

Responses to reviewer

Reviewer comments are in **bold**. Our responses are labelled with [R] and authors' actions with [A]. Line numbers in the responses correspond to the revised manuscript with track-changes. Modifications to the manuscript are in blue.

Reviewer 1

Zhou et al. describe a series of laboratory flow-tube experiments analyzing sulfate formation via heterogeneous reaction of SO₂ and several types of photo-active organic particles. The results are interesting, demonstrate the utility of a novel analytical method (single-particle aerosol mass spectrometry) for observing particle-phase sulfate formation, and add to the rapidly growing body of works exploring atmospheric sulfate formation. I believe this paper merits publication in ACP after several major and minor comments are addressed, potentially involving additional experimentation. My comments are outlined below.

[R0] We thank the reviewer for the valuable feedback and constructive suggestions. Detailed responses are given below.

Major comments

I believe the authors need to more clearly highlight the apparent role of RH in these experiments and to more thoroughly explore the role that RH plays in the observed reactions. At line 221 the authors discuss that vanillin-coated particles produced substantially less sulfate at 20% RH relative to the 80% RH used in other experiments. RH therefore seems to be an important factor in affecting organic photosensitizer-initiated sulfate formation, but RH isn't mentioned as a factor in the abstract or the experimental description in the introduction. More thoroughly investigating the role that variable RH has on photosensitizer-initiated SO₂ oxidation would be very important to better understanding the significance of this pathway in ambient environments. Additionally, at line 158 the authors discuss potential SO₂ oxidants and note the possibility for oxidants that form from H₂O; does the apparent RH dependence point to H₂O as a secondary oxidant source following initial photo-excitation?

[R1] Thank you for your comments. We agree that the role of RH in the experimental system should have been better addressed. Firstly, the reaction between photoexcited SO₂ molecules and H₂O can produce secondary OH radicals (Kroll et al., 2018). However, this reaction played a negligible role in this study because we did not see effective sulfate formation in the control experiment using BA-coated particles as

seeds in the presence of SO₂ (Figure 2). Furthermore, Corral Arroyo et al. (2018) also reported that the particle-phase photosensitized radical production was promoted at higher RH due to the presence of more water as plasticizers and reduced particulate viscosity. In our system, the photosensitizers have low solubility and hygroscopicity, resulting in limited available dissolved VL to trigger photosensitization and possibly limited dissolved SO₂. In addition, lower RH could result in higher particulate viscosity, which hinders molecular diffusion and reaction (Kroll et al., 2018; González Palacios et al., 2016; Corral Arroyo et al., 2018). We have added this information to the text. In this study, the low RH experiments were conducted for the externally mixed VL and nitrate system to study whether the relative atmospheric importance of particulate photosensitization and nitrate photolysis are still the same as those under high RH conditions, given that nitrate concentration in droplets may be much higher under low RH. We found that sulfate formation was on VL-coated particles but not on externally mixed nitrate particles under both high and low RH conditions (Figure 4 and Figure S10). Quantitative examinations of the RH-dependent sulfate formation for photosensitization reaction is useful for future work.

[A1] We have added the potential RH effect on the photosensitized reaction after line 271: “When RH decreased to 20%, a significant reduction in the average RPAs from 0.26 to 0.002 was observed for VL-coated particles (Figure S10), [attributable to the fewer dissolved VL for sulfate formation since VL has low solubility and hygroscopicity and the limited SO₂ dissolution \(Liu et al., 2021b\)](#). In addition, lower RH could result in higher particulate viscosity, which hinders molecular diffusion and reaction (Kroll et al., 2018; González Palacios et al., 2016; Corral Arroyo et al., 2018). A systematic study of the effect of RH [on the particle-phase photosensitized reaction is desirable](#). Overall, sulfate formation was found on VL-coated particles but not on externally mixed nitrate particles [at both high and low RH in our study](#).”

I have several questions about sulfate signal variability, mass spectral variability inherent to the SPAMS, and particle size.

Line 110, section 2.2: how much variability are there in SPAMS spectra? E.g., how much variability in absolute peak area would be expected for monodisperse sulfate particles? What is the expected detection efficiency of the SPAMS for the observed size ranges of particles? Is it possible that any of the presented results are biased from low number statistics due to low particle detection efficiency and/or low numbers of particles? Does particle-phase water have any effect on desorption/ionization and RPAs/APAs? Even if some of these aspects of the SPAMS have been discussed in more detail previously some discussion here is necessary to fully understand and evaluate the presented results.

[R2] The relative peak area (RPA) of sulfate in photosensitizer coated particles has an average standard deviation of 11% across different size bins (Figure S7). The absolute peak area is more sensitive to the variability in ion intensities associated with particle-laser interactions than RPA (Gross et al., 2000; Hatch et al., 2014), and therefore it is not estimated here. The ionization efficiency of SPAMS to detect atmospheric aerosol particles in the size range of 250-2000 nm was above 30% on average (Li et al., 2011). Taking the ionization efficiency into consideration, the number of detected/ionized particles for each experiment condition was around 1000-3000, which is sufficient for systematically identifying the heterogeneous reaction products (Liang et al., 2022; Qi et al., 2019). Before entering the SPAMS, the particles passed through a diffusion dryer to reduce the matrix effects from water (Neubauer et al., 1998).

[A2] To better understand the results, more details of the SPAMS have been added after line 130: “The sized particles were then 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 velocities. The produced positive and negative molecular fragments were analyzed by a Z-shaped bipolar time-of-flight mass spectrometer (Pratt et al., 2009; Li et al., 2011). The ionization efficiency of SPAMS to detect 250-2000 nm atmospheric aerosol particles was above 30% on average (Li et al., 2011). The number of ionized particles for each experiment condition was around 1000-3000, sufficient for systematically identifying the heterogeneous reaction products (Liang et al., 2022; Qi et al., 2019). Furthermore, each experiment was repeated, as reflected in Figure S6. Single particle size and mass spectral analysis were performed using the Computational Continuation Core (COCO) toolkit based on MATLAB software. The number percentage and relative peak area (RPA, defined as the fractional contribution of the targeted ion peak area to the sum of all ion peak areas) were applied to indicate the variations of the amount of different species (e.g., sulfate) in individual particles (Hu et al., 2022). Sulfate-containing particles were distinguished by m/z -97 [HSO_4^-] or m/z -96 [SO_4^-] (Guazzotti et al., 2001; Liang et al., 2022). In addition, an adaptive resonance theory based neural network algorithm (ART-2a) (Li et al., 2011) was used to separate and cluster particles in external and internal mixtures according to the similarities in individual mass spectra of single particles. Before entering the SPAMS, the particles passed through a diffusion dryer to reduce the matrix effects from water (Neubauer et al., 1998).”

There seems to be a lot of spread in the sulfate RPAs within the experiments (Line 146/Figure 2). Do the authors have a theory for this spread? Is SO₂ oxidation less efficient on some particles? Is there substantial spread in flow tube residence time? Is this just due to particle-to-particle variation in SPAMS ionization?

[R3] The spread in the sulfate RPA for a specific experimental condition in Figure 2 is mainly due to the RPA differences for particles of different sizes (Figure S7). As we have discussed in line 257 that the reactive uptake comprises the diffusion of SO₂ molecules, followed by oxidation of SO₂ at/near the surface or in the bulk of the particles. The decreased sulfate RPA with increasing particle size suggested the photosensitized sulfate formation at/near the surface of VL-coated particles, probably due to the prevalence of surface reactions or diffusional limitations of SO₂ in larger particles, especially in the poorly hygroscopic and potentially viscous VL matrix. Even though the sulfate RPA was size dependent, it generally exhibited the same descending order of DMB>VL>SyrAld>BA in each size bin (Figure S7). In Figure 2, the RPA and number percentage for each specific experimental condition was calculated by taking an average of RPAs and number percentages in different size bins in Figure S7.

[A3] For clarity, we had added after line 170 that “Although the coating thickness estimated by particle size increase spanned a wide range from 100 nm to 2.2 μm, the number percentage and RPA of sulfate generally exhibited the same trend for the studied photosensitizers in each size bin (Figures S7). Figure 2 shows the average RPA of sulfate (circles) and the number percentage of sulfate-containing particles (diamonds) in DMB-, VL-, SyrAld- and BA-coated particles at dark and different UV intensities in the presence of SO₂, and the corresponding SO₂ consumption normalized by the average total particle surface area concentration before and after UV irradiation in the OFR detected by SPAMS (crosses). The RPA and number percentage of sulfate for each experimental condition were calculated by taking the average of those values in different size bins in Figure S7. Hence the potential uneven coating thickness has been incorporated in the averages, which show consistent trends in Figure 2. The average number percentages of sulfate-containing particles in DMB- and VL- coated particles are considerably higher (> 84%) under both I₁ and I₄ UV irradiances than under dark (< 2%). SyrAld-coated particles gave a slightly lower percentage of sulfate-containing particles of 43% and 83% at I₁ and I₄ UV irradiances. Upon increase of photon flux densities (I₁ to I₄), the RPA of sulfate increases for DMB-, VL- and SyrAld-coated particles, which is in line with the enhanced normalized SO₂ consumptions. The number percentage and RPA of sulfate exhibited a similar descending order of DMB>VL>SyrAld>BA in each size bin (Figure S7). Our observed trend of sulfate formation potential is in line with the secondary organic aerosol mass yield for syringol oxidation by ³C* of DMB (114%), VL (111%) and SyrAld (78%) in the literature (Smith et al., 2016; Smith et al., 2014).”

On lines 172-174 the authors discuss an apparent size component to the efficiency of sulfate formation. Figure S4 clearly shows that the SPAMS sizing effectively captures the expected size distribution of the PSLs, but what size range do organic-coated particles span before sulfate formation begins? To put another

way, how uniform is the population size distribution after becoming coated in organics? Do these results suggest that sulfate formation occurred unevenly across the particle population? Are there any instrumental factors that may influence the apparent size-dependent sulfate production efficiency? E.g., is it possible that larger particles are only partially ionized by the SPAMS and this skews the observed RPAs?

[R4] [A4] We did not obtain a uniform population for the organic-coated particles. However, we indeed considered the effect of the particle size on the sulfate RPA and please see details in the response [R3]. For the instrumental factor, the laser energy used in this study was 0.5 mJ, which is widely used and sufficiently strong to ionize ambient and laboratory-generated particles (Li et al., 2022; Zhang et al., 2023). Furthermore, Liu et al. (2021a) reported that ionic peak integrity was the best when the laser energy was about 0.5 mJ.

At lines 209-211 the authors discuss the difficulties in using absolute peak areas to draw conclusions about sulfate signal. Are there circumstances where it would be feasible to translate the absolute peak area to some mass (or mass range) of sulfate and therefore be more quantitative about the amount of sulfate present in a particle? Would this be possible after observing APAs of size-selected sulfate particles and taking into account particle sizes measured by the SPAMS? Alternatively, is there a way to be reasonably quantitative about sulfate production rate from the studied photosensitizers, based on measurements like the amount of depleted SO₂ and particle surface area?

[R5] Single-particle mass spectrometry instruments can characterize the composition of individual aerosol particles in real-time. Their unique ability to determine the mixing state of the particles enables qualitative assessment of chemical transformation based on the mass spectra of single particles but not the average composition of an ensemble of particles. However, quantitative measurements by single-particle mass spectrometry systems are inherently problematic because ion formation from laser desorption-ionization is not a well-controlled process and gives rise to considerable particle-to-particle variability (Froyd et al., 2019; Hinz and Spengler, 2007). Recently, some studies have attempted to quantify the mass fractions for chemical species in single particles by combining colocated measurements of single particle mass spectrometry and HR-ToF-AMS measurements (Healy et al., 2014). In our current study, using SPAMS alone is subject to different sensitivities for chemical species due to differences in their ionization and matrix effects and therefore cannot provide a quantitative sulfate production rate. However, our focus is to report the possibility of aerosol phase SO₂ oxidation by model biomass burning photosensitizers at single particle level and compare the relative atmospheric importance of particulate photosensitization and nitrate

photolysis in sulfate formation. We thank the reviewer for the suggestions of using the measured SO₂ depletion for further analysis. However, we cannot rule out SO₂ dissolution without oxidation to form sulfate. We agree that the quantitative information about sulfate production rate from photosensitizers is valuable and will be the subject of our future work. We have also modified the title of the paper to emphasize that our analysis is based on the single particle mixing state, but not mass concentration analysis.

[A5] We have added after line 283 that “The quantitative sulfate production rate via aerosol phase SO₂ oxidation by model photosensitizer is limited by SPAMS measurements in the current study, which focuses on single particle mixing state analysis. Further quantitative studies would be useful.”

We have modified the title of the paper as follows: Sulfate formation via aerosol phase SO₂ oxidation by model biomass burning photosensitizers: 3,4-dimethoxybenzaldehyde, vanillin and syringaldehyde using single particle mixing state analysis

The authors note on lines 174-176 that the sulfate formation efficiency follows a similar trend as SOA formation from reaction between the three photosensitizers and syringol. What did the authors of the previous works attribute the difference in SOA production to? Would this be reasonable within the current system? Are there any other reasonable parameters that would influence the efficacy of SO₂ oxidation by these photosensitizers? E.g., absorption spectra, quenching efficiency, particle phase state or physical attributes.

[R6] [A6] We have added the potential reasons for the different sulfate formation efficiency after line 185: “Specifically, DMB has a higher quantum yield and longer lifetime of ³C* compared to VL (Felber et al., 2021), which can result in a higher sulfate formation efficiency. On the other hand, the direct photodegradation rate constant was higher for SyrAld than VL, likely suppressing the concentration of SyrAld in droplets/ particles and the photosensitized oxidation (Smith et al., 2016). However, photosensitization is still a research field for atmospheric chemistry with broad uncertainties (Felber et al., 2021). Further quantitative work on the quantum yield, lifetime, and the decay and quenching rate constants of the ³C* is needed.”

Minor comments

General: I suggest adding subsections to the “Results and Discussion” to more clearly organize the different materials in this section, as some of the transitions within and between paragraphs are abrupt.

[R7] [A7] Thank you for your suggestions and we have organized the paragraph and added subtitles.

Line 58: what properties make vanillin a typical aromatic carbonyl sensitizer? Or is it just a photosensitizer that's often used in studies?

[R8] [A8] An important class of photosensitizers is aromatic carbonyl compounds (Felber et al., 2021). Vanillin is an aromatic carbonyl and is well-known and widely used in photosensitization studies (Mabato et al., 2022; Felber et al., 2021; Smith et al., 2016).

Lines 85-86: is the estimated organic coating thickness shown anywhere?

[R9] [A9] This has been mentioned in line 170. Although the coating thickness estimated by particle size increase spanned a wide range from 100 nm to 2.2 μm , the number percentage and RPA of sulfate generally exhibited the same trend for the studied compounds in each size bin (Figures S7).

Line 151: what is the presence of (minor) sulfate under dark conditions attributed to?

[R10] [A10] The negligible sulfate formation in the dark may be due to the autooxidation of SO_2 by oxygen.

Line 155: are any sulfite (SO_3) signals observed in the mass spectra? It doesn't appear so based on Figure 1 but it's a little difficult to tell. Would sulfite signals be expected to be visible while examining heterogeneous SO_2 oxidation?

[R11] [A11] we observed rather small m/z -80 [SO_3^-] peak (i.e., $\text{RPA} < 0.06$) in the mass spectra. However, it is more likely due to fragmentation of the formed sulfate rather than dissolved SO_2 , as it is only observed under UV conditions but not dark. Almost no sulfate formed under dark conditions.

Line 179: can the O_2 -free environment influence any aspect of the ionization process?

[R12] [A12] Like other typical mass spectrometers, the pumping scheme inside the SPAMS ensures the high vacuum environments with the pressure of 5×10^{-5} Torr in the sizing region and 7×10^{-7} Torr in the

mass spectrometer region, where ionization process takes place (Li et al., 2011). Therefore, the O₂ free environment would not influence the ionization process.

Line 181: although the absolute changes in RPA are smaller for syringaldehyde particles, is the relative change similar to that for vanillin and DMB? Additionally, do the results in N₂ imply that direct 3C* oxidation of SO₂ can occur but is slower than pathways with O₂?

[R13] Figure 3 compared the distribution of RPA for DMB-, VL- and SyrAld-coated particles under air and N₂ conditions, and it is clear 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. More specifically, when replacing air by pure N₂, the number fraction of particles with sulfate RPA large than 0.2 decreased by more than 40% for DMB- and VL- coated particles (I₄) but by only 14% for SyrAld-coated particles. Our results suggested the involvement of O₂ and the potential important role of secondary oxidants in sulfate formation and also the lower ability of direct 3C* oxidation of SO₂ to produce large sulfate RPA. The relative importance of the direct 3C* and secondary oxidants in sulfate production varies among the different compounds, as reflected by the distribution of sulfate RPA in Figure 3. For example, secondary oxidants could be more important in the DMB system than the SyrAld system.

[A13] We modified the sentence on line 224: “Upon the increase of UV intensity (from I₁ to I₄), the number fraction of particles with sulfate RPA larger than 0.2 only slightly increased in N₂-saturated conditions, and particles with RPA of 0-0.2 dominated the population, [indicating the lower ability of direct 3C* oxidation of SO₂ to produce large sulfate RPA. The relative importance of the direct 3C* and secondary oxidants in sulfate production varies among the different compounds, as reflected by the distribution of sulfate RPA in Figure 3. For example, secondary oxidants could be more important in the DMB system than the SyrAld system.”](#)

Line 186: specify what type of system Wang et al. (2020) was exploring.

[R14] [A14] We have added related information in line 229 as follows: “In contrast, Wang et al. (2020) reported that switching from air to N₂ resulted in similar S(IV) oxidation rates, indicating that the direct reaction of SO₂ with 3C* was more significant than that with the secondary oxidants [for 4-\(benzoyl\)benzoic acid.](#)”

Lines 188-189: have similar variations in 3C* reactions rates from different sources towards the same analyte been observed previously?

[R15] [A15] Yes. Wang et al. (2020) observed different reaction rate constants between 3C* from different sources and SO₂, with xanthone exhibiting the highest rate constant and followed by acetophenone, flavone and 4-(benzoyl)benzoic acid. We have added this reference.

Line 193: can the decrease in organic ion RPA also be consistent with ion scavenging by newly produced sulfate?

[R16] [A16] No, as the decrease in RPA of parent ions in Figure S8 was indicated by their peaks in the positive spectra, whereas sulfate was detected in negative mass spectra. This has been mentioned in the figure caption.

Line 195: the location of the material following “Note...” seems odd and incongruous with the rest of the paragraph.

[R17] [A17] We agree that the phase state information mentioned here does not fit the paragraph, and therefore we have moved this information to the method part. Please see details in the next [R18].

Lines 195-199: the authors seem to be implying that they do not expect the organic-coated PSLs to undergo substantial growth at the RH values used. If this is correct, please state so directly. Any other statements the authors intend to make here on particle physical characteristics should be clearly stated.

[R18] [A18] We apologize that the location of the particle phase state discussion (originally in lines 195-199) led to confusion. The original lines 195-199, which better fit the method part, have been moved to line 99 as follows. In addition, we have added discussions: “Depending on the experiment, the RH in the OFR was regulated at ~80% or 20% to achieve different content of aerosol water by passing HEPA-filtered and activated-carbon-denuded compressed air or pure N₂ through water bubblers. Note that the photosensitizers may be (polymorphic) solid or semi-solid due to their low solubility and hygroscopicity, even at 80% RH (Kavuru et al., 2016; Hussain et al., 2001). For example, Mochida and Kawamura (2004) reported that pyrolysis products of lignin with -COOH, including vanillic acid and syringic acid, showed no hygroscopic growth even at RH of more than 90%. They also proposed that other pyrolysis products with chemical structures such as -CHO may have even lower hygroscopicity than -COOH and would not show measurable particle growth. Though we could not observe the phase states of the particles, both aerosol liquid water in (partially) deliquescent particles and surface adsorbed water content on solid particles at 80% RH were expected to be higher than at 20% RH (Rubasinghege and Grassian, 2013).”

Line 203: to clarify, are the vanillin-coated particles here still PSLs?

[R19] [A19] Yes, VL-coated particles are VL coated on the PSL condensation nuclei.

Line 205: would pH and the identity of the NO₃⁻ counterion (e.g., H⁺, NH₄⁺) potentially influence SO₂ oxidation?

[R20] Yes, SO₂ dissolution is not favorable under acidic environments (Gen et al., 2019), so the counterion could play a role directly through pH. However, at 80% 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 of SO₂ is not expected to play an important role in the different sulfate formation observed for KNO₃ and VL in this study. Furthermore, since the solubility of SO₂ may be limited in the acidic nitrate particles such as ammonium nitrate, the sulfate formation in KNO₃ particles could represent an upper limit of contribution from nitrate photolysis in the atmosphere. Another potential impact of counterion on SO₂ oxidation is via the ionic strength of the solution (Liu et al., 2021b). Divalent cations (e.g., Ca²⁺) afford higher ionic strength than monovalent cations (e.g., Na⁺), but the interaction between Ca²⁺ and nitrate will shift the nitrate absorption band away from actinic wavelengths with increasing concentration (i.e., ionic strength) (Roca et al., 2008). Nevertheless, divalent cations were not used in our experiments and hence ionic strength variations due to the use of different counterions do not affect our conclusion that photosensitization prevails nitrate photolysis in SO₂ oxidation in our experimental conditions.

[A20] We have added the pH information after line 266, “At 80% 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 of SO₂ is not expected to play an important role in the different sulfate formation observed for KNO₃ and VL in this study.”

Line 210: is there any possibility for the different photosensitizers/organic particle matrices to lead to different sulfate ionization efficiencies and RPAs?

[R21] Matrix effect inherently exists in SPAMS measurements, which limits the SPAMS to provide quantitative results. Lacking robust accurate absolute concentration measurements, the relative intensity has been accepted to qualitatively represent chemical composition variations on particles (Gross et al., 2000; Li et al., 2017). We also noted that the variation in relative peak area (RPA) was smaller than in the absolute peak area (APA), even though some studies found that the RPA values may also be affected by the inherent variability of particle compositions due to matrix effects within particles (Reinard and Johnston, 2008).

[A21] We have added the potential matrix effect after line 255: “However, APA is more sensitive to the variability in ion intensities associated with particle-laser interactions than RPA (Gross et al., 2000; Hatch et al., 2014; Zhou et al., 2022). The variation in RPA was smaller than that in the APA, even though some studies found that the RPA values may also be affected by the inherent variability of particle compositions due to matrix effects within particles (Reinard and Johnston, 2008; Zhou et al., 2016).”

Line 214: it's not clear that the KNO₃ particles are deliquesced. Freney al. (2009) observed continuous growth with increasing RH for KNO₃ particles and a deliquescence RH of 90% for dried particles (in line with prior works cited in Freney et al.). Therefore, I don't believe the direct comparison to the sulfate formation in aqueous droplets used in Gen et al. (2019) is valid, and this comparison and discussion of photosensitizer vs nitrate SO₂ oxidation should be caveated with this information.

[R22] [A22] The KNO₃ wet aerosols were generated using an atomizer (TSI 9032), and introduced to the OFR (80% RH) without passing a dryer (as shown in Figure S2b). It has been reported that more than 96% of the KNO₃ particles from nebulization exhibit no efflorescence relative humidity (ERH) (Freney et al., 2009; M.-J. Lee, 2011). Therefore, we considered the KNO₃ particles were deliquescent.

Line 224: is there a reason to suspect that oxalic acid/KNO₃ mixtures might affect SO₂ oxidation differently than pure KNO₃ particles?

[R23] [A23] When mixed with organics, the physicochemical properties of nitrate particles such as pH may change, which may, in turn, affect the nitrate photolysis effectiveness. The oxalic/KNO₃ mixtures represent a slightly more complicated nitrate photolysis system that contains one of the most abundant water soluble organic compounds. No sulfate formation was observed in oxalic/ KNO₃ particles, just as in pure nitrate particles, but we did not speculate on the detailed mechanism.

Line 238-239: “qualitatively more efficient” under the studied conditions: wet aerosols at 80% RH.

[R24] [A24] We have added the studied experimental conditions.

Line 250: are photosensitizers emitted or formed in non-BB environments, for example urban environments where multifunctional aromatics are common emissions and high NO_x levels are common?

[R25] [A25] Yes, photosensitizer particles exist in urban environments. Polycyclic aromatic hydrocarbons (PAHs) as constituents of urban grime act as potential photosensitizers (Gomez Alvarez et al., 2012; Vione

et al., 2006). Furthermore, Wang et al. (2021) reported that naphthalene-derived secondary organic aerosols exhibited interfacial photosensitizing properties.

Reference

- Corral Arroyo, P., Bartels-Rausch, T., Alpert, P. A., Dumas, S. p., Perrier, S. b., George, C., and Ammann, M.: Particle-phase photosensitized radical production and aerosol aging, *Environmental science & technology*, 52, 7680-7688, 2018.
- Felber, T., Schaefer, T., He, L., and Herrmann, H.: Aromatic Carbonyl and Nitro Compounds as Photosensitizers and Their Photophysical Properties in the Tropospheric Aqueous Phase, *The Journal of Physical Chemistry A*, 125, 5078-5095, 2021.
- Freney, E. J., Martin, S. T., and Buseck, P. R.: Deliquescence and efflorescence of potassium salts relevant to biomass-burning aerosol particles, *Aerosol Science and Technology*, 43, 799-807, 2009.
- Froyd, K. D., Murphy, D. M., Brock, C. A., Campuzano-Jost, P., Dibb, J. E., Jimenez, J.-L., Kupc, A., Middlebrook, A. M., Schill, G. P., and Thornhill, K. L.: A new method to quantify mineral dust and other aerosol species from aircraft platforms using single-particle mass spectrometry, *Atmospheric Measurement Techniques*, 12, 6209-6239, 2019.
- Gen, M., Zhang, R., Huang, D. D., Li, Y., and Chan, C. K.: Heterogeneous oxidation of SO₂ in sulfate production during nitrate photolysis at 300 nm: effect of pH, relative humidity, irradiation intensity, and the presence of organic compounds, *Environmental Science & Technology*, 53, 8757-8766, 2019.
- González Palacios, L., Corral Arroyo, P., Aregahegn, K. Z., Steimer, S. S., Bartels-Rausch, T., Nozière, B., George, C., Ammann, M., and Volkamer, R.: Heterogeneous photochemistry of imidazole-2-carboxaldehyde: HO₂ radical formation and aerosol growth, *Atmospheric Chemistry and Physics*, 16, 11823-11836, 2016.
- Gross, D. S., Gälli, M. E., Silva, P. J., and Prather, K. A.: Relative sensitivity factors for alkali metal and ammonium cations in single-particle aerosol time-of-flight mass spectra, *Analytical Chemistry*, 72, 416-422, 2000.
- Guazzotti, S. A., Coffee, K. R., and Prather, K. A.: Continuous measurements of size-resolved particle chemistry during INDOEX-Intensive Field Phase 99, *Journal of Geophysical Research: Atmospheres*, 106, 28607-28627, 2001.
- Hatch, L. E., Pratt, K. A., Huffman, J. A., Jimenez, J. L., and Prather, K. A.: Impacts of aerosol aging on laser desorption/ionization in single-particle mass spectrometers, *Aerosol Science and Technology*, 48, 1050-1058, 2014.
- Healy, R. M., Riemer, N., Wenger, J. C., Murphy, M., West, M., Poulain, L., Wiedensohler, A., O'Connor, I. P., McGillicuddy, E., and Sodeau, J. R.: Single particle diversity and mixing state measurements, *Atmospheric Chemistry and Physics*, 14, 6289-6299, 2014.
- Hinz, K. P., and Spengler, B.: Instrumentation, data evaluation and quantification in on-line aerosol mass spectrometry, *Journal of Mass Spectrometry*, 42, 843-860, 2007.
- Hu, X., Guo, Z., Sun, W., Lian, X., Fu, Y., Meng, H., Zhu, Y., Zhang, G., Wang, X., and Xue, L.: Atmospheric Processing of Particulate Imidazole Compounds Driven by Photochemistry, *Environmental Science & Technology Letters*, 9, 265-271, 2022.
- Hussain, K., Thorsen, G., and Malthe-Sørensen, D.: Nucleation and metastability in crystallization of vanillin and ethyl vanillin, *Chemical engineering science*, 56, 2295-2304, 2001.
- Kavuru, P., Grebinoski, S. J., Patel, M. A., Wojtas, L., and Chadwick, K.: Polymorphism of vanillin revisited: the discovery and selective crystallization of a rare crystal structure, *CrystEngComm*, 18, 1118-1122, 2016.

Kroll, J. A., Frandsen, B. N., Kjaergaard, H. G., and Vaida, V.: Atmospheric hydroxyl radical source: Reaction of triplet SO₂ and water, *The Journal of Physical Chemistry A*, 122, 4465-4469, 2018.

Li, J., Xu, T., Lu, X., Chen, H., Nizkorodov, S. A., Chen, J., Yang, X., Mo, Z., Chen, Z., and Liu, H.: Online single particle measurement of fireworks pollution during Chinese New Year in Nanning, *Journal of Environmental Sciences*, 53, 184-195, 2017.

Li, L., Huang, Z., Dong, J., Li, M., Gao, W., Nian, H., Fu, Z., Zhang, G., Bi, X., and Cheng, P.: Real time bipolar time-of-flight mass spectrometer for analyzing single aerosol particles, *International Journal of Mass Spectrometry*, 303, 118-124, 2011.

Li, X., Li, L., Zhuo, Z., Zhang, G., Du, X., Li, X., Huang, Z., Zhou, Z., and Cheng, Z.: Bioaerosol identification by wide particle size range single particle mass spectrometry, *EGUsphere*, 1-16, 2022.

Liang, Z., Zhou, L., Infante Cuevas, R. A., Li, X., Cheng, C., Li, M., Tang, R., Zhang, R., Lee, P. K., and Lai, A. C.: Sulfate Formation in Incense Burning Particles: A Single-Particle Mass Spectrometric Study, *Environmental Science & Technology Letters*, 2022.

Liu, C., Li, B., Liu, C., Li, M., and Zhou, Z.: Analysis of single-cell microbial mass spectra profiles from single-particle aerosol mass spectrometry, *Rapid Communications in Mass Spectrometry*, 35, e9069, 2021a.

Liu, T., Chan, A. W., and Abbatt, J. P.: Multiphase oxidation of sulfur dioxide in aerosol particles: implications for sulfate formation in polluted environments, *Environmental Science & Technology*, 55, 4227-4242, 2021b.

M.-J. Lee, H.-J. J., H.-J. Eom, S. Maskey, H. K. Kim, and C.-U. Ro: Hygroscopic behavior of individual NaNO₃ particles, <https://acp.copernicus.org/preprints/11/C11055/2011/acpd-11-C11055-2011-supplement.pdf>, 2011.

Mabato, B. R. G., Lyu, Y., Ji, Y., Li, Y. J., Huang, D. D., Li, X., Nah, T., Lam, C. H., and Chan, C. K.: Aqueous secondary organic aerosol formation from the direct photosensitized oxidation of vanillin in the absence and presence of ammonium nitrate, *Atmospheric Chemistry and Physics*, 22, 273-293, 2022.

Mochida, M., and Kawamura, K.: Hygroscopic properties of levoglucosan and related organic compounds characteristic to biomass burning aerosol particles, *Journal of Geophysical Research: Atmospheres*, 109, 2004.

Neubauer, K. R., Johnston, M. V., and Wexler, A. S.: Humidity effects on the mass spectra of single aerosol particles, *Atmospheric Environment*, 32, 2521-2529, 1998.

Pratt, K. A., Mayer, J. E., Holecek, J. C., Moffet, R. C., Sanchez, R. O., Rebotier, T. P., Furutani, H., Gonin, M., Fuhrer, K., and Su, Y.: Development and characterization of an aircraft aerosol time-of-flight mass spectrometer, *Analytical chemistry*, 81, 1792-1800, 2009.

Qi, X., Pang, X., Hong, Y., Wang, Y., Lou, S., Feng, J., Cheng, P., and Zhou, Z.: Real-time analysis of the homogeneous and heterogeneous reactions of pyrene with ozone by SPAMS and CRD-EAS, *Chemosphere*, 234, 608-617, 2019.

Reinard, M. S., and Johnston, M. V.: Ion formation mechanism in laser desorption ionization of individual nanoparticles, *Journal of the American Society for Mass Spectrometry*, 19, 389-399, 2008.

Roca, M., Zahardis, J., Bone, J., El-Maazawi, M., and Grassian, V. H.: 310 nm irradiation of atmospherically relevant concentrated aqueous nitrate solutions: Nitrite production and quantum yields, *The Journal of Physical Chemistry A*, 112, 13275-13281, 2008.

Rubasinghege, G., and Grassian, V. H.: Role (s) of adsorbed water in the surface chemistry of environmental interfaces, *Chemical Communications*, 49, 3071-3094, 2013.

Smith, J. D., Sio, V., Yu, L., Zhang, Q., and Anastasio, C.: Secondary organic aerosol production from aqueous reactions of atmospheric phenols with an organic triplet excited state, *Environmental science & technology*, 48, 1049-1057, 2014.

Smith, J. D., Kinney, H., and Anastasio, C.: Phenolic carbonyls undergo rapid aqueous photodegradation to form low-volatility, light-absorbing products, *Atmospheric Environment*, 126, 36-44, 2016.

Vione, D., Maurino, V., Minero, C., Pelizzetti, E., Harrison, M. A., Olariu, R.-I., and Arsene, C.: Photochemical reactions in the tropospheric aqueous phase and on particulate matter, *Chemical Society Reviews*, 35, 441-453, 2006.

Wang, X., Gemayel, R., Hayeck, N., Perrier, S., Charbonnel, N., Xu, C., Chen, H., Zhu, C., Zhang, L., and Wang, L.: Atmospheric photosensitization: a new pathway for sulfate formation, *Environmental Science & Technology*, 54, 3114-3120, 2020.

Wang, X., Gemayel, R., Baboornian, V. J., Li, K., Boreave, A., Dubois, C., Tomaz, S., Perrier, S., Nizkorodov, S. A., and George, C.: Naphthalene-Derived Secondary Organic Aerosols Interfacial Photosensitizing Properties, *Geophysical Research Letters*, 48, e2021GL093465, 2021.

Zhang, Y., Pei, C., Zhang, J., Cheng, C., Lian, X., Chen, M., Huang, B., Fu, Z., Zhou, Z., and Li, M.: Detection of polycyclic aromatic hydrocarbons using a high performance-single particle aerosol mass spectrometer, *Journal of Environmental Sciences*, 124, 806-822, 2023.

Zhou, L., Li, M., Cheng, C., Zhou, Z., Nian, H., Tang, R., and Chan, C. K.: Real-time chemical characterization of single ambient particles at a port city in Chinese domestic emission control area—Impacts of ship emissions on urban air quality, *Science of the Total Environment*, 819, 153117, 2022.

Zhou, Y., Huang, X. H., Griffith, S. M., Li, M., Li, L., Zhou, Z., Wu, C., Meng, J., Chan, C. K., and Louie, P. K.: A field measurement based scaling approach for quantification of major ions, organic carbon, and elemental carbon using a single particle aerosol mass spectrometer, *Atmospheric Environment*, 143, 300-312, 2016.