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1 **Naphthalene-derived secondary organic aerosols interfacial photosensitizing**
2 **properties**

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8
9 **Key points**

- 10 • Naphthalene-derived SOA contains oxygenated aromatic compounds with photosensitizing
11 properties.
- 12 • Photosensitized oxidation of d-limonene and β -pinene by naphthalene-derived SOA results in
13 particle growth.
- 14 • Sulfate is formed through both dark and photosensitized chemical reactions between
15 naphthalene-derived SOA and SO₂.

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19

20 **Abstract**

21 We investigated the photosensitizing properties of secondary organic aerosol (SOA) formed during
22 the hydroxyl radical (OH) initiated oxidation of naphthalene. This SOA was injected into an aerosol
23 flow tube and exposed to UV radiation and gaseous volatile organic compounds or sulfur dioxide
24 (SO_2). The aerosol particles were observed to grow in size by photosensitized uptake of d-limonene
25 and β -pinene. In the presence of SO_2 , a photosensitized production ($0.2\text{-}0.3 \mu\text{g m}^{-3} \text{h}^{-1}$) of sulfate
26 was observed at all relative humidity (RH). Some sulfate also formed on particles in the dark,
27 probably due to the presence of organic peroxides. The dark and photochemical pathways exhibited
28 different trends with RH, unravelling different contributions from bulk and surface chemistry. As
29 naphthalene and other polycyclic aromatics are important SOA precursors in the urban and
30 suburban areas, these dark and photosensitized reactions are likely to play an important role in
31 sulfate and SOA formation.

32 **Plain Language Summary**

33 Organic compounds and sulfate anions are important components of atmospheric fine particles,
34 which play an important role in air quality, visibility, climate, as well as human and ecosystem
35 health. Photosensitized chemistry, which is driven by reactions of electronically excited organic
36 molecules, is a proposed pathway for fine particle growth, producing highly oxygenated
37 compounds and sulfate anions from gaseous volatile organics and sulfur dioxide, a key air pollutant.
38 Aromatic hydrocarbons and their oxidation products are important components of fine particles in
39 urban environments. This work shows that fine particles formed by oxidation of naphthalene, a
40 common aromatic hydrocarbon, possess photosensitizing properties making them efficient
41 catalysts for atmospheric oxidation of sulfur dioxide and volatile organics.

42 **1. Introduction**

43 Organic compounds and sulfate anions are ubiquitous in ambient aerosols, accounting for 20-90%
44 and 10-60% of the fine particulate mass, respectively (Jimenez et al., 2009; Kanakidou et al., 2005).
45 A large fraction of these organic compounds and sulfate are secondary in nature, i.e., they are
46 produced through atmospheric oxidation of volatile organic compounds (VOCs) (Hallquist et al.,
47 2009) and sulfur dioxide (SO₂) (Eatough et al., 1994; Saxena & Seigneur, 1987). Both sulfate and
48 secondary organic aerosol (SOA) significantly impact air quality, climate, as well as human and
49 ecosystem health (Fuzzi et al., 2015; Nel, 2005). Despite extensive research spanning nearly a
50 century, we still do not fully understand all possible pathways for their formation and
51 transformation in the atmosphere (Zhang et al., 2007; Wang et al., 2014).

52 Many previous studies showed that photosensitized chemistry may be an important
53 pathway for promoting the oxidation of VOCs (Kaur et al., 2019; Li et al., 2019a) in atmospheric
54 particles, which can increase the mass of SOA. For example, irradiation of imidazole-2-
55 carboxaldehyde (IC) and humic acid in the presence of various gaseous VOCs, such as d-limonene,
56 has been shown to produce highly oxygenated compounds and thereby initiate aerosol growth by
57 photosensitized mechanisms (Aregahegn et al., 2013; González Palacios et al., 2016; Rossignol et
58 al., 2014; Tsui et al., 2017; Monge et al., 2012). Previous studies have suggested that the
59 photosensitized chemistry of humic-like substances (HULIS) is not fast enough to compete with
60 the conventional free-radical-driven growth under ambient concentrations of d-limonene
61 (Fankhauser et al., 2020). However, while not being a major growth pathway of aerosols,
62 photosensitized processes have the potential to change the particle phase oxidation capacity. For
63 instance, significant amounts of oxygenated molecules with low-volatility have been observed
64 during photosensitized oxidation of some VOCs (Smith et al., 2014; Rossignol et al., 2014; Yu et

65 al., 2014). The importance of such processes is obviously linked to the concentration of triplet state
66 in the condensed phase as underlined by Kaur et al. (2019), who pooled all active triplet state into
67 a one single T* family. In other words, in contrast to well identified radicals (such as OH), the key
68 feature of tropospheric photosensitization is related to numerous compounds with diverse sources.
69 Understanding those is therefore key. To further illustrate this potential importance, it has been
70 shown that photosensitized chemistry involving the humic fraction of aerosols during Chinese haze
71 events can explain a significant fraction of the observed sulfate formation (Wang et al., 2020a).
72 The authors highlighted the specific role played by biomass burning (for cooking and heating
73 during the cold season) as the main source of the aerosol's photosensitizing properties.

74 Naphthalene, emitted primarily from fossil fuel combustion and biomass burning,
75 represents the smallest, most volatile, and most abundant polycyclic aromatic hydrocarbon (PAH)
76 in the atmosphere (Zhang et al., 2012). Naphthalene is ubiquitous in suburban and urban areas,
77 with a median concentration of $0.94 \mu\text{g m}^{-3}$ in 11 U.S. cities (Sudakin et al., 2011). The OH-
78 initiated oxidation of naphthalene produces a number of different oxygenated compounds with high
79 molecular weight and low-volatility, which can partition into particles and contribute to SOA mass
80 (Chan et al., 2009; Kautzman et al., 2010; Riva et al., 2015). Naphthoquinone, a naphthalene
81 oxidation product (McWhinney et al., 2013), is commonly found in atmospheric aerosols (e.g.,
82 Shanghai, China (Wang et al., 2017); Tempe, USA (Delhomme et al., 2008); Kurashiki City, Japan
83 (Oda et al., 2001); Yangtze River channel (Wang et al., 2020b)), and is known to be an efficient
84 photosensitizer, inducing redox chemistry or producing reactive oxygen species (De Lucas et al.,
85 2014; McNeill & Canonica, 2016). SOA derived from oxidation of naphthalene under high-NO_x
86 conditions has been shown to be weakly fluorescent (Lee et al., 2014), resilient to photobleaching
87 (Aiona et al., 2018), efficient in photosensitizing singlet oxygen in aqueous solutions (Manfrin et

88 al., 2019), capable of photosensitized oxidation of halide ions (Gemayel et al., 2021), and
89 moderately effective in photosensitized oxidation of d-limonene (Malecha & Nizkorodov, 2017).
90 It is therefore likely that aerosol particles containing naphthalene oxidation products (as well as
91 oxidation products of PAHs in general) contribute to photosensitized chemistry in the atmosphere.

92 In this study, we investigated the photosensitizing activity of naphthalene-derived SOA
93 using both gaseous VOCs and SO₂ as reaction partners. The naphthalene-derived SOA was
94 generated in a laminar-flow Gothenburg (Go:PAM) oxidation flow reactor, then its
95 photosensitizing properties were investigated by explicitly measuring particle growth in aerosol
96 flow tube (AFT) experiments, in which particles were exposed to near-UV radiation in presence of
97 VOCs or SO₂. Our data suggests that these aerosols do indeed exhibit photosensitized chemistry,
98 by converting SO₂ into sulfate and d-limonene and β-pinene into particle-phase organic products.

99 **2. Materials and Method**

100 As shown in Figure 1, the experimental setup mainly consisted of a Go:PAM oxidation flow reactor
101 and an aerosol flow reactor.

102 **2.1 Go:PAM Description**

103 The Go:PAM flow reactor (9.6 cm inner diameter, 100 cm length) is made of quartz glass and
104 surrounded by two 30 W Philips ultraviolet lamps capable of producing 254 nm radiation (Watne
105 et al., 2018). The gas flow injected into the Go:PAM chamber consisted of 250 mL min⁻¹ of pure
106 air bubbled through hydrogen peroxide (H₂O₂, Sigma Aldrich, 26.4 wt. % in H₂O) solution, 20 mL
107 min⁻¹ of pure air containing naphthalene (Sigma Aldrich, 99%) vapor, 1 L min⁻¹ of humidified air,
108 and 2.78 L min⁻¹ of dry air, leading to a residence time of 1.8 min. The Go:PAM was operated at
109 room temperature in the range of 297±2 K, whilst a fan was used to homogenize and maintain the

110 temperature. As calculated under the above conditions, the relative humidity (RH) and the
111 concentrations of H₂O₂ and naphthalene in the Go:PAM reactor were around 29%, 5.2×10³ ppb,
112 and 5.5×10² ppb, respectively. The collection and analysis of naphthalene-derived SOA and its
113 chemical characteristics are described in Supporting Information Texts S1-S2.

114 **2.2 Aerosol Flow Tube Experiment**

115 The naphthalene-derived SOA air-flow was controlled by a needle valve and sent into a charcoal
116 denuder (100-160 mL min⁻¹) (Sigma Aldrich, Norit RBAA-3) to reduce concentrations of gaseous
117 compounds and then into a differential mobility analyzer (DMA, TSI model 3081, impactor size
118 0.0508 cm) to produce monodispersed particles of desired size (mobility-equivalent diameter). The
119 size selection by DMA further reduced the concentration of gaseous compounds in the flow. The
120 size-selected SOA and VOC or SO₂ (Linde, France) were injected into a temperature-controlled
121 horizontal jacketed aerosols flow tube (AFT) (6 cm internal diameter, 180 cm length) made of
122 Pyrex (Wang et al., 2020a). In order to reduce the evaporative loss of the naphthalene-SOA
123 particles that is known to happen after size selection (Li et al., 2019b; Yli-Juuti et al., 2017), the
124 temperature inside the AFT was kept at 285 K. The RH inside the AFT was calculated based on
125 the measured temperature and RH of the aerosol flow upon exiting the AFT. The AFT was
126 surrounded by eight UV-lamps (Cleo, Philips, Netherlands) with a continuous emission spectrum
127 over 300-420 nm and a total irradiance of 6×10^{15} photon cm⁻² s⁻¹ (Dupart et al., 2012).

128 As shown in Figure 1, the aerosol flow was diluted by a factor of ~2 with pure air before
129 being sent to a scanning mobility particle sizer (SMPS, TSI 3936, impactor size 0.071 cm), an SO₂
130 analyzer (Thermo 43i) and an Aerodyne compact time-of-flight (cTOF) aerosol mass spectrometer
131 (AMS), to characterize the particle size distributions in the range of 15-700 nm, gaseous SO₂
132 concentration, and particle-phase sulfate production, respectively. The diluted aerosol flow was

133 further diluted with pure air before being analyzed by a stander SO₂ analyzer. More details about
134 the SMPS and AMS measurements are provided in the Supporting Information section (Text S3).
135 In some experiments, a selected VOC was continuously injected in the AFT together with the
136 particles. For this purpose, a permeation tube placed in a temperature controlled oven (Dynacal,
137 Valco Instruments Co. Inc., U.S., using VICI Metronics, U.S., Dynacalibrator, model 150) was
138 used to generate a specific concentration of d-limonene or β -pinene (Rossignol et al., 2014). A
139 high-resolution proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS 8000,
140 Ionicon Analytik) was then used to measure their concentrations. The detailed setup and calibration
141 of the PTR-MS were described in a previous study (Kalalian et al., 2020).

142 **3. Results and Discussion**

143 In previously published control experiments, only one VOC or SO₂ was injected into the AFT
144 (without naphthalene-derived SOA) under similar conditions to other experiments (i.e., the same
145 RH, UV exposure, temperature, and residence time). During these experiments, no loss of VOC or
146 SO₂ and no particle formation were observed (Aregahegn et al., 2013), indicating that gas-phase
147 oxidation of the VOC or SO₂ was not taking place in the AFT, due to an absence of gaseous oxidants.

148 In the first series of experiments, naphthalene-derived SOA (~ 5700 particles cm⁻³, median
149 size ~ 46 nm) and SO₂ (1 ppm after dilution) were injected into the AFT with a residence time of
150 16 min at a high RH of 86-90%. Figure 2A shows a typical profile for the evolution of the median
151 and mean diameters of the particles at the outlet of the AFT. Notably, both the median and mean
152 diameters of particles (before UV irradiation) were smaller than selected inlet sizes, indicating
153 some particle evaporation in the first DMA and AFT. A small particle growth was observed once
154 the UV lights were switched on, growing 2 nm in terms of median and mean diameters. In addition,
155 the Diameter Growth Factor (DGF (%) = $((D_p - D_{p0}) / D_p) \times 100$) was calculated for different

156 experimental conditions (see Table 1). As RH decreases to 61-65% and 40-43%, the particle size
157 measurements indicate particle shrinking instead of growth when naphthalene-derived SOA were
158 exposed to 1 ppm SO₂ and UV irradiation. This is likely due to the particle phase undergoing
159 photodegradation when exposed to UV irradiation, resulting in smaller particle sizes. Indeed, it has
160 been shown that the photodegradation of SOA particles could produce small oxygenated VOCs
161 evaporating to the gas phase (Malecha & Nizkorodov, 2016, 2017; Wong et al., 2015). Notably, at
162 RH 40-49%, the DGF was even lower when SOA particles were exposed to SO₂ compared to
163 control experiments, possibly due to the more acidic aerosol phase enhancing the evaporation of
164 small organic acids from particles. Slade et al. (2017) suggested that degradation of SOA under
165 viscous conditions (i.e., low RH), where diffusion into the bulk is prevented, tends to promote the
166 production of multiple generations of oxidation of the same molecule, resulting in fragmentation
167 and evaporation. Such processes could also be occurring in our experiments at low RH when SO₂
168 is present.

169 In the second series of experiments, 100 nm naphthalene-derived SOA particles, up to 6000
170 particles cm⁻³, were size-selected and exposed to 0.8 ppm SO₂ for sulfate production measurement
171 experiments. The particle size-selection was changed (from 46 to 100 nm) due to the low
172 transmission efficiency of the cTOF-AMS for particles less than 60 nm. The total amount of all
173 sulfate was then monitored (the cTOF instrument has limited capabilities to distinguish between
174 the inorganic and organic sulfate). Figure 2B shows that at different RHs, particulate sulfate was
175 produced from both dark and photosensitized chemistry. The dark production of particulate sulfate
176 can be explained by a couple of factors. Firstly, organic peroxides were found to account for ~26.2%
177 of the total naphthalene-SOA mass (Kautzman et al., 2010), which are believed to oxidize SO₂ to
178 sulfate and organosulfates (Wang et al., 2019; Yao et al., 2019; Ye et al., 2018a). In addition,

179 dissolved S(IV) may react with aldehydes and quinones in naphthalene-derived SOA (Kautzman
180 et al., 2010) to produce organosulfonates (LuValle, 1952; Olson & Hoffmann, 1989). All these
181 pathways could contribute to the measured sulfate in the dark, which are in the range of 0.003-0.11
182 $\mu\text{g m}^{-3}$. In addition, a previous study showed that the sulfate production from the reaction between
183 SO_2 and α -pinene-derived SOA exhibits an exponential dependence on RH (Yao et al., 2019),
184 which is similar to the result obtained in the present study (Figure 2B).

185 When the UV lights were switched on, 0.05-0.08 $\mu\text{g m}^{-3}$ of sulfate (i.e., 0.2-0.3 $\mu\text{g m}^{-3} \text{ h}^{-1}$)
186 were produced at all RHs (Figure 2B). However, although the total sulfate production increases as
187 the RH increases, the sulfate production attributable to the photosensitized oxidation at RH 81-84%
188 is the lowest. This indicates a more complex RH dependence on the photochemical mechanism.
189 Saukko et al. (2012) have investigated the physical phase state (solid, semi-solid, or liquid) of SOA
190 derived from various precursors by measuring their bounce behavior after inertial impaction on a
191 solid substrate. The measured bounce fraction was evaluated as a function of RH and SOA
192 oxidation level (O / C). In the case of naphthalene-derived SOA, the bounce factor was indicative
193 of an amorphous solid or semi-solid state, up to RH close to 70%. At greater RH values, this factor
194 decreased, indicating a phase change with particles having a less viscous, more "liquid-like"
195 material. These trends are to be compared with the data shown in Figure 2B, where the dark
196 chemistry was predominant only at high RH. Such chemistry could be driven, among other factors,
197 by the peroxide, aldehyde, and quinone (i.e., naphthoquinone) compounds present in such particles
198 (Kautzman et al., 2010) forming organosulfates, organosulfonates and sulfate (LuValle, 1952;
199 Olson & Hoffmann, 1989; Wang et al., 2019; Yao et al., 2019; Ye et al., 2018a). But the fact that
200 it occurs more efficiently at high RH (i.e., on more liquid particles), points towards a bulk process
201 where the chemistry occurs after solubilization of the incoming SO_2 molecules. In addition, the

202 sulfate formed from dark chemistry can also impact physical properties such as hygroscopicity,
203 acidity, and phase state (Hodas et al., 2015; Saukko et al., 2012), which may further influence the
204 solubility of S(IV) in the aerosol phase.

205 In contrast, the photochemical fraction of sulfate production is reduced at higher RHs but
206 gains in importance at low RH, where potentially the surface, or a small shell close to the surface,
207 is available for reaction. Notably, the previous studies showed that in-particle diffusion is not rate-
208 limiting to SO₂ uptake by α -pinene-derived SOA at low RH (<10%), whilst toluene-derived SOA
209 starts to lose the resistance above 20% RH (Yao et al., 2019; Ye et al., 2016, 2018b). Therefore, a
210 significant diffusion limitation is not expected in the present study. Besides, SO₂ could also be
211 excited into the triplet state (i.e., SO₂) by direct absorption of light with wavelength from 240 to
212 330 nm, which could react with H₂O to produce sulfate (Kroll et al., 2018; Martins-Costa et al.,
213 2018). However, this sulfate formation pathway was shown to be minor significant in our AFT
214 system due to the weak overlap of SO₂ light absorption and spectral irradiance of our lamps (Wang
215 et al., 2020a). Additionally, the bulk chemistry may also consume the existing photosensitizers and
216 explain the reduced fraction of photochemically produced sulfate at high RHs. Thus, at higher RHs
217 sulfate production is dominated by bulk phase solubilization and subsequent oxidation of SO₂,
218 whereas photosensitized oxidation at the surface of the particles dominates at lower RHs.

219 It is notable that the mean particle size of SOA decreased from 93 nm to 85 nm as the RH
220 increased from 37-39% to 81-84% in the dark, possibly due to the moisture-induced changes in
221 SOA morphology or phase and high evaporation of SOA at high RH (Li et al., 2019b; Wilson et
222 al., 2015; Wong et al., 2015; Yli-Juuti et al., 2017), reducing the surface area and volume by ~16%
223 and ~24%, respectively. Figures 2C and 2D show that sulfate production decreases as the light
224 intensity and SO₂ concentration decrease.

225 Traditionally, SO₂ oxidation is known to be mainly driven by gas-phase reactions with OH
226 radicals, ozone, H₂O₂, nitrogen dioxide (NO₂), and transition-metal ions in the aqueous phase
227 (Cheng et al., 2016), whilst interfacial SO₂ oxidation on acidic microdroplets (Hung & Hoffmann,
228 2015) and SO₂ triplet state chemistry (Kroll et al., 2018; Martins-Costa et al., 2018) were also
229 suggested to play a role in the sulfate formation. However, the photosensitized oxidation of SO₂
230 has recently been discussed as an important contributor to sulfate formation on biomass burning
231 type particles (Wang et al., 2020a). Our findings here now extend such observations also to more
232 anthropogenic particles and are posing the question whether such photosensitized processes are
233 widespread.

234 To test whether these particles exhibit photosensitized reactivity toward different partner
235 molecules, we also exposed them to gaseous d-limonene or β -pinene. Control experiments using
236 seed particles containing only ammonium sulfate or ammonium sulfate/succinic acid exposed to
237 limonene and UV light did not lead to particle growth (Aregahegn et al., 2013; Monge et al., 2012).
238 In contrast, as shown in Figure 3 and Table 1, the particle size of naphthalene-derived SOA
239 particles (starting diameter of 37 nm) in the presence of 0.1 ppm limonene increased by 50.8% and
240 58.7% at RH 39-43% and 84-88%, respectively, corresponding to a residence time of 25 min. This
241 is a remarkable amount of growth, implying that particle volume goes up by $(2.0-2.5)^3$ or by a
242 factor of 8-16. In addition, the reaction with 0.8 ppm β -pinene at RH 45-47% and 85-89% resulted
243 in similarly large DGFs of 8.9% and 24.2%. The RH dependence of particle growth is mainly
244 driven by the enhanced solubility of naphthalene-derived SOA (Yao et al., 2019). Such experiments
245 are meant to show that these particles are reactive toward unsaturated VOCs (Aregahegn et al.,
246 2013; Monge et al., 2012), since d-limonene was found to be a more efficient SOA precursor
247 compared to β -pinene, but are not meant to suggest a strong involvement in particle growth in the

248 ambient atmosphere (due to the unrealistic experimental conditions). Similar to the study of
249 Aregahegn et al. (2013), such growth is probably caused by the formation of highly oxygenated
250 products through limonene or β -pinene reacting with the triplet state of the photosensitizers (Monge
251 et al., 2012; Rossignol et al., 2014).

252 For example, the excited photosensitizer can abstract a hydrogen from an organic molecule
253 (i.e., d-limonene or β -pinene), through either a direct transfer or proceed via an electron transfer
254 followed by a proton transfer (Rossignol et al., 2014). Since the initial step triggering the
255 photosensitized uptake is a H-abstraction reaction (and not an addition to a double bond), VOCs
256 having weak C-H bonds will react faster, which is observed here for limonene. The reduced
257 photosensitizer radical can be oxidized to the original ground state in the presence of O_2 , at the
258 same time, producing superoxide radicals ($HO_2^{\cdot}/O_2^{\cdot-}$) (Aregahegn et al., 2013). The photoproduct
259 VOC and photosensitizer radicals can further react with other molecules or be oxidized by HO_2 or
260 O_2 , to produce new products. The study of Rossignol et al. (2014) found that highly oxygenated
261 organic compounds including compounds retaining the same number of carbons as d-limonene
262 were produced from the reaction of the IC triplet state and d-limonene in the aerosol phase through
263 ring-opening and intramolecular isomerization during the limonene oxidation process.

264 Interestingly, both naphthalene-derived SOAs and seed particles containing
265 photosensitizers grow efficiently even at low RH when exposed to limonene and β -pinene VOCs
266 (Table 1) (Aregahegn et al., 2013; Monge et al., 2012). This indicates that the photosensitized
267 processes may occur at the surface and be sustained even on solid or semi-solid particles without
268 passivation. This is in contrast to the expected behavior of a solid where it is expected that the high
269 viscosities promote radical recombination and the surface is expected to be rapidly passivated. It
270 is beyond the capabilities of these experiments to unravel the molecular reason for this observation,

271 but one could speculate that the presence of a photochemically active surface may locally change
272 the nature of the surface or induce chain reactions that may propagate some surface reactivity.
273 Another possibility is the triplet state of these photoactive compounds convert molecular oxygen
274 into reactive oxygen (e.g., O_2^- or 1O_2) sustaining surface reactivity, which would be in agreement
275 with high 1O_2 yield from naphthalene-SOA in aqueous solutions (Manfrin et al., 2019). The
276 produced oxygenated VOC may also form a new phase beneath the surface, thus keeping the
277 surface open for more reactions. This type of liquid-liquid phase separation has been observed for
278 various SOA types even under lower RH conditions observed here (Huang et al., 2021). Whatever
279 the underlying reason, these observations tend to support that the surface of such solid or semi-
280 solid particles will not passivate while being illuminated with actinic light.

281 Notably, the increased DGF under high RH conditions indicates that the underlying
282 photochemical mechanisms are different for the VOCs and for SO_2 . Wang et al. (2020a) suggested
283 a direct reaction of SO_2 with the organic triplet states through different pathways, possibly
284 influenced by pH. On the other hand, Rossignol et al. (2014) suggested that the underlying
285 mechanism for the VOC uptake is H abstraction followed by the production of multiple generation
286 multiple products (by condensed phase autooxidation). As previously mentioned, at low RH, these
287 first-generation products are concentrated at the surface (because they cannot diffuse to the bulk
288 under highly viscous conditions) where they remain fully exposed to oxidants and undergo rapid
289 further oxidation and fragmentation, yielding highly-oxygenated products with lower molar mass.
290 Those may therefore degas (or desorb) preferably at low RH compared to high RH where diffusion
291 into the bulk is possible. Therefore, the different trends between the VOCs and SO_2 is possibly to
292 a combination of mass transport limitations, and different chemistries being influenced by pH.

293 **4. Conclusions**

294 Naphthalene is ubiquitous in suburban and urban areas and its OH radical driven oxidation
295 produces oxygenated aromatic compounds with low volatility forming secondary organic aerosols.
296 Those particles are found to be reactive in the dark toward SO₂ where the reaction of dissolved
297 S(IV) with naphthalene oxidation products such as quinones, aldehydes, and organic peroxides are
298 expected to produce organosulfonates, organosulfates and sulfates. The dark production of sulfate
299 was observed to increase at high humidity and hence on liquid like particles. In addition, these
300 particles possess photosensitizing properties at lower humidity (< 70% RH), and can oxidize SO₂
301 even on solid or semi-solid particles. Moreover, the particle size of naphthalene-derived SOA
302 grows efficiently under irradiation in the presence of VOCs, especially d-limonene. As the RH
303 increases, the photosensitized particle growth becomes more efficient. These results indicate that
304 the formation of sulfate and oxygenated organic compounds through naphthalene-derived SOA
305 photoinduced reactions contribute to the sulfate concentration and size/mass of SOA particles.

306 **Declaration of Competing Interest**

307 The authors declare no conflict of interest.

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314

315 **References**

- 316 Aiona, P. K., Luek, J. L., Timko, S. A., Powers, L. C., Gonsior, M., & Nizkorodov, S. A. (2018).
317 Effect of Photolysis on Absorption and Fluorescence Spectra of Light-Absorbing Secondary
318 Organic Aerosols. *ACS Earth and Space Chemistry*, 2(3), 235–245.
319 <https://doi.org/10.1021/acsearthspacechem.7b00153>
- 320 Allan, J. D., Bower, K. N., Coe, H., Boudries, H., Jayne, J. T., Canagaratna, M. R., et al. (2004).
321 Submicron aerosol composition at Trinidad Head, California, during ITCT 2K2: Its
322 relationship with gas phase volatile organic carbon and assessment of instrument performance.
323 *Journal of Geophysical Research D: Atmospheres*, 109(23), 1–16.
324 <https://doi.org/10.1029/2003JD004208>
- 325 Aregahegn, K. Z., Nozière, B., & George, C. (2013). Organic aerosol formation photo-enhanced
326 by the formation of secondary photosensitizers in aerosols. *Faraday Discussions*, 165, 123–
327 134. <https://doi.org/10.1039/c3fd00044c>
- 328 Canonica, S., Jans, U. R. S., Stemmler, K., & Hoigne, J. (1995). Transformation Kinetics of
329 Phenols in Water: Photosensitization. *Environmental Science & Technology*, 29(7), 1822–
330 1831.
- 331 Chan, A. W. H., Kautzman, K. E., Chhabra, P. S., Surratt, J. D., Chan, M. N., Crounse, J. D., et al.
332 (2009). Secondary organic aerosol formation from photooxidation of naphthalene and
333 alkylnaphthalenes: Implications for oxidation of intermediate volatility organic compounds
334 (IVOCs). *Atmospheric Chemistry and Physics*, 9(9), 3049–3060. <https://doi.org/10.5194/acp-9-3049-2009>
- 336 Cheng, Y., Zheng, G., Wei, C., Mu, Q., Zheng, B., Wang, Z., et al. (2016). Reactive nitrogen
337 chemistry in aerosol water as a source of sulfate during haze events in China. *Science*
338 *Advances*, 2(12), e1601530. <https://doi.org/10.1126/sciadv.1601530>
- 339 Delhomme, O., Millet, M., & Herckes, P. (2008). Determination of oxygenated polycyclic aromatic
340 hydrocarbons in atmospheric aerosol samples by liquid chromatography-tandem mass
341 spectrometry. *Talanta*, 74(4), 703–710. <https://doi.org/10.1016/j.talanta.2007.06.037>
- 342 Dupart, Y., King, S. M., Nekat, B., Nowak, A., Wiedensohler, A., Herrmann, H., et al. (2012).
343 Mineral dust photochemistry induces nucleation events in the presence of SO₂. *Proceedings*
344 *of the National Academy of Sciences*, 109(51), 20842–20847.
345 <https://doi.org/10.1073/pnas.1212297109>
- 346 Eatough, D. J., Caka, F. M., & Farber, R. J. (1994). The Conversion of SO₂ to Sulfate in the
347 Atmosphere. *Israel Journal of Chemistry*, 34(3–4), 301–314.
348 <https://doi.org/10.1002/ijch.199400034>
- 349 Fankhauser, A. M., Bourque, M., Almazan, J., Marin, D., Fernandez, L., Hutheesing, R., et al.
350 (2020). Impact of Environmental Conditions on Secondary Organic Aerosol Production from
351 Photosensitized Humic Acid. *Environmental Science & Technology*, 54(9), 5385–5390.
352 <https://doi.org/10.1021/acs.est.9b07485>
- 353 Fuzzi, S., Baltensperger, U., Carslaw, K., Decesari, S., Denier Van Der Gon, H., Facchini, M. C.,
354 et al. (2015). Particulate matter, air quality and climate: Lessons learned and future needs.
355 *Atmospheric Chemistry and Physics*, 15(14), 8217–8299. <https://doi.org/10.5194/acp-15-8217-2015>
- 357 Gemayel, R., Emmelin, C., Perrier, S., Tomaz, S., Baboosian, V. J., Fishman, D. A., et al. (2021).
358 Quenching of ketone triplet excited states by atmospheric halides. *Environmental Science:*
359 *Atmospheres*, 1(1), 31–44. <https://doi.org/10.1039/d0ea00011f>

360 González Palacios, L., Corral Arroyo, P., Aregahegn, K. Z., Steimer, S. S., Bartels-Rausch, T.,
361 Nozière, B., et al. (2016). Heterogeneous photochemistry of imidazole-2-carboxaldehyde:
362 HO₂ radical formation and aerosol growth. *Atmospheric Chemistry and Physics*, 16(18),
363 11823–11836. <https://doi.org/10.5194/acp-16-11823-2016>

364 Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., et al. (2009).
365 The formation, properties and impact of secondary organic aerosol: Current and emerging
366 issues. *Atmospheric Chemistry and Physics*, 9(14), 5155–5236. <https://doi.org/10.5194/acp-9-5155-2009>

368 Hodas, N., Zuend, A., Mui, W., Flagan, R. C., & Seinfeld, J. H. (2015). Influence of particle-phase
369 state on the hygroscopic behavior of mixed organic-inorganic aerosols. *Atmospheric*
370 *Chemistry and Physics*, 15(9), 5027–5045. <https://doi.org/10.5194/acp-15-5027-2015>

371 Huang, G., Liu, Y., Shao, M., Li, Y., Chen, Q., Zheng, Y., et al. (2019). Potentially Important
372 Contribution of Gas-Phase Oxidation of Naphthalene and Methylnaphthalene to Secondary
373 Organic Aerosol during Haze Events in Beijing. *Environmental Science and Technology*,
374 53(3), 1235–1244. <https://doi.org/10.1021/acs.est.8b04523>

375 Huang, Y., Mahrt, F., Xu, S., Shiraiwa, M., Zuend, A., & Bertram, A. K. (2021). Coexistence of
376 three liquid phases in individual atmospheric aerosol particles. *Proceedings of the National*
377 *Academy of Sciences*, 118(16), e2102512118. <https://doi.org/10.1073/pnas.2102512118>

378 Hung, H. M., & Hoffmann, M. R. (2015). Oxidation of Gas-Phase SO₂ on the Surfaces of Acidic
379 Microdroplets: Implications for Sulfate and Sulfate Radical Anion Formation in the
380 Atmospheric Liquid Phase. *Environmental Science and Technology*, 49(23), 13768–13776.
381 <https://doi.org/10.1021/acs.est.5b01658>

382 Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., et al.
383 (2009). Evolution of organic aerosols in the atmosphere. *Science*, 326(5959), 1525–1529.
384 <https://doi.org/10.1126/science.1180353>

385 Kalalian, C., Abis, L., Depoorter, A., Lunardelli, B., Perrier, S., & George, C. (2020). Influence of
386 indoor chemistry on the emission of mVOCs from *Aspergillus niger* molds. *Science of the*
387 *Total Environment*, 741, 140148. <https://doi.org/10.1016/j.scitotenv.2020.140148>

388 Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., et al.
389 (2005). Organic aerosol and global climate modelling: a review. *Atmospheric Chemistry and*
390 *Physics*, 5(4), 1053–1123. <https://doi.org/10.5194/acp-5-1053-2005>

391 Kaur, R., Hudson, B. M., Draper, J., Tantillo, D. J., & Anastasio, C. (2019). Aqueous reactions of
392 organic triplet excited states with atmospheric alkenes. *Atmospheric Chemistry and Physics*,
393 19(7), 5021–5032. <https://doi.org/10.5194/acp-19-5021-2019>

394 Kautzman, K. E., Surratt, J. D., Chan, M. N., Chan, A. W. H., Hersey, S. P., Chhabra, P. S., et al.
395 (2010). Chemical composition of gas- and aerosol-phase products from the photooxidation of
396 naphthalene. *Journal of Physical Chemistry A*, 114(2), 913–934.
397 <https://doi.org/10.1021/jp908530s>

398 Kroll, J. A., Frandsen, B. N., Kjaergaard, H. G., & Vaida, V. (2018). Atmospheric Hydroxyl
399 Radical Source: Reaction of Triplet SO₂ and Water. *Journal of Physical Chemistry A*, 122(18),
400 4465–4469. <https://doi.org/10.1021/acs.jpca.8b03524>

401 Kuang, B. Y., Yeung, H. S., Lee, C. C., Griffith, S. M., & Yu, J. Z. (2018). Aromatic formulas in
402 ambient PM_{2.5} samples from Hong Kong determined using FT-ICR ultrahigh-resolution mass
403 spectrometry. *Analytical and Bioanalytical Chemistry*, 410(24), 6289–6304.
404 <https://doi.org/10.1007/s00216-018-1239-8>

405 Lee, H. J., Aiona, P. K., Laskin, A., Laskin, J., & Nizkorodov, S. A. (2014). Effect of solar radiation
406 on the optical properties and molecular composition of laboratory proxies of atmospheric

407 brown carbon. *Environmental Science and Technology*, 48(17), 10217–10226.
408 <https://doi.org/10.1021/es502515r>

409 Li, S., Jiang, X., Roveretto, M., George, C., Liu, L., Jiang, W., et al. (2019a). Photochemical aging
410 of atmospherically reactive organic compounds involving brown carbon at the air–aqueous
411 interface. *Atmospheric Chemistry and Physics*, 19(15), 9887–9902.
412 <https://doi.org/10.5194/acp-19-9887-2019>

413 Li, Z., Tikkanen, O. P., Buchholz, A., Hao, L., Kari, E., Yli-Juuti, T., & Virtanen, A. (2019b).
414 Effect of Decreased Temperature on the Evaporation of α -Pinene Secondary Organic Aerosol
415 Particles. *ACS Earth and Space Chemistry*, 3(12), 2775–2785.
416 <https://doi.org/10.1021/acsearthspacechem.9b00240>

417 Lin, P., Rincon, A. G., Kalberer, M., & Yu, J. Z. (2012). Elemental composition of HULIS in the
418 Pearl River Delta Region, China: Results inferred from positive and negative electrospray
419 high resolution mass spectrometric data. *Environmental Science and Technology*, 46(14),
420 7454–7462. <https://doi.org/10.1021/es300285d>

421 De Lucas, N. C., Ruis, C. P., Teixeira, R. I., Marçal, L. L., Garden, S. J., Corrêa, R. J., et al. (2014).
422 Photosensitizing properties of triplet furano and pyrano-1,2- naphthoquinones. *Journal of*
423 *Photochemistry and Photobiology A: Chemistry*, 276, 16–30.
424 <https://doi.org/10.1016/j.jphotochem.2013.11.010>

425 LuValle, J. E. (1952). The Reaction of Quinone and Sulfite.I. Intermediates. *Journal of the*
426 *American Chemical Society*, 74(12), 2970–2977. <https://doi.org/10.1021/ja01132a005>

427 Malecha, K. T., & Nizkorodov, S. A. (2016). Photodegradation of Secondary Organic Aerosol
428 Particles as a Source of Small, Oxygenated Volatile Organic Compounds. *Environmental*
429 *Science and Technology*, 50(18), 9990–9997. <https://doi.org/10.1021/acs.est.6b02313>

430 Malecha, K. T., & Nizkorodov, S. A. (2017). Feasibility of Photosensitized Reactions with
431 Secondary Organic Aerosol Particles in the Presence of Volatile Organic Compounds. *Journal*
432 *of Physical Chemistry A*, 121(26), 4961–4967. <https://doi.org/10.1021/acs.jpca.7b04066>

433 Manfrin, A., Nizkorodov, S. A., Malecha, K. T., Getzinger, G. J., McNeill, K., & Borduas-
434 Dedekind, N. (2019). Reactive Oxygen Species Production from Secondary Organic Aerosols:
435 The Importance of Singlet Oxygen. *Environmental Science and Technology*, 53(15), 8553–
436 8562. research-article. <https://doi.org/10.1021/acs.est.9b01609>

437 Martins-Costa, M. T. C., Anglada, J. M., Francisco, J. S., & Ruiz-López, M. F. (2018).
438 Photochemistry of SO₂ at the Air-Water Interface: A Source of OH and HOSO Radicals.
439 *Journal of the American Chemical Society*, 140(39), 12341–12344.
440 <https://doi.org/10.1021/jacs.8b07845>

441 McNeill, K., & Canonica, S. (2016). Triplet state dissolved organic matter in aquatic
442 photochemistry: Reaction mechanisms, substrate scope, and photophysical properties.
443 *Environmental Science: Processes and Impacts*, 18(11), 1381–1399.
444 <https://doi.org/10.1039/c6em00408c>

445 McWhinney, R. D., Zhou, S., & Abbatt, J. P. D. (2013). Naphthalene SOA: Redox activity and
446 naphthoquinone gas-particle partitioning. *Atmospheric Chemistry and Physics*, 13(19), 9731–
447 9744. <https://doi.org/10.5194/acp-13-9731-2013>

448 Monge, M. E., Rosenørn, T., Favez, O., Müller, M., Adler, G., Riziq, A. A., et al. (2012).
449 Alternative pathway for atmospheric particles growth. *Proceedings of the National Academy*
450 *of Sciences of the United States of America*, 109(18), 6840–6844.
451 <https://doi.org/10.1073/pnas.1120593109>

452 Nel, A. (2005). ATMOSPHERE: Enhanced: Air Pollution-Related Illness: Effects of Particles.
453 *Science*, 308(5723), 804–806. <https://doi.org/10.1126/science.1108752>

454 Oda, J., Nomura, S., Yasuhara, A., & Shibamoto, T. (2001). Mobile sources of atmospheric
455 polycyclic aromatic hydrocarbons in a roadway tunnel. *Atmospheric Environment*, 35(28),
456 4819–4827. [https://doi.org/10.1016/S1352-2310\(01\)00262-X](https://doi.org/10.1016/S1352-2310(01)00262-X)

457 Olson, T. M., & Hoffmann, M. R. (1989). Hydroxyalkylsulfonate formation: Its role as a S(IV)
458 reservoir in atmospheric water droplets. *Atmospheric Environment (1967)*, 23(5), 985–997.
459 [https://doi.org/10.1016/0004-6981\(89\)90302-8](https://doi.org/10.1016/0004-6981(89)90302-8)

460 Osburn, C. L., & Morris, D. P. (2003). Photochemistry of chromophoric dissolved organic matter
461 in natural waters. In E. W. Helbling & H. Zagarese (Eds.), *UV Effects in Aquatic Organisms*
462 *and Ecosystems* (Vol. 1, pp. 185–218). The Royal Society of Chemistry.
463 <https://doi.org/10.1039/9781847552266-00185>

464 Riva, M., Robinson, E. S., Perraudin, E., Donahue, N. M., & Villenave, E. (2015). Photochemical
465 aging of secondary organic aerosols generated from the photooxidation of polycyclic aromatic
466 hydrocarbons in the gas-phase. *Environmental Science and Technology*, 49(9), 5407–5416.
467 <https://doi.org/10.1021/acs.est.5b00442>

468 Rossignol, S., Aregahegn, K. Z., Tinel, L., Fine, L., Nozière, B., & George, C. (2014). Glyoxal
469 induced atmospheric photosensitized chemistry leading to organic aerosol growth.
470 *Environmental Science and Technology*, 48(6), 3218–3227.
471 <https://doi.org/10.1021/es405581g>

472 Sarangi, B., Aggarwal, S. G., Sinha, D., & Gupta, P. K. (2016). Aerosol effective density
473 measurement using scanning mobility particle sizer and quartz crystal microbalance with the
474 estimation of involved uncertainty. *Atmospheric Measurement Techniques*, 9(3), 859–875.
475 <https://doi.org/10.5194/amt-9-859-2016>

476 Saukko, E., Lambe, A. T., Massoli, P., Koop, T., Wright, J. P., Croasdale, D. R., et al. (2012).
477 Humidity-dependent phase state of SOA particles from biogenic and anthropogenic
478 precursors. *Atmospheric Chemistry and Physics*, 12(16), 7517–7529.
479 <https://doi.org/10.5194/acp-12-7517-2012>

480 Saxena, P., & Seigneur, C. (1987). On the oxidation of SO₂ to sulfate in atmospheric aerosols.
481 *Atmospheric Environment (1967)*, 21(4), 807–812. [https://doi.org/10.1016/0004-](https://doi.org/10.1016/0004-6981(87)90077-1)
482 [6981\(87\)90077-1](https://doi.org/10.1016/0004-6981(87)90077-1)

483 Slade, J. H., Shiraiwa, M., Arangio, A., Su, H., Pöschl, U., Wang, J., & Knopf, D. A. (2017). Cloud
484 droplet activation through oxidation of organic aerosol influenced by temperature and particle
485 phase state. *Geophysical Research Letters*, 44(3), 1583–1591.
486 <https://doi.org/10.1002/2016GL072424>

487 Smith, J. D., Sio, V., Yu, L., Zhang, Q., & Anastasio, C. (2014). Secondary organic aerosol
488 production from aqueous reactions of atmospheric phenols with an organic triplet excited state.
489 *Environmental Science and Technology*, 48(2), 1049–1057.
490 <https://doi.org/10.1021/es4045715>

491 Sudakin, D. L., Stone, D. L., & Power, L. (2011). Naphthalene mothballs: Emerging and recurring
492 issues and their relevance to environmental health. *Current Topics in Toxicology*, 7(541), 13–
493 19.

494 Tsui, W. G., Rao, Y., Dai, H. L., & McNeill, V. F. (2017). Modeling Photosensitized Secondary
495 Organic Aerosol Formation in Laboratory and Ambient Aerosols. *Environmental Science and*
496 *Technology*, 51(13), 7496–7501. <https://doi.org/10.1021/acs.est.7b01416>

497 Wang, S., Zhou, S., Tao, Y., Tsui, W. G., Ye, J., Yu, J. Z., et al. (2019). Organic Peroxides and
498 Sulfur Dioxide in Aerosol: Source of Particulate Sulfate. *Environmental Science and*
499 *Technology*, 53(18), 10695–10704. <https://doi.org/10.1021/acs.est.9b02591>

500 Wang, X., Hayeck, N., Brüggemann, M., Yao, L., Chen, H., Zhang, C., et al. (2017). Chemical

501 Characteristics of Organic Aerosols in Shanghai: A Study by Ultra-High-Performance Liquid
502 Chromatography Coupled with Orbitrap Mass Spectrometry. *Journal of Geophysical*
503 *Research: Atmospheres*, 1–20. <https://doi.org/10.1002/2017JD026930>

504 Wang, X., Gemayel, R., Hayeck, N., Perrier, S., Charbonnel, N., Xu, C., et al. (2020a).
505 Atmospheric Photosensitization: A New Pathway for Sulfate Formation. *Environmental*
506 *Science & Technology*, 54(6), 3114–3120. <https://doi.org/10.1021/acs.est.9b06347>

507 Wang, X., Hayeck, N., Brüggemann, M., Abis, L., Riva, M., Lu, Y., et al. (2020b). Chemical
508 Characteristics and Brown Carbon Chromophores of Atmospheric Organic Aerosols Over the
509 Yangtze River Channel: A Cruise Campaign. *Journal of Geophysical Research: Atmospheres*,
510 125(16), 1–13. <https://doi.org/10.1029/2020JD032497>

511 Wang, X. K., Rossignol, S., Ma, Y., Yao, L., Wang, M. Y., Chen, J. M., et al. (2016). Molecular
512 characterization of atmospheric particulate organosulfates in three megacities at the middle
513 and lower reaches of the Yangtze River. *Atmospheric Chemistry and Physics*, 16(4), 2285–
514 2298. <https://doi.org/10.5194/acp-16-2285-2016>

515 Wang, Y., Zhang, Q., Jiang, J., Zhou, W., Wang, B., He, K., et al. (2014). Key Role of Nitrate in
516 Phase Transitions of Urban Particles: Implications of Important Reactive Surfaces for
517 Secondary Aerosol Formation. *Journal of Geophysical Research: Atmospheres*, 425–440.
518 <https://doi.org/10.1002/2013JD021426>. Received

519 Watne, Å. K., Psichoudaki, M., Ljungström, E., Le Breton, M., Hallquist, M., Jerksjö, M., et al.
520 (2018). Fresh and Oxidized Emissions from In-Use Transit Buses Running on Diesel,
521 Biodiesel, and CNG. *Environmental Science and Technology*, 52(14), 7720–7728.
522 <https://doi.org/10.1021/acs.est.8b01394>

523 Wilson, J., Imre, D., Beránek, J., Shrivastava, M., & Zelenyuk, A. (2015). Evaporation kinetics of
524 laboratory-generated secondary organic aerosols at elevated relative humidity. *Environmental*
525 *Science and Technology*, 49(1), 243–249. <https://doi.org/10.1021/es505331d>

526 Wong, J. P. S., Zhou, S., & Abbatt, J. P. D. (2015). Changes in secondary organic aerosol
527 composition and mass due to photolysis: Relative humidity dependence. *Journal of Physical*
528 *Chemistry A*, 119(19), 4309–4316. <https://doi.org/10.1021/jp506898c>

529 Yao, M., Zhao, Y., Hu, M., Huang, D., Wang, Y., Yu, J. Z., & Yan, N. (2019). Multiphase
530 Reactions between Secondary Organic Aerosol and Sulfur Dioxide: Kinetics and
531 Contributions to Sulfate Formation and Aerosol Aging. *Environmental Science and*
532 *Technology Letters*, 6(12), 768–774. <https://doi.org/10.1021/acs.estlett.9b00657>

533 Ye, J., Abbatt, J. P. D., & Chan, A. W. H. (2018a). Novel pathway of SO₂ oxidation in the
534 atmosphere: reactions with monoterpene ozonolysis intermediates and secondary organic
535 aerosol. *Atmospheric Chemistry and Physics*, 18(8), 5549–5565. <https://doi.org/10.5194/acp-18-5549-2018>

536

537 Ye, Q., Robinson, E. S., Ding, X., Ye, P., Sullivan, R. C., & Donahue, N. M. (2016). Mixing of
538 secondary organic aerosols versus relative humidity. *Proceedings of the National Academy of*
539 *Sciences of the United States of America*, 113(45), 12649–12654.
540 <https://doi.org/10.1073/pnas.1604536113>

541 Ye, Q., Upshur, M. A., Robinson, E. S., Geiger, F. M., Sullivan, R. C., Thomson, R. J., & Donahue,
542 N. M. (2018b). Following Particle-Particle Mixing in Atmospheric Secondary Organic
543 Aerosols by Using Isotopically Labeled Terpenes. *Chem*, 4(2), 318–333.
544 <https://doi.org/10.1016/j.chempr.2017.12.008>

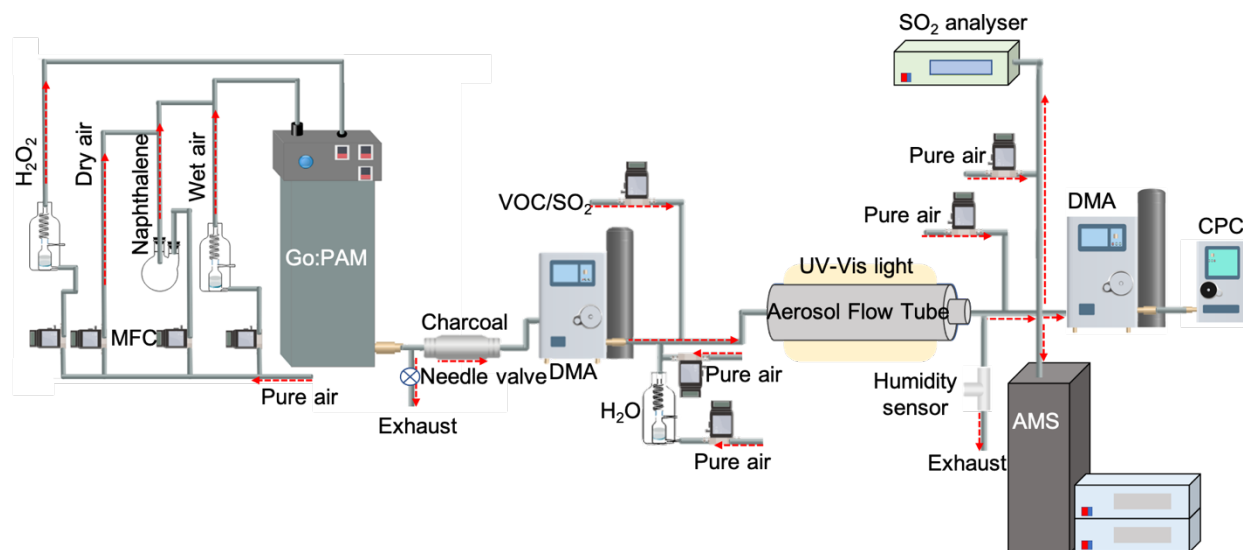
545 Yli-Juuti, T., Pajunoja, A., Tikkanen, O. P., Buchholz, A., Faiola, C., Väisänen, O., et al. (2017).
546 Factors controlling the evaporation of secondary organic aerosol from α -pinene ozonolysis.
547 *Geophysical Research Letters*, 44(5), 2562–2570. <https://doi.org/10.1002/2016GL072364>

548 Yu, L., Smith, J., Laskin, A., Anastasio, C., Laskin, J., & Zhang, Q. (2014). Chemical
549 characterization of SOA formed from aqueous-phase reactions of phenols with the triplet
550 excited state of carbonyl and hydroxyl radical. *Atmospheric Chemistry and Physics*, 14(24),
551 13801–13816. <https://doi.org/10.5194/acp-14-13801-2014>
552 Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Allan, J. D., Coe, H., Ulbrich, I., et al. (2007).
553 Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-
554 influenced Northern Hemisphere midlatitudes. *Geophysical Research Letters*, 34(13), 1–6.
555 <https://doi.org/10.1029/2007GL029979>
556 Zhang, Z., Lin, L., & Wang, L. (2012). Atmospheric oxidation mechanism of naphthalene initiated
557 by OH radical. A theoretical study. *Physical Chemistry Chemical Physics*, 14(8), 2645–2650.
558 <https://doi.org/10.1039/c2cp23271e>
559

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562 Figures



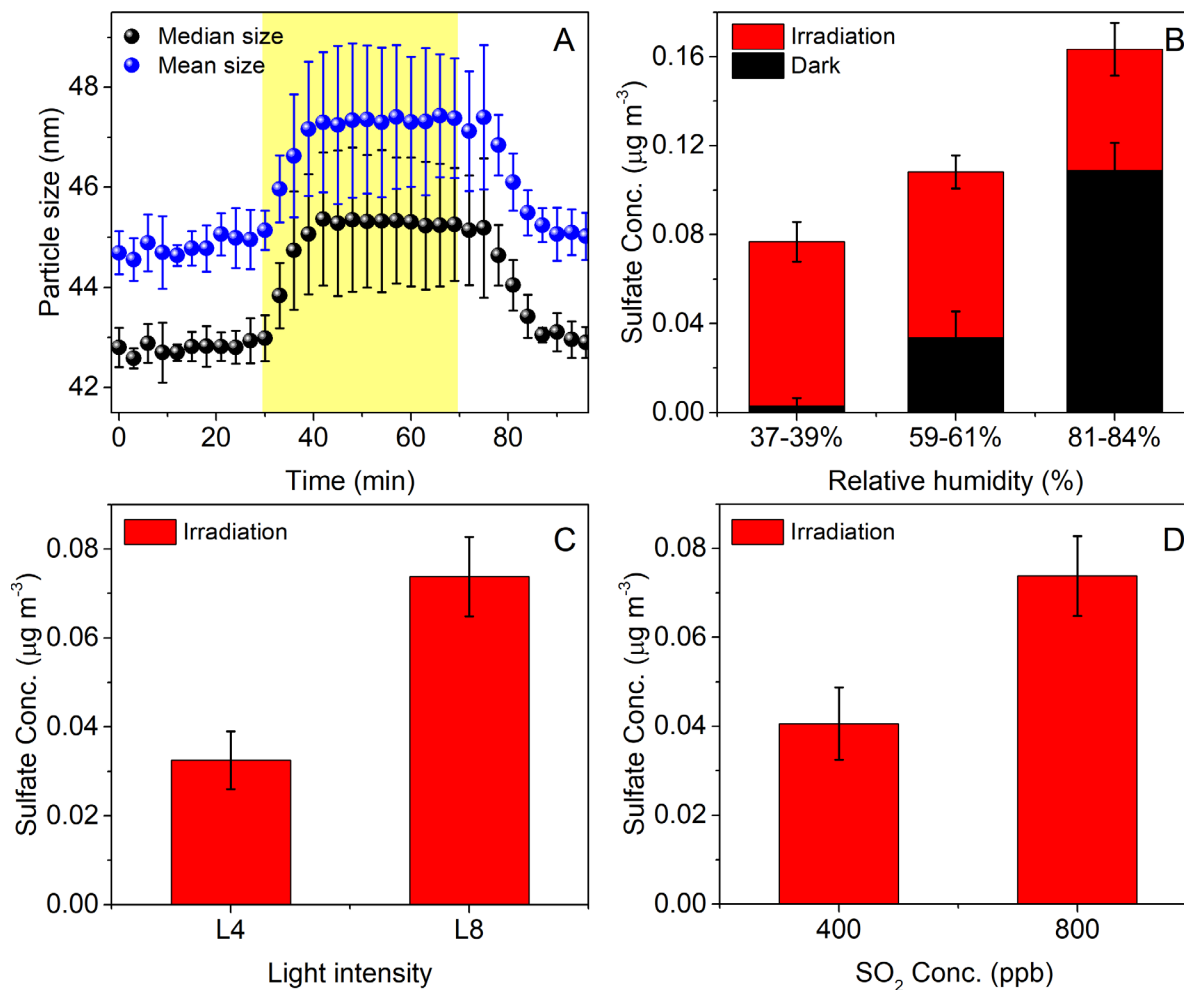
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564 **Figure 1.** Schematic of the experimental setup with the Go:PAM flow and aerosol flow reactors.

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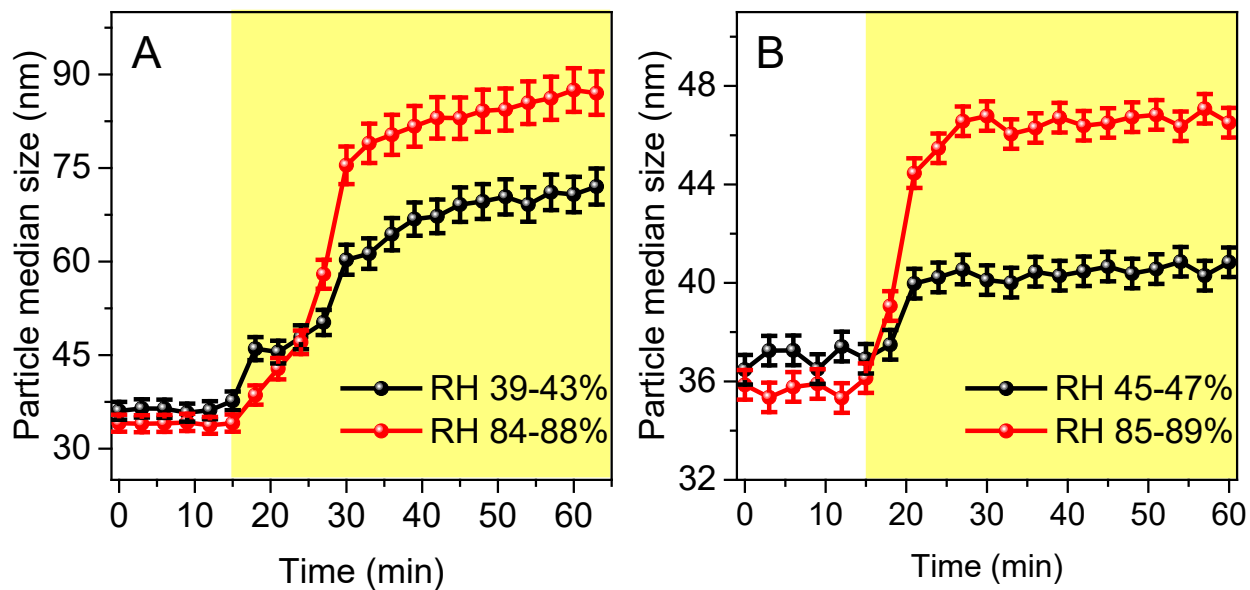
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570 **Figure 2.** Median and mean diameter ($\pm 2\sigma$) growths of naphthalene-derived SOA exposed to UV
 571 light and SO_2 for 16 min in the AFT (A). The yellow region corresponds to the irradiation time.
 572 Sulfate production as measured by the cTOF-AMS of naphthalene-derived SOA exposed to SO_2 at
 573 different RH (B), under different light intensities (C), and with different SO_2 concentrations (D).
 574 L4 means four lamps were turned on; and L8 means eight lamps were turned on.

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 577 **Figure 3.** Median diameter ($\pm 2\sigma$) growths of Nap-derived SOA exposed to UV-A light and 0.1
 578 ppm d-limonene (A) and 0.8 ppm β -pinene for 30 min in the AFT. The yellow region corresponds
 579 to the irradiation time.

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588 **Table 1.** Median Diameter Growth Factor (DGF, %) of naphthalene-derived SOA with different
 589 gaseous compounds and RH. D_{p0} , initial particle median diameter; D_p , particle median diameter
 590 after irradiation.

Gaseous compounds	Concentration (ppm)	Residence time (min)	RH	D_{p0} (nm)	D_p (nm)	DGF (%)
None	0	16	47-49%	44.1±0.2	43.5±0.3	-1.4
	0	16	68-71%	43.8±0.3	42.2±0.4	-3.8
	0	16	85-89%	42.4±0.2	41.4±0.3	-2.4
SO ₂	1	16	40-43%	44.8±0.2	43.0±0.3	-4.2
	1	16	61-65%	42.5±0.2	41.3±0.8	-2.9
	1	16	86-90%	42.8±0.4	44.7±0.7	4.3
	0.7	16	86-90%	42.9±0.2	43.9±0.2	2.3
	0.4	16	86-90%	42.9±0.2	43.1±0.2	0.5
d-Limonene	0.1	25	39-43%	36.4±0.7	71.4±1.3	50.8
	0.1	25	84-88%	34.0±0.2	85.4±1.6	58.7
β-pinene	0.8	25	45-47%	37.0±0.4	40.6±0.3	8.9
	0.8	25	85-89%	35.7±0.3	47.1±0.3	24.2

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