1	Sulfate formation via aerosol phase SO ₂ oxidation by model biomass
2	burning photosensitizers: 3,4-dimethoxybenzaldehyde, vanillin and
3	syringaldehyde using single particle mixing state analysis
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19 Abstract. Atmospheric oxidation of sulfur dioxide (SO₂) to sulfate has been widely investigated by means of gas phase and 20 in-cloud chemistry studies. Recent field measurements have shown significant sulfate formation in cloud-free environments 21 with high aerosol loadings. As an important fraction of biomass burning aerosol components, particulate phenolic and non-22 phenolic aromatic carbonyls may initiate photosensitized aerosol multiphase oxidation of SO₂, of which our knowledge 23 however is still in its nascent stage. In this study, on the basis of single-particle aerosol mass spectrometry (SPAMS) 24 measurements, we find evident sulfate formation in the biomass burning-derived photosensitizer particles under UV and SO₂ 25 exposure, attributable to photosensitized oxidation of S(IV), while almost no sulfate was observed under dark and existence 26 of SO₂. The efficiency of sulfate production under UV irradiation, represented by the number percentage of sulfate-containing 27 particles (99-43%) and sulfate relative peak area (RPA) (0.67-0.12) in single particle spectra, in descending order, were 3,4-28 dimethoxybenzaldehyde (DMB), vanillin (VL) and syringaldehyde (SyrAld). Internal mixtures of VL and potassium nitrate 29 gave a slightly lower number percentage and RPA of sulfate than VL particles alone. In externally mixed VL and potassium 30 nitrate particles, sulfate was predominantly formed on the former, confirming that sulfate formation via photosensitization 31 prevails over that via nitrate photolysis. Our results suggest that photosensitized oxidation of S(IV) could make an important 32 contribution to aerosol sulfate formation, especially in areas influenced by biomass burning.

33

34 1. Introduction

35 Sulfate is a key component of fine particulate matter in the atmosphere, which impacts air quality, climate, and human and 36 ecosystem health (Nel, 2005; Fuzzi et al., 2015; Grantz et al., 2003). Traditional atmospheric models, including the gas-phase 37 oxidation of sulfur dioxide (SO₂) by hydroxyl radical (OH) (Calvert et al., 1978) and stabilized Criegee intermediates (Cheng 38 et al., 2016) and a series of aqueous, in-cloud oxidation of SO₂, underpredict the sulfate production during heavy pollution 39 episodes in China (Zheng et al., 2015; Zhang et al., 2015; Wang et al., 2014; Liu and Abbatt, 2021). Although the liquid water 40 content (LWC) is generally much lower in aerosol particles than in fog and cloud droplets, it was reported that aerosol 41 multiphase oxidation processes are important, especially in polluted and high relative humidity (RH) conditions (Liu et al., 42 2021; Liu et al., 2020). The typical oxidants involved in multiphase oxidation of S(IV) in aerosol particles include dissolved 43 ozone (O₃) (Hoffmann and Calvert, 1985), hydrogen peroxide (H₂O₂) (Hoffmann and Calvert, 1985), transition metal ions

(TMIs, i.e., Fe (III) and Mn(II)) (Ibusuki and Takeuchi, 1987; Harris et al., 2013; Alexander et al., 2009; Martin and Good, 1991), methyl hydrogen peroxide (Walcek and Taylor, 1986) and peroxyacetic acid (Walcek and Taylor, 1986). To narrow the gap between the measured and modeled sulfate production, new chemical pathways have been suggested involving nitrogen dioxide (NO₂) (Wang et al., 2016; Cheng et al., 2016), organic peroxides (Yao et al., 2019; Ye et al., 2018), oxidants from particulate nitrate photolysis (Gen et al., 2019a, b; Zhang et al., 2020), and hypohalous acid (HOX, e.g., HOCl and HOBr) (Liu and Abbatt, 2020). However, the missing sulfate source has still remained unclear and controversial.

50 Photosensitization in atmospheric aerosols has been recently proposed to initiate novel chemistry in the formation of 51 secondary pollutants (George et al., 2015). Upon irradiation, atmospheric photosensitizers such as aromatic carbonyls can 52 generate triplet excited states (³C*) (Canonica et al., 1995; Anastasio et al., 1996; Smith et al., 2014; Kaur and Anastasio, 53 2018; Kaur et al., 2019; Smith et al., 2016), which can oxidize phenols at higher rates compared to OH, particularly under 54 acidic conditions (Smith et al., 2014). In addition to being an oxidant, 3C* can also react with O2 to generate secondary 55 oxidants, such as singlet oxygen ($^{1}O_{2}$), superoxide (O_{2}^{-}), hydroperoxyl radical ($^{+}HO_{2}$), and hydroxyl radicals (^{+}OH) (Corral 56 Arroyo et al., 2018; Dalrymple et al., 2010; George et al., 2018). Biomass burning is an important source of aromatic 57 carbonyls (Rogge et al., 1998; Nolte et al., 2001; Schauer et al., 2001), and the concentrations of phenolic and non-phenolic 58 carbonyls are comparable in biomass burning smoke (Simoneit et al., 1993; Anastasio et al., 1996). Direct photosensitized 59 oxidation of vanillin (a typical aromatic carbonyl photosensitizer) has been reported as an important pathway to form aqueous 60 secondary organic aerosol in areas influenced by biomass burning, with reaction products dominated by brown carbon 61 chromophores (Mabato et al., 2022; Mabato et al., 2023). However, only limited studies focused on the role of biomass 62 burning-derived photosensitizers in S(IV) oxidation. Wang et al. (2020) reported that photosensitized chemistry involving the 63 humic fraction of aerosols during Chinese haze events could explain a significant fraction of the observed sulfate formation, 64 which highlighted the potential photosensitizing properties played by biomass burning particles. Naphthalene, emitted 65 primarily from fossil fuel combustion and biomass burning, can be oxidized by hydroxyl radicals to form secondary organic 66 aerosol (SOA), which was observed to possess interfacial photosensitizing properties (Wang et al., 2021). These recent studies 67 have advanced our understanding of the photosensitized processes, but the types of photosensitizers from biomass burning are 68 diverse and their properties are complex, limiting us from further assessing the importance of photosensitized sulfate formation 69 in the dynamic ambient atmosphere. In this study, we investigate sulfate formation via aerosol phase SO₂ oxidation by biomass 70 burning-derived aromatic carbonyl photosensitizers, including both non-phenolic (3,4-dimethoxybenzaldehyde, DMB) and 71 phenolic photosensitizers (vanillin, VL and syringaldehyde, SyrAld) with similar molar absorptivity at atmospheric relevant 72 wavelengths (Figure S1, Supporting information), in an oxidation flow reactor (OFR) utilizing a single particle aerosol mass 73 spectrometer (SPAMS). Nitrate photolysis has been reported as a typical sulfate formation pathway initiated by particulate 74 photoactive compounds, similar to photosensitization (Gen et al., 2022). The objectives of this study are to semi-quantitatively 75 evaluate the extent of sulfate formation in photosensitizer particles and qualitatively compare the relative atmospheric 76 importance of particulate photosensitization and nitrate photolysis in sulfate formation.

77

2. Methods

79 2.1 Materials and experimental setup

80 A vaporization - condensation method was used to coat photosensitizing or non-photosensitizing species on 0.3 µm polystyrene 81 latex sphere (PSL) particles (Thermo Fisher Scientific Inc., MA) (Qi et al., 2019). A detailed experimental setup is shown in 82 Figure S2a and the initial experimental conditions are summarized in Table S1. All chemicals, including DMB (Acros 83 Organics, 99+%), VL (Acros Organics, 99%), SyrAld (Sigma Aldrich, 98%), benzoic acid (BA, Acros Organics, 99.6%), 84 potassium nitrate (KNO₃, Sigma Aldrich, 99+%) and oxalic acid (Sigma Aldrich, 99.9+%) were used as purchased. The 85 structures of the chemicals used are provided in Table S2. PSL particles were selected as condensation nuclei due to their 86 chemically and thermally inert nature. Their size did not change upon passing through the dryer or glass bottle at 120°C oil 87 bath or exposure to SO₂ or UV irradiation (Figure S3). In addition, PSL particles are difficult to be ionized and do not 88 complicate the interpretation of mass spectra. PSL condensation nuclei were generated by using a constant output atomizer 89 (TSI 3076) with pure N_2 gas (>99.995 %), and a portion of the particles passed through a diffusion dryer at a flow rate of 300 90 mL min⁻¹ to achieve RH <10%. The dried particles subsequently passed through a heated glass bottle (inlet about 2 inches 91 above the bottom) containing ~0.5g of either DMB, VL, SyrAld or BA at the bottom. The heating temperatures of the glass 92 bottle were regulated using an oil bath near the melting points of the chemicals. The generated organic vapor condensed to 93 form coatings onto the PSL particles. The coating thickness was estimated by the measured particle size increase by the

94 SPAMS. For control experiments with PSL-only particles, the particles passed through the same glass bottle containing no 95 chemicals. Photosensitizing (DMB, VL, SyrAld) (Smith et al., 2015, 2016; Smith et al., 2014) and non-photosensitizing 96 (BA) (Smith et al., 2015) species coated particles or uncoated PSL-only particles were then introduced into an OFR (volume 97 of approximately 7.2 L) and mixed with SO₂ gas. SO₂ was delivered by a flow of around 11 mL min⁻¹ (203 ppm, mixing with 98 pure N₂, Scientific Gas Engineering Co., Ltd.) to achieve the SO₂ concentration of around 750 ppb in the OFR. Depending on 99 the experiment, the RH in the OFR was regulated at ~80% or 20% to achieve different content of aerosol water by passing 100 HEPA-filtered and activated-carbon-denuded compressed air or pure N₂ through water bubblers. Note that the photosensitizers 101 may be (polymorphic) solid or semi-solid due to their low solubility and hygroscopicity, even at 80% RH (Kavuru et al., 2016; 102 Hussain et al., 2001). For example, Mochida and Kawamura (2004) reported that pyrolysis products of lignin with -COOH, 103 including vanillic acid and syringic acid, showed no hygroscopic growth even at RH of more than 90%. They also proposed 104 that other pyrolysis products with chemical structures such as -CHO may have even lower hygroscopicity than -COOH and 105 would not show measurable particle growth. Though we could not observe the phase states of the particles, both aerosol liquid 106 water in (partially) deliquescent particles and surface adsorbed water content on solid particles at 80% RH were expected to 107 be higher than at 20% RH (Rubasinghege and Grassian, 2013). Experiments under air enable the generation of secondary 108 oxidants. Conversely, the N₂ experiments would inhibit the formation of secondary oxidants, which can lead to triplets-driven 109 reactions (Chen et al., 2020). The total flow in the OFR was around 3 L min⁻¹, resulting in a residence time of ~ 2.5 min. There 110 are four UVA lamps (Shenzhen Guanhongrui Technology Co., Ltd.) with a continuous emission spectrum over 310-420 nm 111 surrounding the OFR. We conducted experiments with one and four lamps to provide a total irradiance of about 1.1×10^{15} (I₁) 112 and 3.8×10^{15} (I₄) photon cm⁻² s⁻¹, respectively (see details in Supporting information, Text S1); and dark control experiments 113 were performed with UV lamps off. Each experiment lasted around 20 minutes. In the absence of light and SO₂, there was no 114 change in the mass spectra of coated particles (Figure S4). At the outlet of the OFR, SO₂ concentration was monitored by a 115 SO₂ analyzer (Teledyne, T100, USA), and the size and chemical composition of individual aerosol particles were analyzed by 116 a single particle aerosol mass spectrometry (SPAMS, Hexin Analytical Instrument Co., Ltd, China). This single particle 117 technique allows us to study the mixing state of the particles. KNO3 was widely observed in biomass burning plumes (Zauscher 118 et al., 2013). Internally mixed particles of photosensitizing species and KNO₃ were generated by atomizing aqueous solutions 119 of KNO₃ with several drops of PSL suspension, followed by passing through a dryer and then the heated glass bottle containing 120 photosensitizing species as described above (Figure S2a). Externally mixed particles were generated with a second atomizer 121 (TSI 9032), and the generated KNO₃ or KNO₃-oxalic acid mixed particles were mixed with photosensitizing species coated 122 particles in a stainless-steel chamber ($\phi_3 \times 8''$) before introduction to the OFR (Figure S2b).

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124 2.2 SPAMS and data analysis

125 A detailed description of the operational principle of SPAMS has been provided elsewhere (Li et al., 2011). Briefly, aerosol 126 particles were introduced into the SPAMS through an orifice and aerodynamic lens and consecutively irradiated by two laser 127 beams, where their aerodynamic diameter were determined through the velocity and flight time. The sized particles were then 128 desorbed and ionized by a pulsed 266 nm laser (0.5 mJ), which was triggered at the precise time on the basis of the particle 129 velocities. The produced positive and negative molecular fragments were analyzed by a Z-shaped bipolar time-of-flight mass 130 spectrometer (Pratt et al., 2009; Li et al., 2011). The ionization efficiency of SPAMS to detect 250-2000 nm atmospheric 131 aerosol particles was above 30% on average (Li et al., 2011). The number of ionized particles for each experiment condition 132 was around 1000-3000, sufficient for systematically identifying the heterogeneous reaction products (Liang et al., 2022; Qi et 133 al., 2019). Furthermore, each experiment was repeated, as reflected in Figure S6. Single particle size and mass spectral analysis 134 were performed using the Computational Continuation Core (COCO) toolkit based on MATLAB software. The number 135 percentage and relative peak area (RPA, defined as the fractional contribution of the targeted ion peak area to the sum of all 136 ion peak areas) were applied to indicate the variations of the amount of different species (e.g., sulfate) in individual 137 particles (Hu et al., 2022). Sulfate-containing particles were distinguished by m/z -97 [HSO4-] or m/z-96 [SO4-] (Guazzotti et 138 al., 2001; Liang et al., 2022). In addition, an adaptive resonance theory based neural network algorithm (ART-2a) (Li et al., 139 2011) was used to separate and cluster particles in external and internal mixtures according to the similarities in individual 140 mass spectra of single particles. Before entering the SPAMS, the particles passed through a diffusion dryer to reduce the matrix 141 effects from water (Neubauer et al., 1998).

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144 **3. Results and discussion**

145 Photosensitized SO₂ uptake and sulfate formation

146 Figure 1a shows the changes in SO_2 concentration ($[SO_2]$) in the presence of PSL particles coated with various types of 147 photosensitizing (DMB, VL and SyrAld) and non-photosensitizing (BA) species under dark and UV irradiation conditions. In 148 Figure 1a, for UV condition, only time traces of SO₂ under I₄ UV irradiance were shown for clarity, and I₁ UV irradiance cases 149 can be found in Figure S5. Except stated otherwise, results shown in the following discussions were obtained at 80% RH. The 150 steady concentration of SO₂ in the OFR was at around 750 ppb under dark conditions. Upon exposure to UV light, a rapid drop 151 in the SO₂ concentration was observed in the presence of DMB- and VL-coated particles, indicating photoinduced uptake of 152 SO₂ on these particles. Wang et al. (2021) suggested that the photosensitized chemical reactions between naphthalene-derived 153 SOA and SO₂ likely occur at/near the particle surface. In this study, the SO₂ consumption under UV irradiation for DMB and 154 VL coated particles increased with the surface area of SPAMS detected particles in the OFR (Figure 1a and S6) (R²=0.84-155 0.99). Total surface area concentrations in the range of 7×10^4 - 2×10^5 μ m² m⁻³ are denoted by "small", in 2×10^5 - 6×10^5 μ m² 156 m^{-3} as "medium", and larger than $6 \times 10^5 \mu m^2 m^{-3}$ as "large". These values fall within the urban background and indoor air 157 ranges but are slightly lower than urban pollution ranges (Willeke and Whitby, 1975; Hudda and Fruin, 2016; Qi et al., 2008). 158 SO_2 consumption per unit surface area concentration also increased with higher UV irradiance (Figure S6). Only slight SO_2 159 consumption under UV irradiation was observed in the presence of SyrAld-coated particles and no observable decrease in SO2 160 concentrations in the absence of photosensitizing species, i.e., BA-coated particles and PSL-only particles, was found. The 161 average mass spectra of DMB-, VL-, SyrAld- and BA-coated single particles under dark and UV irradiation in the presence of 162 SO_2 are shown in Figure 1b, characterized by their respective parent ions (in either neutral, protonated or deprotonated form) 163 and expected smaller organic fragment ions. PSL-only particles do not ionize and no mass spectra were observed (Qi et al., 164 2019). No sulfate was formed under dark condition, consistent with the stable SO_2 concentrations observed. However, upon 165 exposure to UV irradiation, the RPA of sulfate (97HSO4- and 96SO4-) increased significantly, accompanied by the slight decrease 166 of RPA of the parent ions of ¹⁶⁵C₉H₉O₃^{+/-}, ¹⁵³C₈H₉O₃^{+/-}, ¹⁸¹C₉H₉O₄^{+/-} for DMB-, VL- and SyrAld-coated particles respectively. 167 Mabato et al. (2022) reported direct photosensitized oxidation of photosensitizers, which can generate oxygenated products 168 such as functionalized monomers and oxygenated ring-opening products. In this study, we observed the peak of ${}^{181}C_9H_9O_4^+$ 169 (DMB+O) upon UV irradiation, but the identification of organic products was generally limited by laser-induced fragmentation 170 in the SPAMS. Although the coating thickness estimated by particle size increase spanned a wide range from 100 nm to 2.2 171 µm, the number percentage and RPA of sulfate generally exhibited the same trend for the studied photosensitizers in each size 172 bin (Figures S7). Figure 2 shows the average RPA of sulfate (circles) and the number percentage of sulfate-containing particles 173 (diamonds) in DMB-, VL-, SyrAld- and BA-coated particles at dark and different UV intensities in the presence of SO₂, and 174 the corresponding SO₂ consumption normalized by the average total particle surface area concentration before and after UV 175 irradiation in the OFR detected by SPAMS (crosses). The RPA and number percentage of sulfate for each experimental 176 condition were calculated by taking the average of those values in different size bins in Figure S7. Hence the potential uneven 177 coating thickness has been incorporated in the averages, which show consistent trends in Figure 2. The average number 178 percentages of sulfate-containing particles in DMB- and VL- coated particles are considerably higher (> 84%) under both I_1 179 and I₄ UV irradiances than under dark (< 2%). SyrAld-coated particles gave a slightly lower percentage of sulfate-containing 180 particles of 43% and 83% at I_1 and I_4 UV irradiances. Upon increase of photon flux densities (I_1 to I_4), the RPA of sulfate 181 increases for DMB-, VL- and SyrAld-coated particles, which is in line with the enhanced normalized SO₂ consumptions. The 182 number percentage and RPA of sulfate exhibited a similar descending order of DMB>VL>SyrAld>BA in each size bin (Figure 183 S7). The pHs of the DMB (6.01±0.06), VL (6.15±0.12) and SyrAld (5.97±0.10) particles were similar. Our observed trend of 184 sulfate formation potential is in line with the secondary organic aerosol mass yield for syringol oxidation by ³C* of DMB 185 (114%), VL (111%) and SyrAld (78%) in the literature (Smith et al., 2016; Smith et al., 2014). Specifically, DMB has a higher 186 quantum yield and longer lifetime of ³C^{*} compared to VL (Felber et al., 2021), which can result in a higher sulfate formation 187 efficiency. On the other hand, the direct photodegradation rate constant was higher for SyrAld than VL, likely suppressing the 188 concentration of SyrAld in droplets/ particles and the photosensitized oxidation (Smith et al., 2016). However, 189 photosensitization is still a research field for atmospheric chemistry with broad uncertainties (Felber et al., 2021). Further 190 quantitative work on the quantum yield, lifetime, and the decay and quenching rate constants of the ${}^{3}C^{*}$ is needed.

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The loss of SO₂ associated with the synchronous sulfate production in single DMB-, VL- and to a lesser extent, SyrAld-coated particles was likely attributed to the photosensitization-induced oxidation of S(IV) (i.e., SO₂, HSO₃⁻, and SO₃²⁻). Specifically, UV irradiation could excite photosensitizers from their ground state to singlet excited state, then rapidly relax to a triplet state via intersystem crossing (George et al., 2015; Gomez Alvarez et al., 2012). S(IV) could be oxidized to sulfate directly by ${}^{3}C^{*}$, or by the secondary oxidants (e.g., ${}^{1}O_{2}$, O_{2}^{-} /HO₂ and ${}^{\circ}OH$) produced from the excited molecules and O_{2} /water. Wang et al. (2020) observed sulfate production from direct reactions between triplets of 4-(benzoyl) benzoic acid, humic acid and their salts, and hydrated S(IV).

198 In our previous study, we have reported the enhanced SO₂ oxidation and sulfate formation in incense and mosquito 199 coil burning particles (Liang et al., 2022), as surrogates of biomass burning organic aerosol, BBOA (Li et al., 2012; Zhang et 200 al., 2014), under light, when compared with dark conditions. The number percentage of sulfate-containing particles increased 201 from around 50% under dark to around 90% after UV irradiation (Figure 2). Incense burning particles contain a variety of 202 photosensitizers, e.g., DMB, VL and SyrAld (Peng et al., 2020; Liu and Sun, 1988; Liang et al., 2022), which could oxidize 203 SO₂ via photosensitization. In contrast to Liang et al. (2022), we did not observe sulfate formation under dark in the current 204 study. Their much higher percentage of sulfate-containing particles under dark was likely due to the gaseous oxidants in 205 incense-burning plumes in their experiments. Furthermore, as mentioned earlier, in the control experiment using BA-coated 206 particles as seeds in the presence of SO₂, neither the RPA of sulfate nor the number percentage of sulfate-containing particles 207 changed upon irradiation. This indicates that the direct photoexcitation of SO₂ in the presence of water leading to the formation 208 of OH and subsequently sulfate plays a negligible role (Kroll et al., 2018; Martins-Costa et al., 2018; Wang et al., 2021).

209 The potential role of secondary oxidants

The triplet excited state (${}^{3}C^{*}$) of aromatic carbonyls can react with O₂ in air-saturated conditions via either energy transfer to form ${}^{1}O_{2}$ or electron transfer to form O₂[•], which can further react with H⁺ ion to produce H₂O₂ and [•]OH (Dalrymple et al., 2010). Therefore, the absence of O₂ in N₂ saturated experiments would inhibit the formation of secondary oxidants. Figure 3 shows that replacing air by pure N₂ substantially shifted the distribution of RPA for DMB- and VL-coated particles toward the lower end, while SyrAld-coated particles exhibited slight changes. For example, DMB-coated particles with sulfate RPA larger than 0.6 were dominant and comprised more than 52% of total particles in air, but sulfate RPA of 0-0.2 accounts for more than 73% of the total particles in N₂ under both UV irradiances. This suggests the involvement of O₂ and the 217 potentially important role of secondary oxidants in sulfate formation. Upon the increase of UV intensity (from I_1 to I_4), the 218 number fraction of particles with sulfate RPA larger than 0.2 only slightly increased in N₂-saturated conditions, and particles 219 with RPA of 0-0.2 dominated the population, indicating the lower ability of direct ³C^{*} oxidation of SO₂ to produce large sulfate 220 RPA. The relative importance of the direct 3C* and secondary oxidants in sulfate production varies among the different 221 compounds, as reflected by the distribution of sulfate RPA in Figure 3. For example, secondary oxidants could be more 222 important in the DMB system than the SyrAld system. In contrast, Wang et al. (2020) reported that switching from air to N_2 223 resulted in similar S(IV) oxidation rates, indicating that the direct reaction of SO₂ with ³C^{*} was more significant than that with 224 the secondary oxidants for 4-(benzovl)benzoic acid. This discrepancy is possibly due to the different reactivities of ${}^{3}C^{*}$ from 225 different photosensitizing chemicals towards SO₂ (Wang et al., 2020). In air, DMB-coated particles exhibited the strongest 226 SO₂ oxidation potential with 88% of the total particles having sulfate RPA larger than 0.2 (I₁), followed by VL- (41%) and 227 SyrAld- (15%) coated particles. Upon exposure to simulated sunlight, SyrAld and VL have been shown to undergo apparent 228 direct photodegradation, but DMB exhibits smaller or almost no loss in illuminated solution mixed with non-carbonyl phenols 229 or benzene-diols (Smith et al., 2016, 2015; Smith et al., 2014; Mabato et al., 2023; Mabato et al., 2022). This is generally 230 consistent with the decrease of RPA of parent ions in this study (Figure S8). The rapid direct photodegradation of phenolic 231 carbonyls (VL and SyrAld) can reduce their concentrations in the particles and limits the formation of sulfate.

232 Relative importance of particulate photosensitization and nitrate photolysis in sulfate formation

233 Nitrate is a ubiquitous constituent of atmospheric aerosol particles (Chan and Yao, 2008). Multiphase photochemical 234 oxidation of SO₂ by the photolysis of particulate nitrate could make an important contribution to aerosol sulfate formation (Gen 235 et al., 2019b, a). To qualitatively compare the relative atmospheric importance of photosensitization and nitrate photolysis in 236 sulfate formation, external mixtures of VL-coated particles and KNO₃ particles were exposed to SO₂ and UV irradiation at 80% 237 RH. VL was used for comparison owing to its moderate sulfate formation potential among the three photosensitizers tested. 238 Potassium was the dominant cation in biomass burning plumes (Jahn et al., 2021; Frenev et al., 2009; Zhang et al., 2022), and 239 therefore KNO₃ was selected as the model nitrate salt. RPA of sulfate for VL-coated particles and KNO₃ particles at different 240 sizes in the external mixture were compared in Figure 4a. VL-coated particles exhibited an average sulfate RPA of 0.26, with 241 an overall inverse relationship with particle size, while the sulfate absolute peak areas (APA) are moderately higher for large 242 particles. The APA is proportional to the absolute number of ions detected and a larger sulfate APA may indicate a larger 243 amount of sulfate formed. However, APA is more sensitive to the variability in ion intensities associated with particle-laser 244 interactions than RPA (Gross et al., 2000; Hatch et al., 2014; Zhou et al., 2022). The variation in RPA was smaller than that 245 in the APA, even though some studies found that the RPA values may also be affected by the inherent variability of particle 246 compositions due to matrix effects within particles (Reinard and Johnston, 2008; Zhou et al., 2016). The reactive uptake 247 comprises the diffusion of SO_2 molecules, followed by oxidation of SO_2 at/near the surface or in the bulk of the particles. The 248 decreased sulfate RPA with increasing particle size suggested the photosensitized sulfate formation at/near the surface of VL-249 coated particles, probably due to the prevalence of surface reactions or diffusional limitations of SO₂ in larger particles, 250 especially in the poorly hygroscopic and potentially viscous VL matrix. We cannot exclude the occurrence of bulk phase 251 reaction in the organic moiety, though it was likely less efficient than the surface reaction. In contrast, deliquescent KNO₃ 252 particles (Figure S9) exhibited RPAs of 0, suggesting that nitrate photolysis plays a negligible role in our study, although the 253 concentration of [NO₃⁻] in KNO₃ particles at 80% RH was estimated to be 6.3 M by AIOMFAC 254 (http://www.aiomfac.caltech.edu) (Zuend et al., 2008), almost 100 times higher than the solubility of VL (~66 mM). At 80% 255 RH, the pH of KNO₃ particles was 6.38 ± 0.07 , comparable to that of VL (pH = 6.15 ± 0.12). Thus, pH-dependent partitioning 256 of SO₂ is not expected to play an important role in the different sulfate formation observed for KNO₃ and VL in this study. 257 The prevailing sulfate formation in VL particles over KNO₃ particles is likely due to the much lower integrated molar 258 absorptivity of nitrate (~143 M⁻¹ cm⁻¹) compared to VL (2.8×10⁵ M⁻¹ cm⁻¹) over the wavelength range of 300-400 nm (Figure 259 S1). In addition, this also excluded the possibility of sulfate formation in gas phase and small nuclei, which would be expected 260 to have condensed/coagulated on both the photosensitizer and KNO₃ particles. When RH decreased to 20%, a significant 261 reduction in the average RPAs from 0.26 to 0.002 was observed for VL-coated particles (Figure S10), attributable to the fewer 262 dissolved VL for sulfate formation since VL has low solubility and hygroscopicity and the limited SO₂ dissolution (Liu et al., 263 2021). In addition, lower RH could result in higher particulate viscosity, which hinders molecular diffusion and reaction (Kroll 264 et al., 2018; González Palacios et al., 2016; Corral Arroyo et al., 2018). A systematic study of the effect of RH on the particle-265 phase photosensitized reaction is desirable. Overall, sulfate formation was found on VL-coated particles but not on externally

266 mixed nitrate particles at both high and low RH in our study. Oxalic acid is one of the most abundant species of organic 267 aerosols and is commonly found in atmospheric nitrate-containing particles (Mochizuki et al., 2017; Cheng et al., 2017; Yang 268 et al., 2009). We have also conducted experiments with internal mixtures of KNO3 and oxalic acid, which did not show sulfate 269 formation as well (Figure 4b). However, internally mixed VL and KNO₃ yielded 55% sulfate-containing particles and an 270 average sulfate RPA of 0.12. These values fall in between those of pure KNO₃ and VL-coated particles (Figure 4c). As the ion 271 intensity ratio of nitrate to organics of the KNO₃-VL internally mixed particles of similar size decreased, higher sulfate RPAs 272 were found. The quantitative sulfate production rate via aerosol phase SO_2 oxidation by model photosensitizer is limited by 273 SPAMS measurements in the current study, which focuses of single particle mixing state analysis. Further quantitative studies 274 would be useful.

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276 4. Environmental implications

This paper presents insights on aerosol SO₂ oxidation by biomass burning-derived photosensitizers using single particle characterization. Sulfate formation in photosensitizer coated particles, in terms of both number percentage and RPA of sulfate, was significantly higher under UV irradiation than under dark. From dark to UV irradiation, the average number percentages of sulfate-containing particles increased from less than 2% to 43-99%, and sulfate RPA increased from almost 0 to 0.12-0.67 for SyrAld, VL, and DMB-coated particles.

The speciation, concentration, and properties of photosensitizers in ambient particles are still poorly understood, limiting the parameterization of photosensitized sulfate formation. Nevertheless, we observed that sulfate formation via photosensitization is qualitatively more efficient than nitrate photolysis for wet aerosols at 80% RH. Recently, we found that incense burning particles (considered as typical BBOA surrogates) show increases of sulfate-containing particles and sulfate RPAs by ~45% and ~0.35 under UV than dark, respectively, due to photosensitization reactions of SO₂ (Liang et al., 2022). These results are within the ranges of our measurements in this paper. The SO₂ exposure of ~1800 ppb min in the OFR in this study corresponds to a 45 min and 450 min atmospheric SO₂ exposure, taking an ambient RH of 80% and SO₂ concentration

289	of 40 ppb during extreme haze events (Cheng et al., 2016) and 4 ppb in usual days (Chen et al., 2022), respectively. This
290	indicates that after exposure of tens of minutes to hours to SO ₂ , more than 40% of fresh BBOA particles could contain sulfate
291	via photosensitization, especially under high photon flux such as during typical clear days and haze days in Beijing, China,
292	which were around 4 and 1.4 times, respectively, of that in the OFR (I4) (Figure S1). Our finding provides additional
293	experimental support to the potentially important contribution of photosensitized oxidation of S(IV) to aerosol sulfate
294	formation in biomass burning plumes. Future studies of the quantification and mechanism revelation of sulfate formation via
295	photosensitization are needed. In addition, we solely studied three typical biomass burning-derived photosensitizers.
296	Photosensitized sulfate formation on real BBOA particles, which is a complex matrix of organics, is to be explored further.



Figure 1. (a) Time traces of SO₂ in the dark (0-10 min) and under UV irradiation (I₄) (10-20 min) in the presence of DMB-, VL-, SyrAld-, or BA-coated particles and PSL-only particles. The SO₂ consumption is presented as a function of the total surface area concentration of SPAMS detected particles. Total surface area concentrations in the range of 7×10^4 - 2×10^5 µm² m⁻³ are denoted by "small", in 2×10^5 - 6×10^5 µm² m⁻³ as "medium", and larger than 6×10^5 µm² m⁻³ as "large". (b) Average negative and positive mass spectra for the DMB-, VL-, SyrAldand BA-coated particles under dark and UV irradiation (I₁ and I₄) conditions. All experiments were conducted at 80% RH.



Figure 2. Average sulfate relative peak areas (RPAs), and number percentage of sulfate-containing particles for the DMB-, VL-, SyrAldand BA-coated particles, mosquito coil burning, and incense burning particles under dark and UV irradiation conditions in the presence of SO₂. Errors are shown by 95% confidence intervals. SO₂ consumptions normalized by the average total particle surface area concentrations before and after UV irradiation in the OFR detected by SPAMS are shown. Data of incense and mosquito coil burning particles were from Liang et al. (2022). All experiments were conducted at 80% RH.

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318 Figure 3. Distribution of sulfate RPA for DMB-, VL- and SyrAld-coated particles under air and N₂ conditions at different UV intensities in

319 the presence of SO₂.



Figure 4. Sulfate RPA vs. particle diameter detected by the SPAMS for (a) externally mixed VL-coated particles and KNO₃; (b) externally mixed VL-coated particles and KNO₃-oxalic acid particles; and (c) internally mixed VL and KNO₃ particles at 80% RH under UV irradiation (I₁) in the presence of SO₂. The markers are presented as a function of sulfate APA. The color scale in c indicates the ion intensity ratio of nitrate to organics (total negative ion intensity subtracted by nitrate and sulfate intensity) in the negative mass spectra.

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- **334 Data availability.** The data are available upon request to the corresponding author.
- 335 Author contributions. CKC and LZ designed the experiment; LZ and ZL conducted the experiments; LZ and ZL performed
- the data interpretation; LZ, ZL, BRGM, RAIC, RT, ML, CC and CKC wrote the paper. All authors contributed to the paper
- 337 with useful scientific discussions or comments.
- 338 **Competing interests.** The contact author has declared that neither they nor their co-authors have any competing interests.
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