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Measurement of heterogeneous uptake of NO₂ on inorganic particles, sea water and urban grime

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Abstract: Heterogeneous reactions of NO₂ on different surfaces play an important role in atmospheric NO_x removal and HONO formation, having profound impacts on photochemistry in polluted urban areas. Previous studies have suggested that the NO₂ uptake on the ground or aerosol surfaces could be a dominant source for elevated HONO during daytime. However, the uptake behavior of NO₂ varies with different surfaces, and different uptake coefficients were used or derived in different studies. To obtain a more holistic picture of heterogeneous NO₂ uptake on different surfaces, a series of laboratory experiments using different flow tube reactors was conducted, and the NO₂ uptake coefficient (γ) were determined on inorganic particles, sea water and urban grime. The results showed that heterogeneous reactions on those surfaces were generally weak in dark condition, with the measured γ varied from $<10^{-8}$ to 3.2×10^{-7} under different humidity. A photo-enhanced uptake of NO₂ on urban grime were observed, with obvious formation of HONO and NO from the heterogeneous reaction. The photo-enhanced γ was measured to be 1.9×10^{-6} to 5.8×10^{-6} at 5% RH and 5.8×10^{-6} at 70% RH on urban grime, showing a positive RH dependence for both NO₂ uptake and HONO formation. The results demonstrate an important role of urban grime in the daytime NO₂-to-HONO conversion, and could be helpful to explain the unknown daytime HONO source in the polluted urban area.

Keywords: NO₂ uptake; HONO source; heterogeneous uptake coefficient; urban grime

1. Introduction

The heterogeneous reaction of NO₂ on different surfaces acts as an important NO_x sink and also a major source of nitrous acid (HONO), thus affecting the atmospheric nitrogen cycle and photochemistry [1]. Several previous laboratory studies have measured the heterogeneous uptake of NO₂ on inorganic particles, such as SiO₂ [2,3], Al₂O₃ [4,5] and CaCO₃ [6], but the reactivity of NO₂ on inorganic particles (expressed as an uptake coefficient, γ) is usually low (γ lies in the range from $<10^{-8}$ to 10^{-7}). Enhanced reactivity of NO₂ was found when irradiation was involved in the heterogeneous process. For example, the photo-enhanced uptake of NO₂ have been found on polycyclic aromatic hydrocarbons (PAHs) [7-10], humic acid (HA) [11-13], soot [14,15] and mineral dust [3,16]. The photo-enhanced γ is usually within 10^{-7} ~ 10^{-6} , larger than those on inorganic particles at dark by one or two orders of magnitude. Moreover, enhanced HONO formation was also often observed together with the photo-enhanced uptake of NO₂ [7-10,11,12,14].

HONO could act as an important source of hydroxyl radical (OH) through photolysis and therefore plays an important role in the oxidation capacity of the atmosphere. Gas-phase reaction of NO and OH and nocturnal heterogeneous reaction of NO₂ on surfaces have been recognized as the major HONO sources at daytime and nighttime, respectively (e.g. [1,17]). A recent study at a coastal site in Hong Kong has observed that the NO₂-to-HONO conversion rate in the air masses passing

48 over the sea was almost 3 times larger than that in the land air masses, suggesting that the air-sea
49 interaction at the sea surface could be a source of HONO [18]. Some studies also revealed significant
50 unknown daytime sources of HONO that cannot be explained by the traditional gas-phase oxidation
51 process [19], and several potential daytime sources or mechanism have been proposed, including
52 traffic emissions [20,21], photo-enhanced heterogeneous reaction of NO₂ on surfaces containing
53 humic acid, PAHs and soot [7,11,14], photolysis of nitrate [22-25] and nitric acid [26,27], etc.

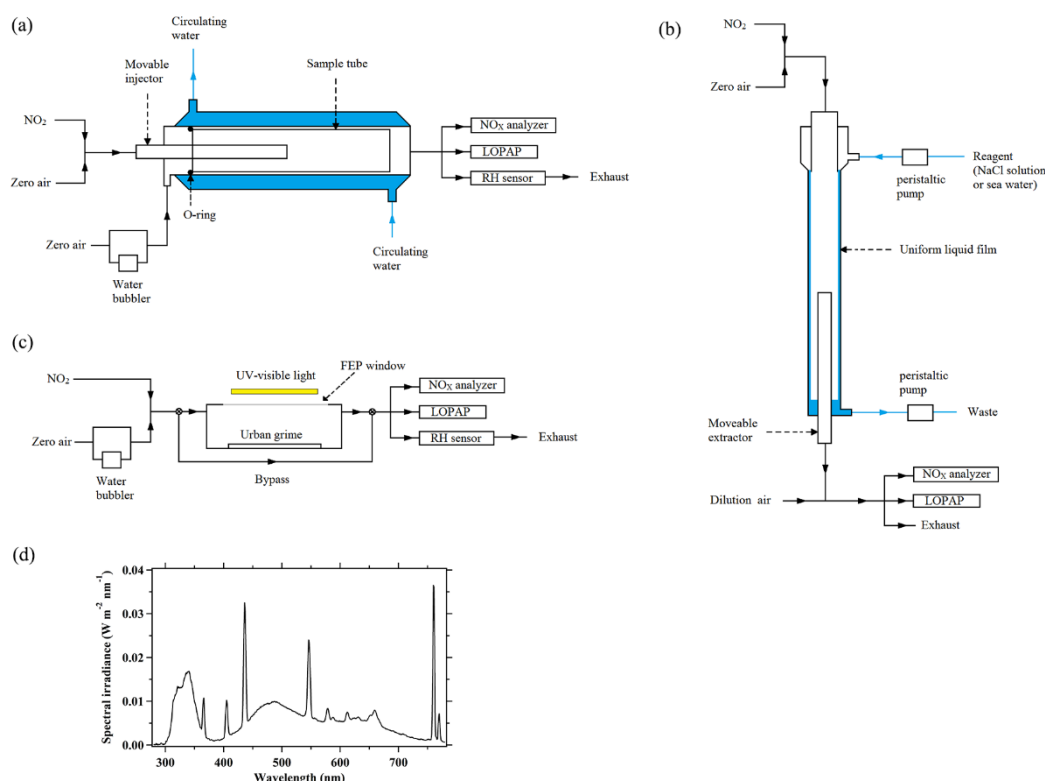
54 In urban area, particles and urban surfaces provide a large surface area for the heterogeneous
55 reactions of trace gases. A model study predicted that in highly urbanized area, the surface area
56 provided by the ground surface could be 3 times larger than the atmospheric aerosol surface, and
57 could be more important for heterogeneous reaction of NO₂ in urban area [28]. Furthermore, urban
58 surfaces such as buildings and roads are usually covered with a film of a complex mixture of organic
59 and inorganic materials, which are called urban grimes [29-32]. A recent study has reported a photo-
60 enhanced uptake of NO₂ and HONO production on real urban grime and , with γ of $(1.1-5.8)\times 10^{-6}$ at
61 RH range of 0% - 90% [33]. As the physical and chemical properties of urban grime vary with
62 locations [29-32], the heterogeneous behavior of NO₂ on more urban grime under different conditions
63 should be investigated [33], in order to better quantify the roles of heterogeneous reactions on urban
64 grime in HONO production and urban air quality, especially for highly urbanized environment with
65 more NO_x emission and building surfaces.

66 In this study, to enrich the present understanding of NO₂ heterogeneous reactivity and to
67 explore the unknown source of HONO, we conducted a series of laboratory experiments on different
68 surfaces. We measured the heterogeneous uptake of NO₂ on SiO₂, Al₂O₃, CaCO₃, NaCl and (NH₄)₂SO₄
69 particle surface by a coated-wall flow tube, and on NaCl solution and sea water surface using a
70 wetted-wall flow tube. We also investigate the NO₂ heterogeneous process and HONO production
71 on urban grimes collected in Hong Kong with high building density and compact urban setting.

72 2. Experiments

73 2.1 Coated wall flow tube

74 A horizontal cylindrical coated-wall flow tube was used to study the NO₂ uptake on solid
75 particles (Figure 1a), and similar apparatus and techniques have been employed and described in
76 many studies [34-36]. The flow tube was made of quartz glass with a length of 34 cm and an inner
77 diameter of 1.6 cm. Powder sample was dissolved in 20.0 mL of deionized water (for MgO, SiO₂,
78 Al₂O₃, and CaCO₃) or ethanol (for NaCl and (NH₄)₂SO₄) and then was dripped into a quartz tube (20.0
79 cm length, 1.1 cm i.d.) and dried for 12 hours in an oven at 373 K. SiO₂ (99.9%), Al₂O₃ (99.9%), CaCO₃
80 (99.9%), NaCl (99.9%), (NH₄)₂SO₄ (99.9%) and ethanol (99.9%) were purchased from Sigma-Aldrich.
81 The specific surface area was measured by nitrogen Brunauer-Emmett-Teller (BET) physisorption
82 (Quantachrome Autosorb-1-C) and was 135.6 m² g⁻¹ for MgO, 4.2 m² g⁻¹ for SiO₂, 12 m² g⁻¹ for Al₂O₃,
83 0.6 m² g⁻¹ for CaCO₃, 0.22 m² g⁻¹ for NaCl, and 0.16 m² g⁻¹ for (NH₄)₂SO₄, respectively. Experiments
84 were carried out at 295 K by thermostatic circulation of water through the outer jacket of the flow
85 tube and the flow tube was covered to shield from the light during the experiments. Zero air was
86 introduced in the flow tube as carrier gas at a flow rate of 0.9 L min⁻¹, ensuring a laminar regime. The
87 RH of the carrier gas was adjusted by a water bubbler. NO₂ (10 ppmv in N₂; 99%; Arkonic) was
88 introduced in the flow tube via a movable injector (with an inner diameter of 0.3 cm) and the NO₂
89 concentration in the total flow was 100 ppbv. At the exit of the flow tube, NO concentration, NO₂
90 concentration and RH were measured.



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Figure 1. Schematic diagrams of (a) the coated wall flow tube system, (b) the wetted wall flow tube system, and (c) the Teflon box reactor system. (d) Spectral irradiance of the UV-visible light measured in the Teflon reactor.

95 2.2 Wetted wall flow tube experiments

96 A wetted wall flow tube system was developed following the design of Behnke et al. [37] and
97 Gutzwiller et al. [38]. The vertical flow tube was made of glass with a length of 120 cm and an inner
98 diameter of 0.8 cm (Figure 1b). Experiments were carried out at 295 K by thermostatic circulation of
99 water through the outer jacket of the flow tube and the flow tube was covered to shield from the light
100 during the experiments. 3.5 wt% NaCl solution was prepared by NaCl (99.9%; Sigma-Aldrich) and
101 deionized water. Sea water was collected at Hok Tsui, Hong Kong in July 30, 2017. Reagent (NaCl
102 solution or sea water) was pumped in at the top of the wetted wall flow tube by a peristaltic pump
103 at a flow rate of 3 ml min⁻¹. Using an annular reservoir dispenser system, the reagent flowed down
104 uniformly on the inner wall of the flow tube and was pumped out at the bottom of the flow tube. A
105 mixture of NO₂ and zero air (NO₂ concentration of 300 ppbv) was introduced in the flow tube at a
106 flow rate of 400 mL min⁻¹, ensuring a laminar regime. Then after contact with the reagent, the gas
107 exited from a Teflon moveable extractor and diluted by dry zero air at a flow rate of 1700 mL min⁻¹.
108 NO, NO₂ and HONO concentrations in the outflow were monitored.

109 2.3 Teflon box reactor experiments

110 A PFA box reactor (inner size of 25×15×5 cm, with a 22.5×12.5 cm FEP window on the top) was
111 used to study the uptake coefficient of NO₂ on urban grime (Figure 1c). The box was covered to shield
112 from the light in the dark experiments or illuminated by an 18 W UV-visible light (Arcadia Products
113 plc.) in the irradiation experiments. A fan outside the reactor was used for cooling the UV-visible
114 light, and the experiments were performed at room temperature around 295K. Before the experiment,
115 the spectral irradiance inside the reactor was measured by a Spectro-Radiometer (specbos 1211UV,
116 JETI Technische Instrumente GmbH.), as shown in figure 1d, and a total irradiance of 2.1 W m⁻² was
117 measured in the wavelength range of 280–780 nm. The photolysis frequency of NO₂, j_{NO_2} , was

118 measured to be $1.8 \times 10^{-4} \text{ s}^{-1}$ by a jNO_2 filter radiometer (Meteorologie Consult). Urban grime samples
 119 were collected by placing $20 \times 10 \text{ cm}$ glass plates underneath a building overhang at the Hong Kong
 120 Polytechnic University from August 21 to September 3, 2017, and the weight of each sample is about
 121 0.01 g . A glass plate with urban grime was placed in the box reactor to investigate NO_2 uptake on
 122 urban grime or a clean glass plate was placed in the blank experiment. NO_2 and zero air were
 123 introduced in the box reactor and the total flow rate was changed from 3 to 5 LPM resulting in
 124 resistant time from 37.5 to 22.5 s. The initial NO_2 concentration was 57 ppbv. A water bubbler was
 125 used to humidify the zero air and adjust the RH. Photolysis experiments of urban grime was also
 126 tested and the experiment setup and conditions were the same as the urban grime experiments except
 127 that only zero air was introduced into the reactor. The NO , NO_2 and HONO concentrations and RH
 128 were measured at the exit of the box reactor.

129 2.4 Instrumentation

130 At the exits of the reactors, NO and NO_2 concentrations were measured by a chemiluminescence
 131 analyzer with a photolytic converter (Thermo, 42i), HONO concentration was measured by a long-
 132 path absorption photometer (QUMA, LOPAP) [39,40] and the relative humidity (RH) was measured
 133 by a RH sensor (Omega, RH-USB). Reacted and fresh urban grime samples were sonicated in 50 mL
 134 Milli-Q water to extract the inorganic compositions and the concentrations of the inorganic ions in
 135 the urban grime samples were measured by an ion chromatograph (Dionex, ICS 1000).

136 2.5 Calculation of uptake coefficient

137 The reaction of NO_2 on different surfaces was assumed to be a pseudo-first-order reaction and
 138 the first-order rate constant (k_{obs}) can be calculated by:

$$k_{\text{obs}} = \ln \left(\frac{(\text{NO}_2)_0}{(\text{NO}_2)_t} \right) / t, \quad (1)$$

139 where $(\text{NO}_2)_0$ is the initial NO_2 concentration and $(\text{NO}_2)_t$ is the NO_2 concentration after the reaction
 140 time t with the surface.

141 The geometric uptake coefficient γ_{geo} of the flow tube experiments can be calculated by:

$$\gamma_{\text{geo}} = \frac{2 r_{\text{tube}} k_{\text{obs}}}{c}, \quad (2)$$

142 where r_{tube} is the radius of the flow tube and c is the average molecular velocity of NO_2 .

143 The Cooney–Kim–Davis (CKD) method was used to correct the gas phase diffusion limitations
 144 in the calculation of the geometric uptake coefficient γ [41,42]. And for the coated wall flow tube
 145 experiments, the true uptake coefficient (γ_{BET}) on particles was calculated by Eq. (3) [36,43].

$$\gamma_{\text{BET}} = \frac{S_{\text{geo}}}{S_{\text{BET}}} \times \text{slope}, \quad (3)$$

146 where S_{geo} is the inner wall surface area of the quartz tube, S_{BET} is the particle sample surface area and
 147 *slope* is the slope of the plot of the geometric uptake coefficient γ versus the sample mass in the linear
 148 regime.

149 The geometric uptake coefficient γ_{geo} in the urban grime experiments was calculated by:

$$\gamma_{\text{geo}} = \frac{4 V_{\text{box}} (k_{\text{obs_grime}} - k_{\text{obs_glass}})}{S_{\text{glass}} c}, \quad (4)$$

150 where $k_{\text{obs_grime}}$ and $k_{\text{obs_glass}}$ are the first-order rate constants measured with the urban grime sample
 151 or with a clean glass plate, the V_{box} is the volume of the box reactor, S_{glass} is the surface area of the
 152 glass plate and c is the average molecular velocity of NO_2 .

153 Yields of NOHO and NO are calculated by:

$$\text{Yield} = \frac{(\Delta \text{Product})_{\text{grime}} - (\Delta \text{Product})_{\text{glass}}}{(\Delta \text{NO}_2)_{\text{grime}} - (\Delta \text{NO}_2)_{\text{glass}}}, \quad (5)$$

154 where $(\Delta\text{Product})_{\text{grime}}$ and $(\Delta\text{Product})_{\text{glass}}$ are the HONO or NO concentrations produced from NO₂
 155 reactions on urban grime or on a clean glass plate; $(\Delta\text{NO}_2)_{\text{grime}}$ and $(\Delta\text{NO}_2)_{\text{glass}}$ are the NO₂ consumed
 156 on urban grime or on a clean glass plate.

157 The flux of HONO production from the urban grime surface was calculated by:

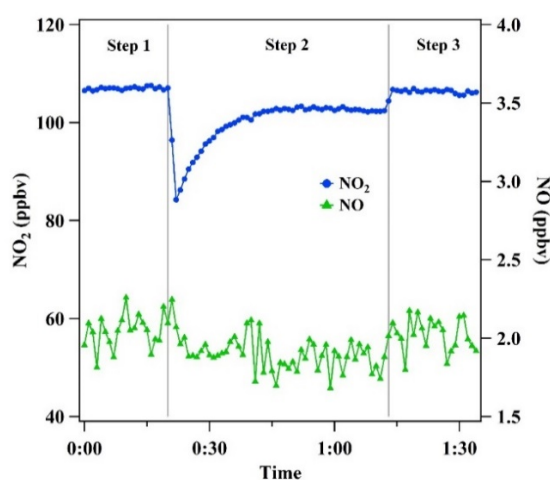
$$\text{Flux} = \frac{((\Delta\text{HONO})_{\text{grime}} - (\Delta\text{HONO})_{\text{glass}})fP}{RTAS_{\text{glass}}}, \quad (6)$$

158 $(\Delta\text{HONO})_{\text{grime}}$ and $(\Delta\text{HONO})_{\text{glass}}$ are the HONO concentration produced from NO₂ uptake on urban
 159 grime or on a clean glass plate; f is the total flow introduced into the box reactor; P is ambient pressure;
 160 R is molar gas constant, taken as 8.314 J mol⁻¹ K⁻¹; T is ambient temperature; A is the Avogadro's
 161 constant; and S_{glass} is the surface area of the glass plate.

162 3. Results and Discussion

163 3.1. NO₂ uptake on inorganic particles

164 Figure 2 shows the typical uptake experiment of NO₂ on inorganic particles, and the measured
 165 true uptake coefficient γ_{BET} on all of the tested inorganic particles are less than 3.2×10^{-7} , as summarized
 166 in Table 1. On each type of particles, experiments were conducted at least at two RH conditions. The
 167 results indicate that the heterogeneous uptake of NO₂ on these inorganic particles are generally weak,
 168 even at high humidity. In Table 1, previous results from other studies on inorganic particles are also
 169 summarized and compared [2-6,44,45]. The pressure and humidity conditions of coated wall flow
 170 tube are much closer to ambient conditions than some techniques such as Knudsen cell reactor used
 171 in the previous studies. The results measured in the present study are slightly higher than previous
 172 studies on the mineral particle surfaces [2-6], except for NaCl [44,45]. The γ_{BET} on NaCl was much
 173 smaller than the values measured in two previous studies using aerosol flow tube ($<10^{-4}$ and 3.7×10^{-4} –
 174 1×10^{-3}) [44,45], and the discrepancy could be partially due to the different experiment techniques and
 175 also the much higher NO₂ concentration (ppm level) in the previous studies. Future experiments
 176 under atmospheric condition are still needed to measure the γ of NO₂ on mixed real ambient aerosols.



177
 178 **Figure 2.** NO₂ uptake on CaCO₃. Blue circles and green triangles represent the NO₂, and NO
 179 concentrations at the exit of the reactor. The grey vertical lines indicate the experimental steps. Step
 180 1: reactor bypass; step 2: CaCO₃ exposed to NO₂ in the dark; step 3: reactor bypass line.

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Table 1. Summary of the NO₂ uptake coefficient on different surfaces.

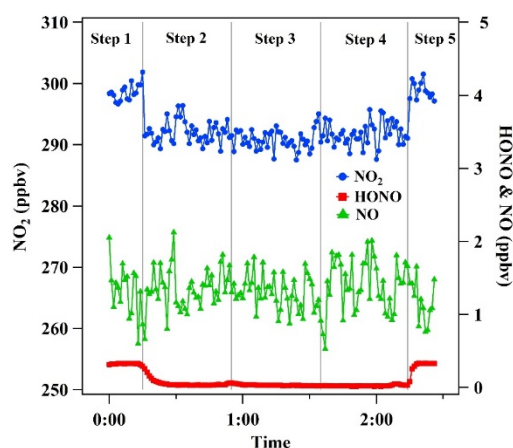
Surface	Irradiation	RH (%)	γ	γ in previous studies	References
SiO ₂	dark	10	$<10^{-8}$	$<10^{-10}$ (dry; Knudsen cell reactor)	[2]

		85	<10 ⁻⁸	<10 ⁻⁹ (RH 25%; coated wall flow tube)	[3]
Al ₂ O ₃	dark	7	3.2×10 ⁻⁸	2 ×10 ⁻⁸ (dry; Knudsen cell reactor)	[4]
		80	1.4×10 ⁻⁸	1.3×10 ⁻⁹ -2.6×10 ⁻⁸ (dry; DRIFTS)	[5]
NaCl	dark	5	<10 ⁻⁸	<10 ⁻⁴ (RH 75%; aerosol flow tube;)	[44]
		85	<10 ⁻⁸	1×10 ⁻³ -3.7×10 ⁻⁴ (RH 50%-90%; aerosol flow tube;)	[45]
CaCO ₃	dark	10	2.5×10 ⁻⁷		
		32	1.8×10 ⁻⁷	(4.25±1.18)×10 ⁻⁹ (dry; DRIFTS)	[6]
		85	3.2×10 ⁻⁷	(6.56±0.34)×10 ⁻⁸ (wet; DRIFTS)	
(NH ₄) ₂ SO ₄	dark	10	<10 ⁻⁸		
		56	<10 ⁻⁸	-	-
		85	<10 ⁻⁸		
3.5 wt% NaCl solution	dark	-	1.4×10 ⁻⁸	-	-
Bulk sea water	dark	-	1.6×10 ⁻⁸	-	-
Urban grime	dark	5	<10 ⁻⁷		
		70	3.1×10 ⁻⁷		
	irradiated	5	1.9×10 ⁻⁶	(1.1±0.2)×10 ⁻⁶ -(5.8±0.7)×10 ⁻⁶ (RH 0% - 90%; coated wall flow	
		70	5.8×10 ⁻⁶	tube)	[33]

183

184 3.2. NO₂ uptake on sea water

185 As discussed before, the sea surface was suggested to be a potential source of HONO [18], thus
186 we used the wetted wall flow tube to investigate the NO₂ uptake on 3.5 wt% NaCl solution and sea
187 water. Figure 3 shows the example result of the NO₂ uptake experiment on sea water. It was
188 supervised to find that HONO production was observed in the flow tube system when NO₂ had not
189 contacted with the sea water surface (step 1). The background HONO was probably produced on the
190 wall of the path tubing. However, when the extractor was pulled down and the NO₂ contacted with
191 the sea water, both concentrations of NO₂ and HONO decreased (step 2-4). And when the contact of
192 the NO₂ with the sea water was stopped, the NO₂ and HONO concentrations returned back to the
193 initial concentrations (step 5). The γ_{geo} of NO₂ on NaCl solution and sea water was then calculated to
194 be 1.4×10⁻⁸ and 1.6×10⁻⁸, respectively (Table 1). These results suggest that the NO₂ uptake on sea water
195 might not be a significant pathway to release gaseous HONO, or the alkaline conditions of sea water
196 could retain the formed acidic HONO in the aqueous phase. Our results cannot help explain the
197 elevated NO₂-to-HONO conversion rate in the air masses passing by sea surfaces observed by Zha et
198 al. [18]. Another possible reason could be that the sea water used in the present study was the bulk
199 water, while at the air–sea interface, there is a sea-surface microlayer (SML) comprised of complex
200 enriched organic matters [46,47], which might be able to promote the heterogeneous conversion of
201 NO₂ to HONO. Further experiment with the sea-surface microlayer is needed to better understand
202 the HONO formation on the sea surface.

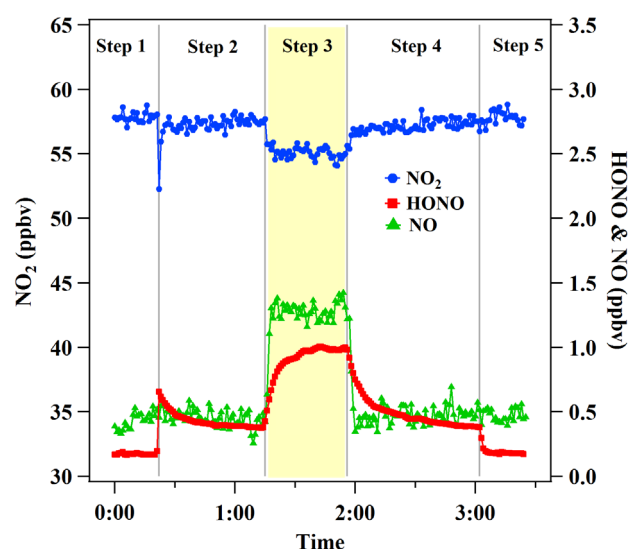


203

204 **Figure 3.** NO₂ uptake on bulk sea water. Blue circles, red squares and green triangles represent the
 205 NO₂, HONO and NO concentrations at the exit of the reactor. The grey vertical lines indicate the
 206 experimental steps. Step 1: the extractor was at top of the wetted wall flow tube, $l = 0$ cm; step 2:
 207 pulling down the extractor and the contact distance $l = 10$ cm; step 3: $l = 20$ cm; step 4: $l = 30$ cm; step
 208 5: the extractor was pushed back to the top of the wetted wall flow tube, $l = 0$ cm.

209 3.3. NO₂ uptake on urban grime

210 Figure 4 shows the steps of one experimental cycle to determine NO₂ uptake on urban grime.
 211 First, NO₂ was not introduced into the box reactor but passed through a bypass line until the NO₂
 212 initial concentration was stable (step 1). Then NO₂ was introduced into the box reactor with the UV-
 213 visible light off (step 2). When the concentration of HONO and NO₂ were stable, the light was turned
 214 on and NO₂ uptake remained constant as long as the light was on (step 3). After that, the light was
 215 turned off (step 4) and NO₂ was bypassed from the box reactor (step 5). When the urban grime was
 216 exposed to NO₂ in the dark condition, NO₂ concentration decreased slightly (step 2 and 4),
 217 corresponding to an uptake coefficient below 3.1×10^{-7} . When the light was turned on, there was an
 218 obvious decrease of NO₂ compared to dark condition, and the NO₂ uptake was constant during the
 219 irradiation (step 3). It suggests a weak uptake and reaction of NO₂ on urban grime in the dark
 220 condition, but an enhanced reaction under irradiation. The γ_{geo} on urban grime under irradiation was
 221 measured to be 1.9×10^{-6} at 5% RH and 5.8×10^{-6} at 70% RH, which shows a clear relative humidity
 222 dependence and is similar to the values of $(1.1\text{--}5.8) \times 10^{-6}$ at RH 0% - 90% reported by Liu et al. [33].



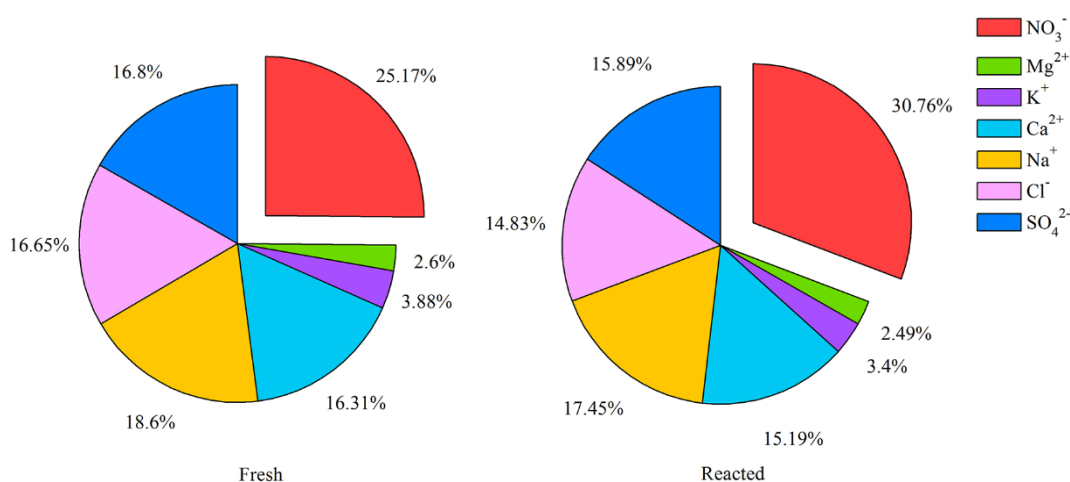
223

224 **Figure 1.** Conversion of NO₂ to HONO and NO on urban grime at 70% RH. Blue circles, red squares
 225 and green triangles represent the NO₂, HONO and NO concentrations at the exit of the reactor. The
 226 grey vertical lines indicate the experimental steps. Step 1: reactor bypass; step 2: urban grime exposed

227 to NO₂ in the dark; step 3: urban grime exposed to NO₂ under the irradiation; step 4: urban grime
228 exposed to NO₂ in the dark; step 5: reactor bypass.

229 Photo-enhanced uptake of NO₂ has also been found on polycyclic aromatic hydrocarbons
230 (PAHs) [7-10], soot [14,15] and mineral dust [3,16]. PAHs were proposed as photosensitizers to get
231 excited under irradiation and react with NO₂, thus promote the NO₂ uptake [14]. Ndour et al. [16]
232 found that TiO₂ can act as photocatalyst and enhance the reactivity of NO₂ on mineral dust under
233 irradiation. The true uptake coefficient (γ_{BET}) measured on soot and mineral dust in previous studies
234 was calculated by measuring BET surface area of particle samples, and thus it may not be comparable
235 to the geometric uptake coefficient on urban grime in the present study. Nevertheless, the γ_{geo} values
236 of $(1.8 \pm 0.3) \times 10^{-6}$ on pyrene/KNO₃ under irradiation at 30-35% RH [9] are lower than the γ_{geo} on urban
237 grime, which have more complex compositions than the proxies used in previous studies. In addition,
238 Baltrusaitis et al. [48] found that NO₂ uptake was enhanced on α -Fe₂O₃ surface under UV irradiation
239 with reduced nitrogen species found on the surface. Mineral species like Fe, which has been found in
240 urban grime [30], along with mixture of PAHs, soot, TiO₂ and other photocatalysts in the urban grime,
241 could significantly contribute to the photo-reactivity of urban grime and promote the NO₂-to-HONO
242 conversion.

243 Formation of HONO and NO were also observed from the NO₂ uptake reactions on urban grime.
244 When urban grime was exposed to NO₂ in the dark condition (cf. step 2 and step 4 in Figure 4), the
245 heterogeneous reaction of NO₂ only produced ~0.22 ppbv of HONO. At step 3, when urban grime
246 was exposed to NO₂ under irradiation, enhanced formations of HONO (~0.86 ppbv) and NO (0.79
247 ppbv) were both observed. Nanayakkara et. al. [22] has shown that the photolysis of nitrate can
248 contribute to HONO formation, so a photolysis experiment without NO₂ input was also carried out
249 in the present study to assess the contribution from nitrate. Photolysis of nitrate in urban grime only
250 contributed to ~0.20 ppbv of HONO, and there was no NO formation during the photolysis
251 experiment, which indicated that NO formation was not due to the photolysis of HONO (figure not
252 shown here). Furthermore, based on the measured photolysis frequency of NO₂ (j_{NO_2} , $1.8 \times 10^{-4} \text{ s}^{-1}$), the
253 photolysis only contributed to a loss of 0.7% of the total NO₂, suggesting that the formation of NO
254 via NO₂ photolysis was also neglected in the present study. Similar to the present study, both
255 formations of HONO and NO have been observed on illuminated PAHs and soot, and were
256 attributed to the photosensitized reactions of NO₂ with PAHs [7-10,14]. The observed HONO and
257 NO could be contributed from the photo-reduction of NO₂ with PAHs or soot in urban grime.
258 However, only HONO formation was observed during the illuminated uptake of NO₂ on urban grime
259 collected in Guangzhou [33], which may suggest the different reactions undergo on the surface of
260 urban grime with different compositions. More experiments under different conditions with urban
261 grime collected from different locations are still needed to better understand the NO₂ uptake and
262 reactions on urban grime. Furthermore, the inorganic ions in the reacted and fresh urban grime was
263 also compared in the present study (Figure 5), and the mass fraction of nitrate in urban grime
264 increased after exposure to NO₂ under irradiation. This indicated that the heterogeneous NO₂ uptake
265 on urban grime also produced particulate nitrate besides the reduced gas phase products.



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Figure 5. Mass fractions of inorganic ions in the fresh urban grime and in the reacted urban grime after the irradiation experiment.

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The yields of NO and HONO on urban grime were calculated from the ratio of the net formation of NO or HONO to the net consumption of NO₂ by Eq.5. The HONO yield was estimated to be 28% at 5% RH and 46% at 70% RH, and the NO yield was estimated to be 16% at 5% RH and 11% at 70% RH under irradiation. The positive correlations of NO₂ uptake and HONO formation with RH, indicating that high RH could enhance the uptake reaction. The amount of the absorbed water on urban grime has been found positively related with RH [23]. The absorbed water could enhance the uptake by increasing the mobility of reagents [50] or reducing the viscosity of the surface [51]. Such changes in mobility of reagents and viscosity of the surface could promote the reaction of NO₂ and the release of volatile products.

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3.4. Atmospheric implication on HONO unknown source

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The photo-enhanced HONO formation via NO₂ uptake could influence the oxidation capacity of the urban atmosphere, as an important source of OH radical (e.g. [52]). The flux of HONO production under irradiation can be calculated from the experiments, and it was determined to be 1.9×10^9 molecules cm⁻² s⁻¹ at 5% RH and 5.3×10^9 molecules cm⁻² s⁻¹ at 70% RH. Given in an urban area with 57 ppbv of NO₂ in a 10 m width street and 20 m height building covered with urban grime, an estimation of HONO source strength from urban grime could give 0.25 ppbv h⁻¹ at 5% RH and 0.71 ppbv h⁻¹ at 70% RH. Tang et al. [53] found that there was high daytime missing sources of HONO in Beijing-Tianjin-Heibei region in China and the missing sources reached a maximum of 2.5 ppbv h⁻¹. Lee et al. [54] also reported the daytime missing source of HONO maximum of ~2.8 ppbv h⁻¹ in London. Accordingly, in highly urbanized area, urban surfaces covered by urban grime such as buildings and roads provide a large surface area and the NO₂ uptake on the urban grime could be an important source of HONO in daytime, and should be considered in the simulation of HONO levels in future modeling studies.

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In view of the unknown HONO sources observed in different places, many air quality models have incorporated the NO₂ uptake process to better simulating the atmospheric HONO loading, which is of vital importance in assessing the oxidation capacity of the lower troposphere in polluted regions. In some model studies, larger γ were applied to better match the simulated HONO levels to measurements (e.g. [28,55,56]). Nighttime uptake coefficients of 5×10^{-6} and 1×10^{-5} on aerosol surface were used by Zhang et al. [55] and Zhang et al. [56], respectively, following the model setup in Li et al. [57]. Yet, the uptake coefficient in Li et al. [57] was set as 1×10^{-6} according to a laboratory experiment for the NO₂ uptake on pure water and acidic solution [58]. Zhang et al. [28] adopted a large uptake coefficient of 2×10^{-5} on aerosol surface when sunlight was available, while the uptake coefficients reported by the references there ranged from 1.2×10^{-7} to 6×10^{-6} [7,11,14,16]. The CAMQ model adopted the γ_{geo} of 1×10^{-6} measured on tunnel wall by Kurtenbach et al. [20] to simulate the

303 heterogeneous formation of HONO on urban, leaves, and particle surfaces [59-61]. However, the real
304 surface of the porous residue on the tunnel wall was not taken into consideration in γ_{geo} , and thus the
305 true uptake coefficient on the residue particles should be smaller than the measured γ_{geo} [20], which
306 should be only suitable for geometric surfaces such as ground and building surfaces. Besides, several
307 model studies also used the γ_{geo} measured by Kurtenbach et al. [20] as the γ_{BET} on particles [62-64].
308 Instead, the true uptake coefficient on particles such as γ_{BET} or γ measured in aerosol flow tube with
309 directly measured particle surface area should be used in such cases. Inappropriate usages of γ of
310 NO_2 in air quality models could lead to misestimates of HONO. Therefore, more direct measurement
311 of γ of NO_2 with real ambient aerosol and urban grime with mixture composition are needed. The
312 uptake of NO_2 on different surfaces with different γ values also should be separately treated in the
313 air quality models.

314 4. Conclusions

315 Heterogeneous uptake of NO_2 on different surfaces is an important process in controlling the
316 NO_x removal from the atmosphere, and accurate representation of the NO_2 uptake coefficient in air
317 quality models is of paramount importance for predicting the atmospheric NO_x cycling and
318 photochemistry. In the present study, we measured the NO_2 uptake on different surfaces, including
319 inorganic particles, sea water and urban grime, using three different flow tube reactors. The reactivity
320 of NO_2 was found very weak in dark condition on such surfaces. But UV-visible illumination
321 enhanced the NO_2 uptake on urban grime by two orders of magnitude. HONO and NO formations
322 were observed from the photo-enhanced NO_2 uptake on urban grime. The flux of HONO production
323 from irradiated urban grime was determined to be $1.9\text{-}5.3 \times 10^9$ molecules $\text{cm}^{-2} \text{s}^{-1}$ at RH of 5% to 70%,
324 which could lead to a daytime HONO source of 0.25-0.71 ppbv h^{-1} in a presumptive urban street. The
325 photo-enhanced NO_2 uptake on urban grime could increase the daytime HONO levels in the polluted
326 urban atmosphere, and should be considered in future experimental and modeling studies.

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329 original draft preparation, C.Y.; writing—review and editing, T.W., Z.W., Q.M., C.G., and C.Y.; supervision,
330 T.W.; project administration, T.W. and C.G.; funding acquisition, T.W. All authors have read and agreed to the
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338 References

- 339 1. Finlayson-Pitts, B.J.; Wingen, L.M.; Sumner, A.L.; Syomin, D.; Ramazan, K.A. The heterogeneous
340 hydrolysis of NO_2 in laboratory systems and in outdoor and indoor atmospheres: An integrated mechanism.
341 *Physical Chemistry Chemical Physics* **2003**, *5*, 223-242.
- 342 2. Underwood, G.M.; Song, C.H.; Phadnis, M.; Carmichael, G.R.; Grassian, V.H. Heterogeneous reactions of
343 NO_2 and HNO_3 on oxides and mineral dust: A combined laboratory and modeling study. *Journal of*
344 *Geophysical Research: Atmospheres* **2001**, *106*, 18055-18066.
- 345 3. Ndour, M.; Nicolas, M.; D'Anna, B.; Ka, O.; George, C. Photoreactivity of NO_2 on mineral dusts originating
346 from different locations of the sahara desert. *Physical chemistry chemical physics : PCCP* **2009**, *11*, 1312-1319.
- 347 4. Underwood, G.; Miller, T.; Grassian, V. Transmission FT-IR and Knudsen cell study of the heterogeneous
348 reactivity of gaseous nitrogen dioxide on mineral oxide particles. *The Journal of Physical Chemistry A* **1999**,
349 *103*, 6184-6190.
- 350 5. Börensen, C.; Kirchner, U.; Scheer, V.; Vogt, R.; Zellner, R. Mechanism and kinetics of the reactions of NO_2
351 or HNO_3 with alumina as a mineral dust model compound. *The Journal of Physical Chemistry A* **2000**, *104*,
352 5036-5045.

- 353 6. Li, H.J.; Zhu, T.; Zhao, D.F.; Zhang, Z.F.; Chen, Z.M. Kinetics and mechanisms of heterogeneous reaction
354 of NO₂ on CaCO₃ surfaces under dry and wet conditions. *Atmos. Chem. Phys.* **2010**, *10*, 463-474.
- 355 7. George, C.; Strekowski, R.S.; Kleffmann, J.; Stemmler, K.; Ammann, M. Photoenhanced uptake of gaseous
356 NO₂ on solid-organic compounds: A photochemical source of HONO? *Faraday Discussions* **2005**, *130*, 195-
357 210.
- 358 8. Brigante, M.; Cazoir, D.; D'Anna, B.; George, C.; Donaldson, D.J. Photoenhanced uptake of NO₂ by pyrene
359 solid films. *The Journal of Physical Chemistry A* **2008**, *112*, 9503-9508.
- 360 9. Ammar, R.; Monge, M.E.; George, C.; D'Anna, B. Photoenhanced NO₂ loss on simulated urban grime.
361 *Chemphyschem : a European journal of chemical physics and physical chemistry* **2010**, *11*, 3956-3961.
- 362 10. Cazoir, D.; Brigante, M.; Ammar, R.; D'Anna, B.; George, C. Heterogeneous photochemistry of gaseous
363 NO₂ on solid fluoranthene films: A source of gaseous nitrous acid (HONO) in the urban environment.
364 *Journal of Photochemistry and Photobiology A: Chemistry* **2014**, *273*, 23-28.
- 365 11. Stemmler, K.; Ammann, M.; Donders, C.; Kleffmann, J.; George, C. Photosensitized reduction of nitrogen
366 dioxide on humic acid as a source of nitrous acid. *Nature* **2006**, *440*, 195-198.
- 367 12. Stemmler, K.; Ndour, M.; Elshorbany, Y.; Kleffmann, J.; D'anna, B.; George, C.; Bohn, B.; Ammann, M. Light
368 induced conversion of nitrogen dioxide into nitrous acid on submicron humic acid aerosol. *Atmospheric*
369 *Chemistry and Physics* **2007**, *7*, 4237-4248.
- 370 13. Han, C.; Yang, W.; Wu, Q.; Yang, H.; Xue, X. Heterogeneous photochemical conversion of NO₂ to HONO
371 on the humic acid surface under simulated sunlight. *Environmental science & technology* **2016**, *50*, 5017-5023.
- 372 14. Monge, M.E.; D'Anna, B.; Mazri, L.; Giroir-Fendler, A.; Ammann, M.; Donaldson, D.J.; George, C. Light
373 changes the atmospheric reactivity of soot. *Proceedings of the National Academy of Sciences of the United States*
374 *of America* **2010**, *107*, 6605-6609.
- 375 15. Guan, C.; Li, X.; Zhang, W.; Huang, Z. Identification of nitration products during heterogeneous reaction
376 of NO₂ on soot in the dark and under simulated sunlight. *The journal of physical chemistry. A* **2017**, *121*, 482-
377 492.
- 378 16. Ndour, M.; D'Anna, B.; George, C.; Ka, O.; Balkanski, Y.; Kleffmann, J.; Stemmler, K.; Ammann, M.
379 Photoenhanced uptake of NO₂ on mineral dust: Laboratory experiments and model simulations.
380 *Geophysical Research Letters* **2008**, *35*.
- 381 17. Kleffmann, J. Daytime sources of nitrous acid (HONO) in the atmospheric boundary layer. *Chemphyschem :*
382 *a European journal of chemical physics and physical chemistry* **2007**, *8*, 1137-1144.
- 383 18. Zha, Q.; Xue, L.; Wang, T.; Xu, Z.; Yeung, C.; Louie, P.K.K.; Luk, C.W.Y. Large conversion rates of NO₂ to
384 HNO₂ observed in air masses from the south china sea: Evidence of strong production at sea surface?
385 *Geophysical Research Letters* **2014**, *41*, 7710-7715.
- 386 19. Su, H.; Cheng, Y.; Oswald, R.; Behrendt, T.; Trebs, I.; Meixner, F.X.; Andreae, M.O.; Cheng, P.; Zhang, Y.;
387 Poschl, U. Soil nitrite as a source of atmospheric HONO and OH radicals. *Science* **2011**, *333*, 1616-1618.
- 388 20. Kurtenbach, R.; Becker, K.H.; Gomes, J.A.G.; Kleffmann, J.; Lorzer, J.C.; Spittler, M.; Wiesen, P.; Ackermann,
389 R.; Geyer, A.; Platt, U. Investigations of emissions and heterogeneous formation of HONO in a road traffic
390 tunnel. *Atmospheric Environment* **2001**, *35*, 3385-3394.
- 391 21. Liang, Y.; Zha, Q.; Wang, W.; Cui, L.; Lui, K.H.; Ho, K.F.; Wang, Z.; Lee, S.-c.; Wang, T. Revisiting nitrous
392 acid (HONO) emission from on-road vehicles: A tunnel study with a mixed fleet. *Journal of the Air & Waste*
393 *Management Association* **2017**, *67*, 797-805.
- 394 22. Nanayakkara, C.E.; Jayaweera, P.M.; Rubasinghege, G.; Baltrusaitis, J.; Grassian, V.H. Surface
395 photochemistry of adsorbed nitrate: The role of adsorbed water in the formation of reduced nitrogen
396 species on alpha-Fe₂O₃ particle surfaces. *The journal of physical chemistry. A* **2014**, *118*, 158-166.
- 397 23. Baergen, A.M.; Donaldson, D.J. Photochemical renoxification of nitric acid on real urban grime.
398 *Environmental science & technology* **2013**, *47*, 815-820.
- 399 24. Ye, C.; Gao, H.; Zhang, N.; Zhou, X. Photolysis of nitric acid and nitrate on natural and artificial surfaces.
400 *Environmental science & technology* **2016**, *50*, 3530-3536.
- 401 25. Ye, C.; Zhang, N.; Gao, H.; Zhou, X. Photolysis of particulate nitrate as a source of HONO and NO_x.
402 *Environmental science & technology* **2017**, *51*, 6849-6856.
- 403 26. Zhou, X.; Gao, H.; He, Y.; Huang, G.; Bertman, S.B.; Civerolo, K.; Schwab, J. Nitric acid photolysis on
404 surfaces in low-NO_x environments: Significant atmospheric implications. *Geophysical research letters* **2003**,
405 *30*.

- 406 27. Laufs, S.; Kleffmann, J. Investigations on HONO formation from photolysis of adsorbed HNO₃ on quartz
407 glass surfaces. *Physical chemistry chemical physics : PCCP* **2016**, *18*, 9616-9625.
- 408 28. Zhang, L.; Wang, T.; Zhang, Q.; Zheng, J.; Xu, Z.; Lv, M. Potential sources of nitrous acid (HONO) and their
409 impacts on ozone: A WRF-Chem study in a polluted subtropical region. *Journal of Geophysical Research:*
410 *Atmospheres* **2016**, *121*, 3645-3662.
- 411 29. Baergen, A.M.; Styler, S.A.; van Pinxteren, D.; Muller, K.; Herrmann, H.; Donaldson, D.J. Chemistry of
412 urban grime: Inorganic ion composition of grime vs particles in Leipzig, Germany. *Environmental science &*
413 *technology* **2015**, *49*, 12688-12696.
- 414 30. Lam, B.; Diamond, M.L.; Simpson, A.J.; Makar, P.A.; Truong, J.; Hernandez-Martinez, N.A. Chemical
415 composition of surface films on glass windows and implications for atmospheric chemistry. *Atmospheric*
416 *Environment* **2005**, *39*, 6578-6586.
- 417 31. Butt, C.M.; Diamond, M.L.; Truong, J.; Ikonomidou, M.G.; Ter Schure, A.F. Spatial distribution of
418 polybrominated diphenyl ethers in southern Ontario as measured in indoor and outdoor window organic
419 films. *Environmental science & technology* **2004**, *38*, 724-731.
- 420 32. Liu, Q.-T.; Chen, R.; McCarry, B.E.; Diamond, M.L.; Bahavar, B. Characterization of polar organic
421 compounds in the organic film on indoor and outdoor glass windows. *Environmental science & technology*
422 **2003**, *37*, 2340-2349.
- 423 33. Liu, J.; Li, S.; Mekic, M.; Jiang, H.; Zhou, W.; Loisel, G.; Song, W.; Wang, X.; Gligorovski, S. Photoenhanced
424 uptake of NO₂ and HONO formation on real urban grime. *Environmental Science & Technology Letters* **2019**.
- 425 34. Han, C.; Liu, Y.; He, H. Role of organic carbon in heterogeneous reaction of NO₂ with soot. *Environmental*
426 *science & technology* **2013**, *47*, 3174-3181.
- 427 35. Liu, Y.; Han, C.; Ma, J.; Bao, X.; He, H. Influence of relative humidity on heterogeneous kinetics of NO₂ on
428 kaolin and hematite. *Physical chemistry chemical physics : PCCP* **2015**, *17*, 19424-19431.
- 429 36. Ma, Q.; Wang, T.; Liu, C.; He, H.; Wang, Z.; Wang, W.; Liang, Y. SO₂ initiates the efficient conversion of
430 NO₂ to HONO on MgO surface. *Environmental science & technology* **2017**, *51*, 3767-3775.
- 431 37. Behnke, W.; George, C.; Scheer, V.; Zetzsch, C. Production and decay of ClNO₂ from the reaction of gaseous
432 N₂O₅ with NaCl solution: Bulk and aerosol experiments. *Journal of Geophysical Research: Atmospheres* **1997**,
433 *102*, 3795-3804.
- 434 38. Gutzwiller, L.; Arens, F.; Baltensperger, U.; Gaggeler, H.W.; Ammann, M. Significance of semivolatile
435 diesel exhaust organics for secondary HONO formation. *Environmental science & technology* **2002**, *36*, 677-
436 682.
- 437 39. Heland, J.; Kleffmann, J.; Kurtenbach, R.; Wiesen, P. A new instrument to measure gaseous nitrous acid
438 (HONO) in the atmosphere. *Environmental science & technology* **2001**, *35*, 3207-3212.
- 439 40. Xu, Z.; Wang, T.; Wu, J.; Xue, L.; Chan, J.; Zha, Q.; Zhou, S.; Louie, P.K.K.; Luk, C.W.Y. Nitrous acid (HONO)
440 in a polluted subtropical atmosphere: Seasonal variability, direct vehicle emissions and heterogeneous
441 production at ground surface. *Atmospheric Environment* **2015**, *106*, 100-109.
- 442 41. Cooney, D.O.; Kim, S.-S.; Davis, E.J. Analyses of mass transfer in hemodialyzers for laminar blood flow
443 and homogeneous dialysate. *Chemical Engineering Science* **1974**, *29*, 1731-1738.
- 444 42. Murphy, D.M.; Fahey, D.W. Mathematical treatment of the wall loss of a trace species in denuder and
445 catalytic converter tubes. *Analytical Chemistry* **1987**, *59*, 2753-2759.
- 446 43. Underwood, G.; Li, P.; Usher, C.; Grassian, V. Determining accurate kinetic parameters of potentially
447 important heterogeneous atmospheric reactions on solid particle surfaces with a Knudsen cell reactor. *The*
448 *Journal of Physical Chemistry A* **2000**, *104*, 819-829.
- 449 44. Abbatt, J.; Waschewsky, G. Heterogeneous interactions of HOBr, HNO₃, O₃, and NO₂ with deliquescent
450 NaCl aerosols at room temperature. *The Journal of Physical Chemistry A* **1998**, *102*, 3719-3725.
- 451 45. Harrison, R.M.; Collins, G.M. Measurements of reaction coefficients of NO₂ and HONO on aerosol particles.
452 *Journal Of Atmospheric Chemistry* **1998**, *30*, 397-406.
- 453 46. Donaldson, D.J.; George, C. Sea-surface chemistry and its impact on the marine boundary layer.
454 *Environmental science & technology* **2012**, *46*, 10385-10389.
- 455 47. Wurl, O.; Obbard, J.P. A review of pollutants in the sea-surface microlayer (SML): A unique habitat for
456 marine organisms. *Marine pollution bulletin* **2004**, *48*, 1016-1030.
- 457 48. Baltrusaitis, J.; Jayaweera, P.M.; Grassian, V.H. XPS study of nitrogen dioxide adsorption on metal oxide
458 particle surfaces under different environmental conditions. *Physical Chemistry Chemical Physics* **2009**, *11*,
459 8295-8305.

- 460 49. Baergen, A.M.; Donaldson, D.J. Photochemical renoxification of nitric acid on real urban grime.
461 *Environmental science & technology* **2013**, *47*, 815-820.
- 462 50. Rubasinghege, G.; Grassian, V.H. Role(s) of adsorbed water in the surface chemistry of environmental
463 interfaces. *Chemical communications (Cambridge, England)* **2013**, *49*, 3071-3394.
- 464 51. Renbaum-Wolff, L.; Grayson, J.W.; Bateman, A.P.; Kuwata, M.; Sellier, M.; Murray, B.J.; Shilling, J.E.;
465 Martin, S.T.; Bertram, A.K. Viscosity of α -pinene secondary organic material and implications for particle
466 growth and reactivity. *Proceedings of the National Academy of Sciences - PNAS* **2013**, *110*, 8014-8019.
- 467 52. Elshorbany, Y.F.; Kurtenbach, R.; Wiesen, P.; Lissi, E.; Rubio, M.; Villena, G.; Gramsch, E.; Rickard, A.R.;
468 Pilling, M.J.; Kleffmann, J. Oxidation capacity of the city air of Santiago, Chile. *Atmospheric Chemistry And*
469 *Physics* **2009**, *9*, 2257-2273.
- 470 53. Tang, Y.; An, J.; Wang, F.; Li, Y.; Qu, Y.; Chen, Y.; Lin, J. Impacts of an unknown daytime HONO source on
471 the mixing ratio and budget of hono, and hydroxyl, hydroperoxyl, and organic peroxy radicals, in the
472 coastal regions of china. *Atmospheric Chemistry and Physics* **2015**, *15*, 9381-9398.
- 473 54. Lee, J.D.; Whalley, L.K.; Heard, D.E.; Stone, D.; Dunmore, R.E.; Hamilton, J.F.; Young, D.E.; Allan, J.D.;
474 Laufs, S.; Kleffmann, J. Detailed budget analysis of HONO in central London reveals a missing daytime
475 source. *Atmos. Chem. Phys.* **2016**, *16*, 2747-2764.
- 476 55. Zhang, J.; An, J.; Qu, Y.; Liu, X.; Chen, Y. Impacts of potential HONO sources on the concentrations of
477 oxidants and secondary organic aerosols in the Beijing-Tianjin-Hebei region of china. *The Science of the total*
478 *environment* **2019**, *647*, 836-852.
- 479 56. Zhang, J.; Guo, Y.; Qu, Y.; Chen, Y.; Yu, R.; Xue, C.; Yang, R.; Zhang, Q.; Liu, X.; Mu, Y., *et al.* Effect of
480 potential HONO sources on peroxyacetyl nitrate (PAN) formation in eastern china in winter. *Journal of*
481 *environmental sciences (China)* **2020**, *94*, 81-87.
- 482 57. Li, G.; Lei, W.; Zavala, M.; Volkamer, R.; Dusanter, S.; Stevens, P.; Molina, L.T. Impacts of HONO sources
483 on the photochemistry in Mexico City during the MCMA-2006/MILAGO Campaign. *Atmospheric chemistry*
484 *and physics* **2010**, *10*, 6551-6567.
- 485 58. Kleffmann, J.; Becker, K.H.; Wiesen, P. Heterogeneous NO₂ conversion processes on acid surfaces: Possible
486 atmospheric implications. *Atmospheric Environment* **1998**, *32*, 2721-2729.
- 487 59. 1. Binkowski, F.S.; Roselle, S.J. Models-3 Community Multiscale Air Quality (cmaq) model aerosol
488 component 1. Model description. *Journal of Geophysical Research D: Atmospheres* **2003**, *108*.
- 489 60. Byun, D.; Schere, K.L. Review of the governing equations, computational algorithms, and other
490 components of the Models-3 Community Multiscale Air Quality (CMAQ) modeling system. *Applied*
491 *mechanics reviews* **2006**, *59*, 51-76.
- 492 61. Foley, K.M.; Roselle, S.J.; Appel, K.W.; Bhave, P.V.; Pleim, J.E.; Otte, T.L.; Mathur, R.; Sarwar, G.; Young,
493 J.O.; Gilliam, R.C., *et al.* Incremental testing of the Community Multiscale Air Quality (CMAQ) modeling
494 system version 4.7. *Geoscientific model development* **2010**, *3*, 205-226.
- 495 62. Vogel, B.; Vogel, H.; Kleffmann, J.; Kurtenbach, R. Measured and simulated vertical profiles of nitrous
496 acid – part II. Model simulations and indications for a photolytic source. *Atmospheric Environment* **2003**, *37*,
497 2957-2966.
- 498 63. Sarwar, G.; Roselle, S.J.; Mathur, R.; Appel, W.; Dennis, R.L.; Vogel, B. A comparison of CMAQ HONO
499 predictions with observations from the Northeast Oxidant And Particle Study. *Atmospheric environment*
500 (1994) **2008**, *42*, 5760-5770.
- 501 64. Czader, B.H.; Rappenglück, B.; Percell, P.; Byun, D.W.; Ngan, F.; Kim, S. Modeling nitrous acid and its
502 impact on ozone and hydroxyl radical during the Texas Air Quality Study 2006. *Atmospheric chemistry and*
503 *physics* **2012**, *12*, 6939-6951.

504