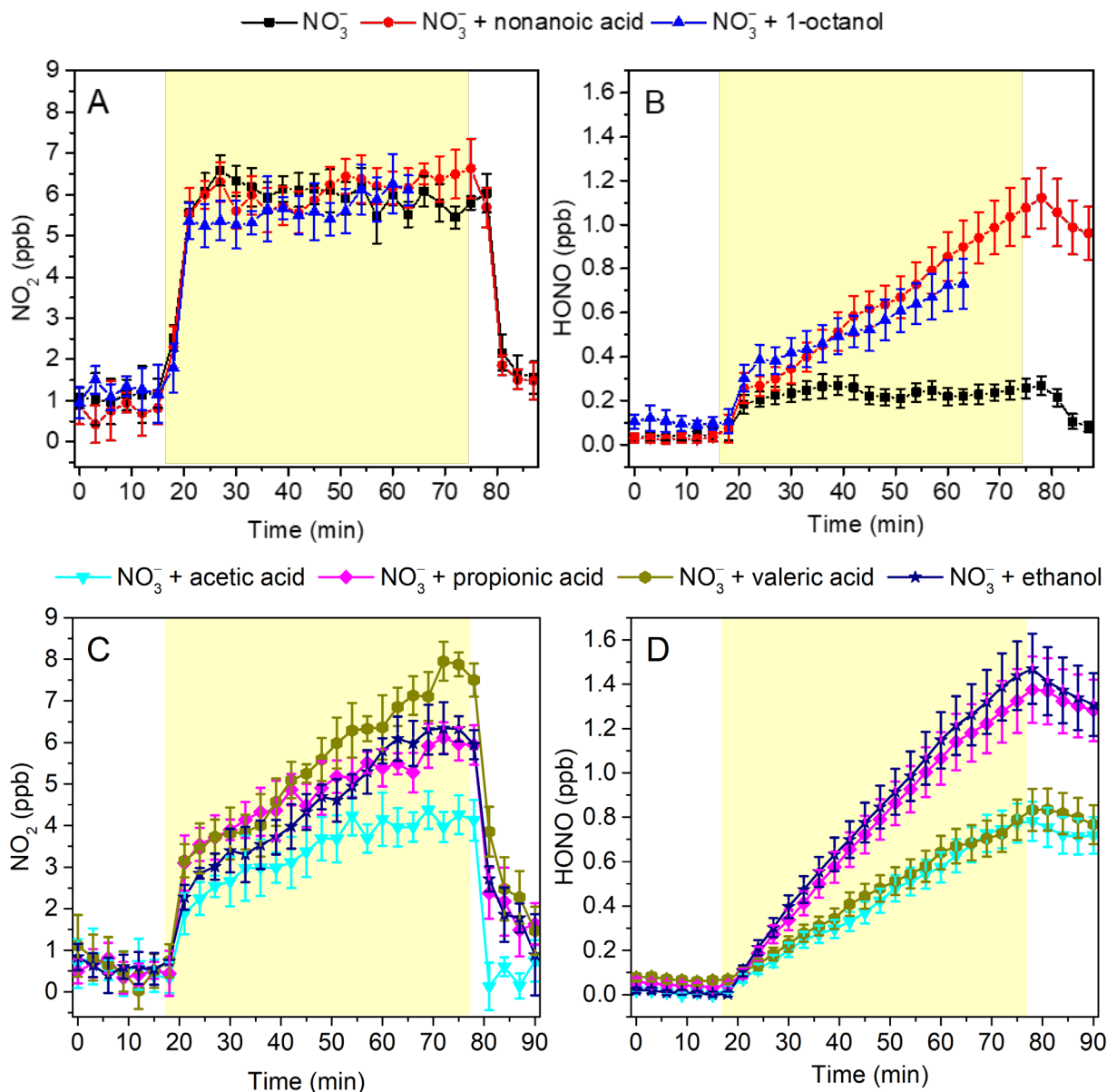
238 REFERENCES

- 239
- 240 (1) Mack, J.; Bolton, J. R. Photochemistry of Nitrite and Nitrate in Aqueous Solution: A
241 Review. *J. Photochem. Photobiol. A Chem.* **1999**, *128* (1–3), 1–13.
- 242 (2) Herrmann, H. On the Photolysis of Simple Anions and Neutral Molecules as Sources of O-
243 /OH, SO_x- and Cl in Aqueous Solution. *Phys. Chem. Chem. Phys.* **2007**, *9* (30), 3935–
244 3964.
- 245 (3) Roca, M.; Zahardis, J.; Bone, J.; El-Maazawi, M.; Grassian, V. H. 310 Nm Irradiation of
246 Atmospherically Relevant Concentrated Aqueous Nitrate Solutions: Nitrite Production and
247 Quantum Yields. *J. Phys. Chem. A* **2008**, *112* (51), 13275–13281.
- 248 (4) Scharko, N. K.; Berke, A. E.; Raff, J. D. Release of Nitrous Acid and Nitrogen Dioxide
249 from Nitrate Photolysis in Acidic Aqueous Solutions. *Environ. Sci. Technol.* **2014**, *48* (20),
250 11991–12001.
- 251 (5) Benedict, K. B.; McFall, A. S.; Anastasio, C. Quantum Yield of Nitrite from the Photolysis
252 of Aqueous Nitrate above 300 Nm. *Environ. Sci. Technol.* **2017**, *51* (8), 4387–4395.
- 253 (6) Zellner, R.; Exner, M.; Herrmann, H. Absolute OH Quantum Yields in the Laser
254 Photolysis of Nitrate, Nitrite and Dissolved H₂O₂ at 308 and 351 Nm in the Temperature
255 Range 278–353 K. *J. Atmos. Chem.* **1990**, *10* (4), 411–425.
- 256 (7) Løgager, T.; Sehested, K. Formation and Decay of Peroxynitric Acid: A Pulse Radiolysis
257 Study. *J. Phys. Chem.* **1993**, *97* (39), 10047–10052.
- 258 (8) Xue, L.; Gu, R.; Wang, T.; Wang, X.; Saunders, S.; Blake, D.; Louie, P. K. K.; Luk, C. W.
259 Y.; Simpson, I.; Xu, Z.; et al. Oxidative Capacity and Radical Chemistry in the Polluted
260 Atmosphere of Hong Kong and Pearl River Delta Region: Analysis of a Severe
261 Photochemical Smog Episode. *Atmos. Chem. Phys.* **2016**, *16* (15), 9891–9903.
- 262 (9) Harris, G. W.; Carter, W. P. L.; Winer, A. M.; Pitts, J. N.; Platt, U.; Perner, D.
263 Observations of Nitrous Acid in the Los Angeles Atmosphere and Implications for
264 Predictions of Ozone-Precursor Relationships. *Environ. Sci. Technol.* **1982**, *16* (7), 414–
265 419.
- 266 (10) Finlayson-Pitts, B. J.; Wingen, L. M.; Sumner, A. L.; Syomin, D.; Ramazan, K. A. The
267 Heterogeneous Hydrolysis of NO₂ in Laboratory Systems and in Outdoor and Indoor
268 Atmospheres: An Integrated Mechanism. *Phys. Chem. Chem. Phys.* **2003**, *5* (2), 223–242.
- 269 (11) Oswald, R.; Behrendt, T.; Ermel, M.; Wu, D.; Su, H.; Cheng, Y.; Breuninger, C.;
270 Moravek, A.; Mougín, E.; Delon, C.; et al. HONO Emissions from Soil Bacteria as a
271 Major Source of Atmospheric Reactive Nitrogen. *Science (80-.)*. **2013**, *341* (6151), 1233–
272 1235.
- 273 (12) Tong, S.; Hou, S.; Zhang, Y.; Chu, B.; Liu, Y.; He, H.; Zhao, P.; Ge, M. Exploring the
274 Nitrous Acid (HONO) Formation Mechanism in Winter Beijing: Direct Emissions and
275 Heterogeneous Production in Urban and Suburban Areas. *Faraday Discuss.* **2016**, *189*,
276 213–230.
- 277 (13) Lee, J. D.; Whalley, L. K.; Heard, D. E.; Stone, D.; Dunmore, R. E.; Hamilton, J. F.;
278 Young, D. E.; Allan, J. D.; Laufs, S.; Kleffmann, J. Detailed Budget Analysis of HONO in
279 Central London Reveals a Missing Daytime Source. *Atmos. Chem. Phys.* **2016**, *16* (5),
280 2747–2764.
- 281 (14) Kleffmann, J. Daytime Sources of Nitrous Acid (HONO) in the Atmospheric Boundary
282 Layer. *ChemPhysChem* **2007**, *8* (8), 1137–1144.
- 283 (15) George, C.; Streckowski, R. S.; Kleffmann, J.; Stemmler, K.; Ammann, M. Photoenhanced
284 Uptake of Gaseous NO₂ on Solid Organic Compounds: A Photochemical Source of

- 285 HONO? *Faraday Discuss.* **2005**, *130* (2), 195.
- 286 (16) Stemmler, K.; Ammann, M.; Donders, C.; Kleffmann, J.; George, C. Photosensitized
287 Reduction of Nitrogen Dioxide on Humic Acid as a Source of Nitrous Acid. *Nature* **2006**,
288 *440* (7081), 195–198.
- 289 (17) Han, C.; Liu, Y.; He, H. Heterogeneous Reaction of NO₂ with Soot at Different Relative
290 Humidity. *Environ. Sci. Pollut. Res.* **2017**, *24* (26), 21248–21255.
- 291 (18) Monge, M. E.; D’Anna, B.; Mazri, L.; Giroir-Fendler, A.; Ammann, M.; Donaldson, D. J.;
292 George, C. Light Changes the Atmospheric Reactivity of Soot. *Proc. Natl. Acad. Sci. U. S.*
293 *A.* **2010**, *107* (15), 6605–6609.
- 294 (19) Zhou, X.; Zhu, L. Role of Nitric Acid Surface Photolysis on Tropospheric Cycling of
295 Reactive Nitrogen Species. *Adv. Atmos. Chem.* **2016**, *1* (2), 271–304.
- 296 (20) Zhou, X.; Gao, H.; He, Y.; Huang, G.; Bertman, S. B.; Civerolo, K.; Schwab, J. Nitric
297 Acid Photolysis on Surfaces in Low-NO_x Environments: Significant Atmospheric
298 Implications. *Geophys. Res. Lett.* **2003**, *30* (23), 10–13.
- 299 (21) Romer, P. S.; Wooldridge, P. J.; Crouse, J. D.; Kim, M. J.; Wennberg, P. O.; Dibb, J. E.;
300 Scheuer, E.; Blake, D. R.; Meinardi, S.; Brosius, A. L.; et al. Constraints on Aerosol
301 Nitrate Photolysis as a Potential Source of HONO and NO_x. *Environ. Sci. Technol.* **2018**,
302 *52* (23), 13738–13746.
- 303 (22) Kleffmann, J.; Gavriloaiei, T.; Hofzumahaus, A.; Holland, F.; Koppmann, R.; Rupp, L.;
304 Schlosser, E.; Siese, M.; Wahner, A. Daytime Formation of Nitrous Acid: A Major Source
305 of OH Radicals in a Forest. *Geophys. Res. Lett.* **2005**, *32* (5), 1–4.
- 306 (23) King, D. W.; Lounsbury, H. a; Millero, F. Rates and Mechanism of Fe(II) Iron
307 Concentrations. *Environ. Sci. Technol.* **1995**, *29* (3), 818–824.
- 308 (24) Akutsu, K.; Nakajima, H.; Katoh, T.; Kino, S.; Fujimori, K. Chemiluminescence of
309 Cypridina Luciferin Analogues. Part 2. Kinetic Studies on the Reaction of 2-Methyl-6-
310 Phenylimidazo[1,2-a]Pyrazin-3(7H)-One (CLA) with Superoxide: Hydroperoxyl Radical
311 Is an Actual Active Species Used to Initiate the Reaction. *J. Chem. Soc. Perkin Trans. 2*
312 **1995**, No. 8, 1699.
- 313 (25) Fujimori, K.; Nakajima, H.; Akutsu, K.; Mitani, M.; Sawada, H.; Nakayama, M.
314 Chemiluminescence of Cypridina Luciferin Analogues. Part 1. Effect of PH on Rates of
315 Spontaneous Autoxidation of CLA in Aqueous Buffer Solutions. *J. Chem. Soc. Perkin*
316 *Trans. 2* **1993**, No. 12, 2405.
- 317 (26) Rose, A. L.; Moffett, J. W.; Waite, T. D. Determination of Superoxide in Seawater Using
318 2-Methyl-6-(4-Methoxyphenyl)-3,7-Dihydroimidazo[1,2-a]Pyrazin-3(7H)-One
319 Chemiluminescence. *Anal. Chem.* **2008**, *80* (4), 1215–1227.
- 320 (27) Rose, A. L.; Webb, E. A.; Waite, T. D.; Moffett, J. W. Measurement and Implications of
321 Nonphotochemically Generated Superoxide in the Equatorial Pacific Ocean. *Environ. Sci.*
322 *Technol.* **2008**, *42* (7), 2387–2393.
- 323 (28) Wang, X.; Gemayel, R.; Hayeck, N.; Perrier, S.; Charbonnel, N.; Xu, C.; Chen, H.; Zhu,
324 C.; Zhang, L.; Wang, L.; et al. Atmospheric Photosensitization: A New Pathway for
325 Sulfate Formation. *Environ. Sci. Technol.* **2020**, acs.est.9b06347.
- 326 (29) Reeser, D. I.; Kwamena, N. O. A.; Donaldson, D. J. Effect of Organic Coatings on Gas-
327 Phase Nitrogen Dioxide Production from Aqueous Nitrate Photolysis. *J. Phys. Chem. C*
328 **2013**, *117* (43), 22260–22267.
- 329 (30) Vione, D.; Maurino, V.; Minero, C.; Pelizzetti, E. Reactions Induced in Natural Waters by
330 Irradiation of Nitrate and Nitrite Ions. *Environ. Photochem. Part II* **2005**, *2* (September),
331 221–253.

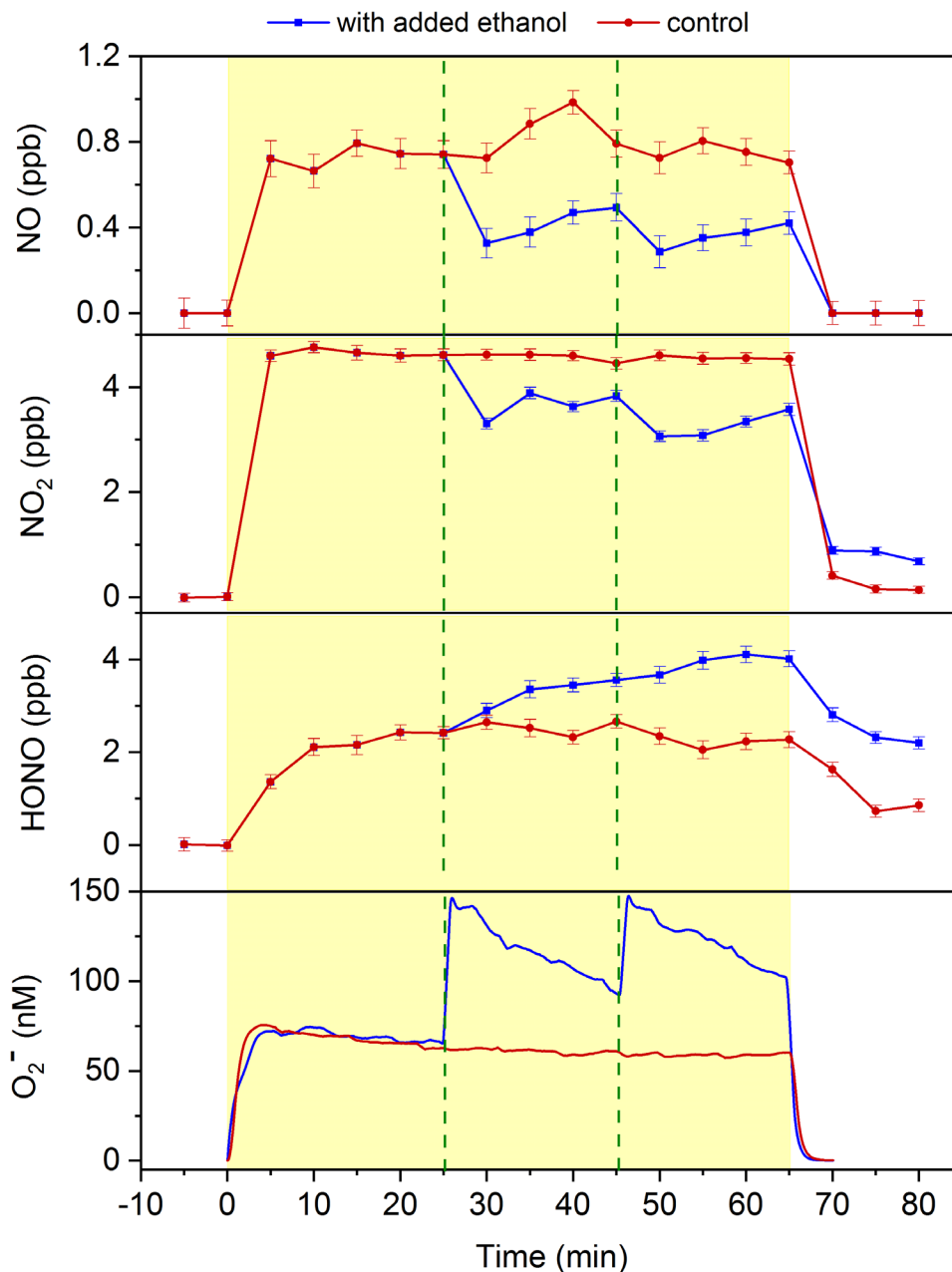
- 332 (31) Sturzbecher-Höhne, M.; Nauser, T.; Kissner, R.; Koppenol, W. H. Photon-Initiated
333 Homolysis of Peroxynitrous Acid. *Inorg. Chem.* **2009**, *48* (15), 7307–7312.
- 334 (32) Goldstein, S.; Lind, J.; Merényi, G. Chemistry of Peroxynitrites as Compared to
335 Peroxynitrates. *Chem. Rev.* **2005**, *105* (6), 2457–2470.
- 336 (33) Abida, O.; Mielke, L. H.; Osthoff, H. D. Observation of Gas-Phase Peroxynitrous and
337 Peroxynitric Acid during the Photolysis of Nitrate in Acidified Frozen Solutions. *Chem.*
338 *Phys. Lett.* **2011**, *511* (4–6), 187–192.
- 339 (34) Bielski, B. H. J.; Cabelli, D. E.; Arudi, R. L.; Ross, A. B. Reactivity of HO₂/O₂⁻ Radicals
340 in Aqueous Solution. *J. Phys. Chem. Ref. Data* **1985**, *14* (4), 1041–1100.
- 341 (35) Lammel, G.; Ferner, D.; Warneck, P. Decomposition of Pernitric Acid in Aqueous
342 Solution. *J. Phys. Chem.* **1990**, *94* (15), 6141–6144.
- 343 (36) Goldstein, S.; Czapski, G.; Lind, J.; Merenyi, G. Mechanism of Decomposition of
344 Peroxynitric Ion (O₂NOO⁻): Evidence for the Formation. *Inorg. Chem.* **1998**, *37* (16),
345 3943–3947.
- 346 (37) Goldstein, S.; Czapski, G. The Reaction of NO· with O₂⁻ and HO₂⁻: A Pulse Radiolysis
347 Study. *Free Radic. Biol. Med.* **1995**, *19* (4), 505–510.
- 348 (38) Gupta, D.; Harish, B.; Kissner, R.; Koppenol, W. H. Peroxynitrate Is Formed Rapidly
349 during Decomposition of Peroxynitrite at Neutral PH. *Dalt. Trans.* **2009**, No. 29, 5730–
350 5736.
- 351 (39) von Sonntag, C.; Schuchmann, H. -P. The Elucidation of Peroxyl Radical Reactions in
352 Aqueous Solution with the Help of Radiation-chemical Methods. *Angew. Chemie Int. Ed.*
353 *English* **1991**, *30* (10), 1229–1253.
- 354 (40) Schuchmann, M. N.; Zegota, H.; Sonntag, C. von. Acetate Peroxyl Radicals, ·O₂CH₂
355 CO₂⁻: A Study on the γ-Radiolysis and Pulse Radiolysis of Acetate in Oxygenated
356 Aqueous Solutions. *Zeitschrift für Naturforsch. B* **1985**, *40* (2), 215–221.
- 357 (41) Karpel Vel Leitner, N.; Dore, M. Hydroxyl Radical Induced Decomposition of Aliphatic
358 Acids in Oxygenated and Deoxygenated Aqueous Solutions. *J. Photochem. Photobiol. A*
359 *Chem.* **1996**, *99* (2–3), 137–143.
- 360 (42) Schuchmann, M. N.; Schuchmann, H. P.; Von Sonntag, C. The PKa Value of the
361 (Carboxymethyl)Peroxyl Radical: The Taft Σ* Constant of the -CH₂O₂· Group. *J. Phys.*
362 *Chem.* **1989**, *93* (13), 5320–5323.
- 363 (43) Goldstein, S.; Lind, J.; Merenyi, G. Reaction of Organic Peroxyl Radicals with NO₂
364 and NO in Aqueous Solution: Intermediacy of Organic Peroxynitrate and Peroxynitrite
365 Species. *J. Phys. Chem. A* **2004**, *108* (10), 1719–1725.
- 366 (44) Nissenson, P.; Knox, C. J. H.; Finlayson-Pitts, B. J.; Phillips, L. F.; Dabdub, D. Enhanced
367 Photolysis in Aerosols: Evidence for Important Surface Effects. *Phys. Chem. Chem. Phys.*
368 **2006**, *8* (40), 4700–4710.
- 369 (45) Wingen, L. M.; Moskun, A. C.; Johnson, S. N.; Thomas, J. L.; Roeselová, M.; Tobias, D.
370 J.; Kleinman, M. T.; Finlayson-Pitts, B. J. Enhanced Surface Photochemistry in Chloride-
371 Nitrate Ion Mixtures. *Phys. Chem. Chem. Phys.* **2008**, *10* (37), 5668–5677.
- 372 (46) Kasibhatla, P.; Sherwen, T.; Evans, M. J.; Carpenter, L. J.; Reed, C.; Alexander, B.; Chen,
373 Q.; Sulprizio, M. P.; Lee, J. D.; Read, K. A.; et al. Global Impact of Nitrate Photolysis in
374 Sea-Salt Aerosol on NO_x, OH, and O₃ in the Marine Boundary Layer. *Atmos. Chem. Phys.*
375 **2018**, *18* (15), 11185–11203.
- 376 (47) Reed, C.; Evans, M. J.; Crilley, L. R.; Bloss, W. J.; Sherwen, T.; Read, K. A.; Lee, J. D.;
377 Carpenter, L. J. Evidence for Renoxification in the Tropical Marine Boundary Layer.
378 *Atmos. Chem. Phys.* **2017**, *17* (6), 4081–4092.

379 **Figures**
380

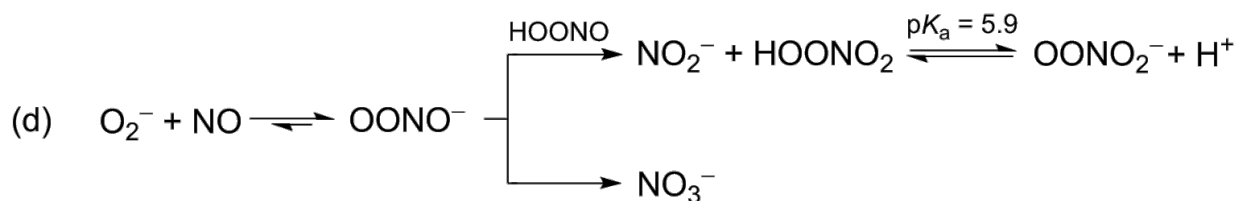
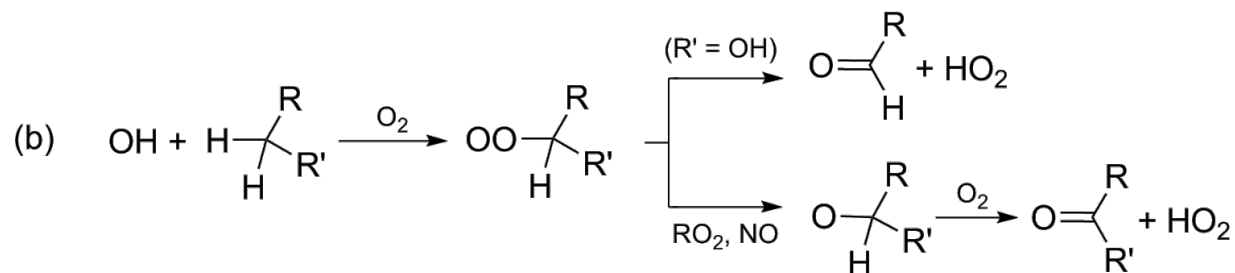
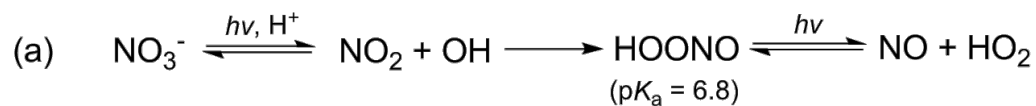


381

382
383 **Figure 1.** $\text{NO}_2(\text{g})$ and $\text{HONO}(\text{g})$ concentration profiles during the irradiation of phosphate
384 buffered nitrate solutions ($\text{pH } 5.8 \pm 0.2$). The production of (A) $\text{NO}_2(\text{g})$ and (B) $\text{HONO}(\text{g})$ is in the
385 presence or absence of NNA or 1-octanol, and the production of (C) $\text{NO}_2(\text{g})$ and (D) $\text{HONO}(\text{g})$ is
386 in the presence of acetic acid, propionic acid, valeric acid, or ethanol, respectively. The yellow
387 region corresponds to the irradiation period (duration 1 hour) starting at time = 16 min.
388



389
 390 **Figure 2.** Simultaneous measurement of NO(g), NO₂(g), HONO(g), and O₂⁻(aq) arising when
 391 solutions of nitrate and nonanoic acid (10 mM, 1 mM, pH 5) are irradiated with UV-visible light.
 392 Green dashed lines indicate points in time when 100 μL aliquots of a solution containing ethanol
 393 (1.5 M) and DTPA (50 μM) were added to initiate HO₂/O₂⁻(aq) formation. For the control
 394 experiment, aliquots of DTPA (50 μM) alone was added to the control. The yellow region
 395 corresponds to the irradiation period.



396

397 **Scheme 1.** Reaction mechanisms for HO_2/O_2^- (aq) and NO_2^- (aq) formation.

398

399

400

401

402

403

404

405

406

407

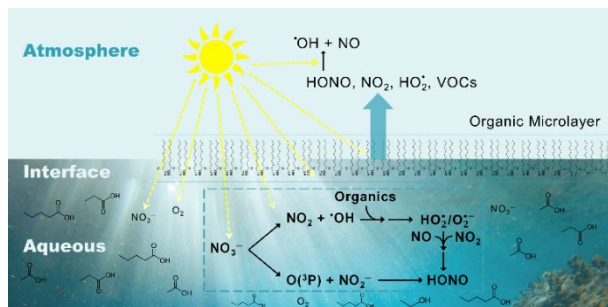
408 **TOC**

409 **For Table of Contents Use Only**

410 Title: Superoxide and nitrous acid production from nitrate photolysis is enhanced by dissolved
411 aliphatic organic matter

412 Authors: Xinke Wang, Evan Z. Dalton, Zachary C. Payne, Sebastien Perrier, Matthieu Riva,

413 Jonathan D. Raff, and Christian George



414