Enhanced Sulfate Formation in Mixed Biomass Burning and Sea-salt ~~Particles~~ Interactions Mediated by Photosensitization: Effects of Chloride, ~~and~~ Nitrogen-containing Compounds and Atmospheric Aging

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Abstract

Discrepancies persist between modeled simulations and measured sulfate concentrations in marine boundary layer, especially when the marine air was influenced by biomass burning plume. However, there is a notable dearth of research conducted on the interactions between sea-salt aerosol and biomass burning plume, impeding a comprehensive understanding of the sulfate formation. ~~Recent research has suggested that photosensitized oxidation can be an effective pathway for the oxidation of SO_2 based on a limited number of model photosensitizers. However, there is a notable dearth of research conducted on complex chemical systems, impeding a comprehensive understanding of sulfate formation in photosensitization.~~ This work studied sulfate formation by mixing real biomass burning (BB) extracts and NaCl, mimicking internal mixtures of BB and sea-salt particles. Significant enhancement of sulfate formation was observed for BB-NaCl particles compared to incense burning (IS)-NaCl particles. For fresh particles, the sulfate formation rate followed the trend of corn straw (CS)-NaCl>rice straw (RS)-NaCl>wheat straw (WS)-NaCl>IS-NaCl. The filter aging ~~Aged particles~~ was ~~were produced~~ achieved by exposing them to $OH^{\bullet}$ through ~~irradiating the filters directly with~~ UV irradiation~~lights~~. Aged particles showed changes in sulfate formation rates, with the highest enhancement by RS-NaCl due to interactions between RS and NaCl. Model experiments spiked

with nitrogen-containing organic compounds (NOCs), such as pyrazine (CHN) and 4-nitrocatechol (CHON), revealed positive effects of chloride in the PS-CHON system and negative effects in the PS-CHN system. Our work suggests that BB reaching or near coastal areas could affect sulfate formation via photosensitizer-mediated reactions, potentially exacerbating air quality concerns.

Keywords: sulfate formation, biomass burning, photosensitization, sea-salt aerosol, chloride

1 Introduction

~~Sulfate is a critical constituent of atmospheric particulate matter, exerting substantial influence on atmospheric radiative forcing, air quality, and human health (Fuzzi et al., 2015; Nel, 2005; Charlson et al., 1992). The commonly recognized sulfate formation mechanisms include gas-phase SO_2 oxidation by OH radicals (Stockwell and Calvert, 1983) and stabilized Criegee intermediates (sCIs) (Mauldin Iii et al., 2012) and multiphase and heterogeneous SO_2 oxidation by H_2O_2, O_3, NO_2, organic peroxides and O_2 catalyzed transition metal ions (TMI) (Seinfeld and Pandis, 2016; Wang et al., 2020a; Liu and Abbatt, 2021; Liu et al., 2020; Wang et al., 2021b). More recently, some new sulfate formation pathways, e.g., in particle nitrate photolysis (Gen et al., 2019a, b), triplet SO_2 chemistry (Donaldson et al., 2016; Gong et al., 2022), SO_2 oxidation on acidic microdroplets (Hung and Hoffmann, 2015), photosensitizer-mediated SO_2 oxidation (Tang et al., 2023; Wang et al., 2020b; Liang et al., 2022; Zhou et al., 2023; Wang et al., 2024c), chlorine photoactivation (Cao et al., 2024), and enhanced chlorine and photosensitization chemistry (Zhang and Chan, 2024) have been proposed. Despite extensive investigations into sulfate formation mechanisms, a substantial disparity persists between modeled simulations and measured sulfate concentrations, especially in marine boundary layer (Wyant et al., 2015) and anthropogenic emission dominated (Wang et al., 2014), highlighting the importance to further study the sulfate formation mechanism in these areas.~~

~~Biomass burning (BB) emits around 34–41 Tg of smoke aerosol annually, making it a significant contributor to both gaseous and particulate pollutants like SO_2, primary organic aerosol (POA), black carbon (BC) and brown carbon (BrC) (Schill et al., 2020; Laskin et al., 2015; Lin et al., 2016; Huang et al., 2022b). The recent~~ Recent fire outbreaks in areas like Canada, Amazonia, and Southeast Australia, together with the increased fire frequency and intensity reports in areas like western US have highlighted the risks of fire, especially biomass burning (BB), to human ~~and animal~~ health and climate change (Bond et al., 2013; Andreae, 2019; Jones et al., 2022). As an agricultural powerhouse, China boasts immense agricultural crop yields, especially in rice, wheat, and corn throughout the country. These crop residues are frequently burned in rural areas for cooking and heating purposes, as well as for land preparation after harvest, resulting in the substantial production of light-absorbing species, such as brown carbon (BrC) (Chen et al., 2017). ~~Atmospheric processes, e.g., atmospheric aging or long-range transport, can alter the chemical compositions and optical properties of BrC, potentially affecting the global climate.~~ Recent studies have reported that ~~the~~ specific BrC species from biomass burning, including~~e.g.,~~ vanillin (VL), acetovanillone, syringaldehyde (SyrAld), can act as photosensitizers (PS) and oxidize SO_2 to sulfate (Zhou et al., 2023; Liang et al., 2024). Atmospheric processes like ~~, e.g., atmospheric~~ aging or long-range transport, can alter the chemical compositions and optical properties of PS ~~BrC~~, potentially affecting the sulfate formation potential. ~~the global climate.~~

Sea-salt aerosol (SSA), with its high particulate matter loadings and extensive surface area, ~~is a crucial atmospheric constituent that~~ plays a significant role in interfacial and multiphase reactions with reactive gases, thereby impacting global radiation balance and air quality in marine and coastal areas (Gantt and Meskhidze, 2013; Chi et al., 2015). Prior research has identified several secondary sulfate formation pathways in SSA, e.g., multiphase SO_2 oxidation by O_3 (Alexander et al., 2012), coexistence of NO_2 (Zhang and Chan, 2023b), PS (Tang et al., 2023), chlorine-PS synergistic effects (Zhang and Chan, 2024), and Cl and OH radicals generated by chlorine photoactivation (Cao et al., 2024), highlighting the importance of NaCl-based photochemistry in sulfate formation.

SSA can frequently mix with organic matter through processes such as sea-to-air emission, photochemical oxidation and atmospheric transport (Liu et al., 2023b). Previous studies have observed ~~high~~ elevated sulfate concentrations ~~and light absorption properties~~ in coastal regions when air masses passed through inland areas due to intensive ~~biomass burning~~BB or other anthropogenic emissions, suggesting the possible interactions between the ~~sea-salt aerosol~~SSA (primarily sodium chloride) and anthropogenic emissions ~~e.g., biomass burning~~ (Qiu et al., 2019; Huang et al., 2018; Wu et al., 2022). ~~For example, Qiu et al. (2019) discovered high absorption Ångström exponent (AAE of 1.46) in coastal city Xiamen, when the air masses passing through Southeast Asia with intense biomass burning.~~ Van Pinxteren et al. (2015) observed an increase in sulfate concentration (2.26 μg m^{-3}) during the RV MARIA S cruise as it approached the African mainland, in contrast to the marine-origin aerosol (1.59 μg m^{-3}), showing significant influence of ~~biomass burning~~BB. Hence, mixing of sea-salt and biomass burning aerosols can happen in coastal regions.

Since the sulfate formation rate depends on the intrinsic properties of the solution matrix and the two main reaction matrixes in marine boundary layer (MBL) were wet aerosol (droplet in our case) and cloud/fog (bulk aqueous), both droplet and aqueous reactions are relevant for studying the aqueous reactions in aerosols and clouds within MBL (Ruiz-Lopez et al., 2020; Herrmann, 2003). Typically, droplet experiments were characterized by high ionic strength (up to >10 M), low liquid water content (10^{-7}-10^{-3} cm^3 m^{-3}) and high surface-to-volume ratio whereas aqueous reactions exhibit the opposite characteristics. Transmission electron microscopy (TEM) studies indicate that most coastal particles are internally mixed, showing a higher proportion of organic and salt mixtures in the presence of biomass burning aerosols, accompanied by an increase in sulfate (Dang et al., 2022; Li et al., 2003). However, discrepancies persist between modeled simulations and measured sulfate concentrations in MBL (Yu et al., 2023). The interactions of sea-salt and BB aerosols, especially in multiphase reactions, can potentially unravel the intricate chemistry of sulfate formation in BB affected MBL. Hence, internal mixtures of inorganic salt and water-soluble organic carbons are often used in reaction studies (Tan et al., 2024).

~~However, the studies on interactions of anthropogenic emission and sea-alt aerosol on sulfate formation are very scarce.~~

~~Prior research has identified several secondary sulfate formation pathways in sea-salt aerosol, e.g., multiphase SO_2 oxidation by O_3 (Alexander et al., 2012), coexistence of NO_2 (Zhang and Chan, 2023b), photosensitizers (Tang et al., 2023), chlorine photosensitizer synergistic effects~~

~~(Zhang and Chan, 2024), and Cl and OH radicals generated by chlorine photoactivation (Cao et al., 2024), highlighting the importance of NaCl-based photochemistry in sulfate formation. Our prior study observed higher sulfate formation for incense burning-NaCl particles than pure NaCl particles (Tang et al., 2023). The follow-up research found magnitudes higher sulfate formation rate (~132 μM s^{-1}) in premixed NH_4Cl+IC (imidazole-2-carboxaldehyde, a model photosensitizer found in secondary organic aerosol) particles than pure NH_4Cl particles (~ 1.8 μM s^{-1}) (Zhang and Chan, 2024). However, the studies on interactions of anthropogenic emission and sea-alt aerosol on sulfate formation are very scarce.~~

In this study, we performed in-situ droplet and aqueous experiments using BB extracts-NaCl mixture to explore the possible interplay between biomass burning and marine aerosols in coastal areas. BB was derived from the burning of rice straw (RS), wheat straw (WS), and corn straw (CS) as well as incense burning (IS). ~~This is supplemented by aqueous reactions using BB extracts and bisulfite to mimic the in-cloud aqueous reactions of biomass burning emission-mediated S(IV) oxidation. The effects of chloride on sulfate formation were also studied.~~ The aims of this study are to: (i) compare the differences in sulfate formation among different kinds of BB-NaCl particles and BB extracts; (ii) ~~evaluate~~ examine the impacts of the atmospheric aging (~~UV~~ OH• aging) on sulfate formation across different BB-NaCl particles and BB extracts; (iii) investigate ~~Investigating~~ the role of chloride ions in BB extracts mediated sulfate formation.

2 Material and methods

2.1 Burning experiments

Three types of commonly used biomass (RS, WS and CS) were cut into small, uniform pieces (~10 cm in length) and dried. About 100 g of the dried biomass materials (~10% moisture content) was then introduced into a traditional~~ly~~ iron stove commonly used in rural areas (Figure S1). The stove was covered with a hood and the biomass was ignited using a propane lighter. The generated BB smoke was collected onto 90-mm quartz filters at 0.9 m^3 min^{-1} for 10 minutes by a custom-made aerosol sampler under mixed combustion condition (include flaming and smoldering, modified combustion efficiency MCE, $0.85 \leq \Delta[CO_2]/(\Delta[CO_2]+\Delta[CO]) \leq 0.95$) (Ting et al., 2018). The sampler was placed at a height of 1 meter above the ground and connected to a $PM_{2.5}$ sampling head through a sampling pump. For incense burning (IS), laboratory generated smoldering smoke was collected on 47-mm quartz filters at a flow rate of ~ 6.0 L min^{-1} for 80 min using a stainless-steel combustion chamber. Note that the different combustion modes of IS and BB are intentionally used to represent the real-world combustion conditions. Our previous study demonstrated that IS was representative of BB based on GC×GC chromatograms and pixel-based partial least squares discriminant analysis ~~Our previous study has demonstrated the similarities (especially in sugars such as levoglucosan and phenols) in GC×GC chromatograms between BB and IS~~ (Tang et al., 2023). Hereafter, we will use BB to represent both the real BB materials and the surrogate materials (IS) unless otherwise specified. After sampling, the collected BB samples (fresh BB) were wrapped by pre-baked aluminum foil (550 ℃ for 6 h) and stored at -20 ℃ until further analysis.

To achieve atmospheric OH• aging, the collected fresh BB filter samples were ~~put into~~placed in a ~~the~~ pre-flushed ~~(zero air, more than 24 h)~~ combustion chamber (zero air, more than 24 h)

and illuminated ~~under~~ with UV lamps for 40 min. We used lamps of 185 nm and 254 nm, the combination of which have been widely used in oxidation flow reactor design and experiments for mimicking atmospheric OH• concentrations (Peng and Jimenez, 2020; Rowe et al., 2020; Tkacik et al., 2014; Hu et al., 2022). The estimated OH exposure was ~2.0×10^{12} molecules cm^{-3} s, equivalent to an atmospheric aging period of 15 days (assuming an average atmospheric OH concentration of 1.5×10^{6} molecules cm^{-3}) (Mao et al., 2009). Detailed characterization of the OH exposure can be found in our previous study (Tang et al., 2023).

2.2 Materials and instrumentation

Aqueous stock solutions of BB samples were prepared by dissolving the collected filters in ultrapure water and subjecting them to ultrasonication in a cooled-water bath three times, each for 20 minutes. The resulting water extracts of the BB were then filtered through 0.22 μm PTFE filters and stored in brown vials at 4°C in a refrigerator. The anions, i.e., chloride, sulfate and nitrate of the BB extracts were analyzed by Dionex ion chromatography (ICS 1100, CA). An aliquot (~0.5 ml) of the BB or IS extracts were used for water-soluble organics detection by ultra-high performance liquid chromatography (Thermo Scientific Dionex UltiMate 3000 UHPLC) coupled with high-resolution Orbitrap Fusion Lumos Tribrid mass spectrometry (Orbitrap HRMS, Thermo Fisher Scientific, USA). The particulate organic matter was also characterized by a thermal desorption module (TDS3, Gerstel) coupled to comprehensive two-dimensional gas chromatography-mass spectrometer (GCMS-TQ™8050 NX, Shimadzu, Japan). UV-Vis spectrometry (UV-3600, Shimadzu, Japan) was employed to examine the absorbance of BB extracts. Total organic carbon (TOC) was measured by total carbon analyzer (TOC-L CPH, Shimadzu, Japan). Metal concentrations were measured by inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7800). Detailed analysis can be found in Text S1. Aqueous stock solution of sodium chloride (≥99.8%, Unichem) was prepared by dissolving the corresponding salt in ultrapure water to obtain a concentration of 1M. The study utilized high purity grade synthetic air and nitrogen supplied by the Linde HKO Ltd., while sulfur dioxide was obtained from the Scientific Gas Engineering Co., Ltd.

2.3 Multiphase and aqueous-phase reactions of S(IV)

~~For~~ In SO_2 uptake experiments, the stock solution of BB extracts was premixed with sodium chloride solution (1M) at a volume ratio of 1:1 and the solutions had pH a of 4-6. A droplet generator (Model 201, Uni-Photon Inc.) was then utilized to ~~generate droplets, which were subsequently~~ deposit~~ed~~ droplets onto a hydrophobic substrate (model 5793, YSI Inc.) for SO_2 uptake experiments. Reactive SO_2 uptake experiments were performed via a flow cell/in-situ Raman system at controlled room temperature (23-25°C). The top and bottom quartz windows of the flow cell were used for Raman analysis and UV irradiation, respectively. The light experiment was performed using a xenon lamp (model 6258, ozone free, 300W, Newport, light intensity of 1318 mW/cm^2), with photon flux of 9.8 $\times10^{15}$ photons cm^{-2} s^{-1} in 280-420 nm received by particles in the flow cell (Zhang and Chan, 2023b). Identical experiments were conducted in the dark, with the lights off and the experimental area kept in complete darkness. The relative humidity (RH) inside the flow cell was adjusted to 80% by mixing dry and wet synthetic air or nitrogen. The particles were then equilibrated at 80% RH for over 60 min and remained liquid throughout the experiment period. SO_2 was introduced into the system to reach

a concentration of 8.0 ppm. The prescribed size used in our in-situ Raman research was 60 ± 5 μm. Despite using particles for droplet experiments that were larger than ambient fine particles, we employed the SO_2 uptake coefficient (γ_{SO_2}) as a kinetic parameter to account for the particle size effects. Comprehensive calculation of γ_{SO2} can be found in our previous studies (Gen et al., 2019b, a; Tang et al., 2023; Zhang et al., 2020a).

Aqueous-phase photochemical reactions were performed using a custom-built quartz photo reactor (Mabato et al., 2023; 2022). Specifically, a 500 mL solution containing 100 ppm bisulfite and 1 ppm BB TOC extracts were continuously mixed using a magnetic stirrer throughout the experiments. Note that the 1 ppm BB TOC and 100 ppm bisulfite align well with the atmospheric-relevant ranges in aqueous aerosols, fogs and clouds, where PS concentration can reach hundreds of micromolar and total sulfur concentration can exceed several millimolar. (Anastasio et al., 1997; Guo et al., 2012; Shen et al., 2012; Rao and Collett, 1995) To achieve air-saturated conditions, synthetic air was continuously introduced to the solutions at a flow rate 0.5 L min^{-1} throughout the experiments. The above mixed solutions were then exposed to radiation via the same xenon lamp as in the droplet experiments. Samples were collected at 1h~~r~~ interval for a total of 8 h for sulfate and bisulfite analysis using ion chromatography.

3 Results and Discussion

3.1 Enhanced sulfate production of BB-NaCl droplets compared to IS-NaCl droplets.

As no sulfate was detected in the dark conditions for any of the experiments, we have focused on the light experiments. Figure 1 depicts the sulfate production by (a) fresh BB-NaCl; (b) aged BB-NaCl droplets as a function of time in the presence of light, air and SO_2 at 80% RH. As our previous study (Tang et al., 2023) has found significantly higher sulfate formation of IS-NaCl droplets over NaCl droplets, here we only focus on the comparison of sulfate formation between different kinds of BB-NaCl droplets and IS-NaCl droplets. ~~Note that sulfate concentration was normalized to the initial TOC concentration of the mixture to facilitate the comparison of sulfate production of different droplet compositions.~~ Regardless of whether the extracts were fresh or aged, the sulfate production by real BB-NaCl droplets was higher than IS-NaCl droplets. Specifically, sulfate formed by fresh (F) BB-NaCl droplets followed the trends of CS_F-NaCl (16.8 ± 2.6 mM $ppmC^{-1}$) >RS_F-NaCl (9.8 ± 0.1mM $ppmC^{-1}$) >WS_F-NaCl (4.2 ± 0.2mM $ppmC^{-1}$) >IS_F-NaCl (0.8 mM $ppmC^{-1}$) after illumination for 1080 min. In aged (A) samples, while BB_A-NaCl is more efficient than IS_A-NaCl in sulfate formation, the order of sulfate formation was different from the fresh samples: RS_A-NaCl (35.2 ± 0.6 mM $ppmC^{-1}$) > CS_A-NaCl (13.0 ± 0.1 mM $ppmC^{-1}$) > WS_A-NaCl (6.0 ± 1.6 mM $ppmC^{-1}$) > IS_A-NaCl (0.6 mM $ppmC^{-1}$). The sulfate enhancement factors of RS_F-NaCl, WS_F-NaCl, and CS_F-NaCl over IS_F-NaCl after 18 h SO_2 uptake ($Sulfate_{BB_F-NaCl/IS_F-NaCl}$) were 11.7, 5.0 and 20.0, respectively. The enhancement of sulfate can also be observed in aged BB samples, with values of 54.3, 9.2 and 20.1 for RS_A-NaCl, WS_A-NaCl, and CS_A-NaCl, respectively. The lower sulfate formation of IS-NaCl droplets than BB-NaCl droplets can be explained by the significantly higher TOC concentration of IS due to the incomplete and smoldering combustion (Table S1). The TOC concentration of the IS

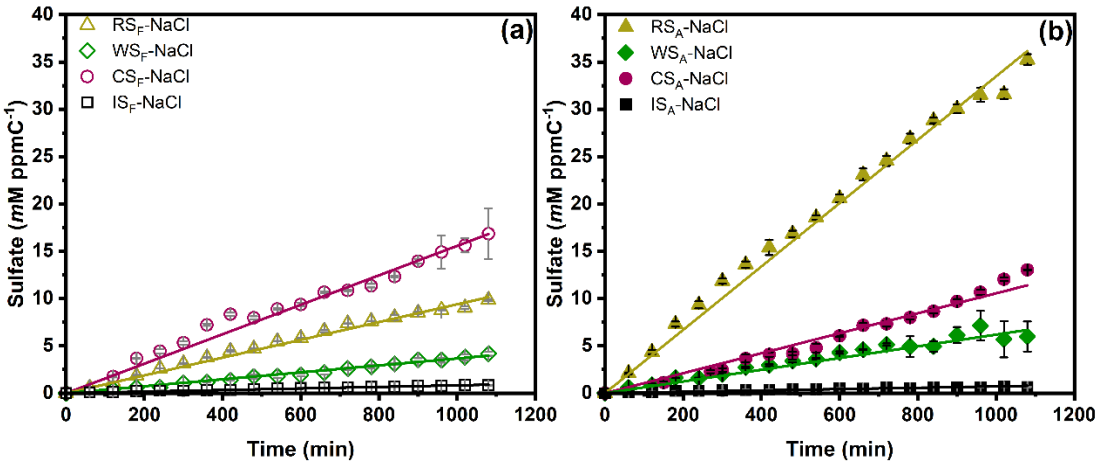
extracts (>550 mg L^{-1}) was nearly an order of magnitude higher than that of the BB extracts (34.0-69.9 mg L^{-1}), while WSOC/(WSOC+∑anions) exhibited a more than tenfold increase in BB extracts than in IS extracts. Previous studies have confirmed that the smoldering condition of BB will result in significantly more organic compounds and less ions than flaming condition (Wang et al., 2020c; Fushimi et al., 2017; Kalogridis et al., 2018; Kim et al., 2018). Additionally, significantly higher polycyclic aromatic hydrocarbons (PAHs) proportion (12.2%-16.6% by intensity) than IS (~5.0%) were observed by GC×GC-MS. Huang et al. (2022a) reported higher ~~polycyclic aromatic hydrocarbons (~~PAHs~~)~~ in BB particulates (CS, WS, RS, >262.5 mg kg^{-1}, >3.7% of organic matter) than in IS particulates (3.3 mg kg^{-1}, 0.9% of organic matter) (Song et al., 2023). Fushimi et al. (2017) and Kim et al. (2021) demonstrated that more PAHs would be emitted under flaming compared to smoldering conditions. PAHs like pyrene, fluoranthene, and phenanthrene have been recognized as PS~~photosensitizers~~ (Jiang et al., 2021; Yang et al., 2021) and are mainly from combustion processes, e.g., pyrosynthesis from aliphatic and aromatic precursors in biomass burning processes and the constituents vary with temperatures and oxygen contents (Pozzoli et al., 2004). The higher percentage of PAHs in BB together with the collection procedure (mixed combustion and higher temperature for real BB while smoldering and lower temperature for IS) suggested the BB materials would generate more PAHs at high temperatures and may contribute to sulfate formation.

Table 1 and Figure S2 presents the reactive (γ_{SO_2}) and normalized reactive SO_2 uptake coefficients ($n\gamma_{SO_2}$) of different BB-NaCl droplets. The γ_{SO_2} obtained in our study are 0.9 - 6.6×10^{-6}, which are consistent but fall on the low side of the reported heterogeneous SO_2 oxidation processes, including nitrate photolysis (10^{-6}-10^{-5}) (Gen et al., 2019b), TMI-catalyzed oxidation (10^{-6}-10^{-4}) (Zhang et al., 2024), NO_2/O_3 oxidation (10^{-6}-10^{-4}) (Zhang et al., 2021a; Zhang and Chan, 2023a) and peroxide oxidation (10^{-6}-10^{-1}) (Wang et al., 2021a; Ye et al., 2018; Yao et al., 2019). Additionally, the reported γ_{SO_2} in our study aligns well with the results obtained from ambient samples in Beijing (Zhang et al., 2020b). The large discrepancy of the reported γ_{SO_2} can be attributed to the differences in aerosol components, particle size, RH, SO_2 and oxidants concentrations. From our results, it appears that sulfate formation from BB-NaCl particles is much less effective than particles under nitrate photolysis. It is interesting to note that Zhou et al. (2023) found particles coated with model PS compounds much more effective in sulfate formation than nitrate particles under photolysis in a PAM reactor. The much shorter residence time in that reactor (2.5 min) and higher PS concentration (~66 mM) than the exposure time of filter samples (40 min) and PS concentration (<250 ppm) in our sulfate experiments may explain the differences in the comparison of PS/BB and nitrate photolysis results. Higher $n\gamma_{SO_2}$ were found for fresh and aged real BB-NaCl than IS-NaCl droplets, following the trend of :CS_F-NaCl (8.8-×-10^{-8} $ppmC^{-1}$)>RS_F-NaCl (6.2-×-10^{-8} $ppmC^{-1}$)>WS_F-NaCl (2.0-×-10^{-8} $ppmC^{-1}$)>IS_F-NaCl (0.61-×-10^{-8} $ppmC^{-1}$) and RS_A-NaCl (2.2-×-10^{-7} $ppmC^{-1}$)>CS_A-NaCl (6.2-×-10^{-8} $ppmC^{-1}$)>WS_A-NaCl (3.5-×-10^{-8} $ppmC^{-1}$)>IS_A-NaCl (0.46-×-10^{-8} $ppmC^{-1}$), respectively.

In our previous study, we observed a significant increase in sulfate formation for IS-NaCl droplets than NaCl droplets, which we attributed to photosensitization (Tang et al., 2023). Considering the fact that BB-NaCl droplets produced sulfate more efficiently than IS-NaCl droplets and NaCl droplets, we explore the underlying mechanisms driving this phenomenon.

Possible reasons include nitrate (from BB extracts or newly formed) photolysis, [Cl^--H_3O^+-O_2] photoexcitation (Cl^- from BB extracts), H_2O_2 oxidation, BC-catalyzed oxidation, reactive nitrogen species oxidation, and organics-driven pathways e.g., HCHO, photosensitizing components, organic peroxide, and TMI-organic oxidation (Ye et al., 2023).

Since there was no nitrate peak in our Raman spectra in all experiments, the potential impact from nitrate photolysis was excluded. Besides, the significantly low Cl^- concentration (0.0002-0.001M) in the original BB extracts (compared to 1M NaCl, Table S1) has minimized the influence of chloride photoexcitation of [Cl^--H_3O^+-O_2] (Cl^- from BB extracts) on the sulfate formation. Reactive nitrogen species e.g., NO_x, HONO and NH_3 were neither introduced nor detected in our system, indicating that the oxidation pathway involving reactive nitrogen species was insignificant. Additionally, the water extraction process has excluded the possibility of BC-catalyzed oxidation. The absence of sulfate formation in dark conditions ruled out the involvement of direct H_2O_2 oxidation and organic peroxide oxidation pathways. The concentrations of TMI did not exhibit a consistent relationship with the sulfate formation observed in both BB_F-NaCl and BB_A-NaCl droplets (Figure ~~S2~~S3), suggesting that the TMI-catalyzed oxidation pathway may not be responsible for the observed phenomenon. Therefore, the most probable reason for the enhancement of sulfate formation by BB-NaCl droplets over NaCl droplets would be the photosensitizing components. Given the complexity and the lack of a method to quantify PS in BB aerosols, using the total TOC concentration as an upper limit for estimating PS concentration is considered a compromise that allows for systematic comparison. Our goal is to compare the photosensitizing ability in different chemical systems, but not to quantify their absolute values. Therefore, the sulfate formation reported here can be considered as the lower limit of photosensitizing capacity. State-of-the-art mass spectrometry analysis including UHPLC-Orbitrap-MS and GC×GC-MS showed the existence of possible ~~photosensitizers~~ PS such as PAHs (e.g., fluoranthene, pyrene, cyclopenta[cd]pyrene, 4-methylphenanthrene, benzo[a]pyrene, perylene, Table S2) and aromatic carbonyls (SyrAld, VL, 3,4-dimethoxybenzaldehyde, acetophenone, acetosyringone, Table S2). Photosensitizing components can directly or indirectly (by forming secondary oxidants in the presence of oxygen) oxidize S(IV) to S(VI). Wang et al. (2020b) proposed a direct oxidation process of S(IV) to sulfate by excited triplet states of photosensitizers (^{3}PS*). To explore the contribution of the direct ^{3}PS* oxidation on sulfate formation, we performed the same sets of experiments in N_2-saturated condition, shown in Figure ~~S3~~2.Under N_2-saturated conditions, secondary oxidants such as HO_2•, OH• oxidation pathway can be ruled out due to the lack of oxygen. Consequently, the sulfate formed under this condition can be considered as the direct PS* oxidation. The BB-NaCl droplets showed only direct PS* oxidation contribution of 3.6% to 22.7%, highlighting the predominant role of secondary oxidants (Tang et al., 2023). For BB_F-NaCl droplets, the contribution of direct PS* followed the trend of WS_F-NaCl (22.7%) > RS_F-NaCl (15.7%) > CS_F-NaCl (7.0%), while for BB_A-NaCl droplets, WS_A-NaCl (10.2%) > CS_A-NaCl (6.7%) > RS_A-NaCl (3.6%) was observed. In summary, regardless of whether fresh or aged, the secondary oxidants triggered by indirect PS* oxidation were the main reason for sulfate formation, highlighting the importance of O_2 in PS* mediated oxidation processes.



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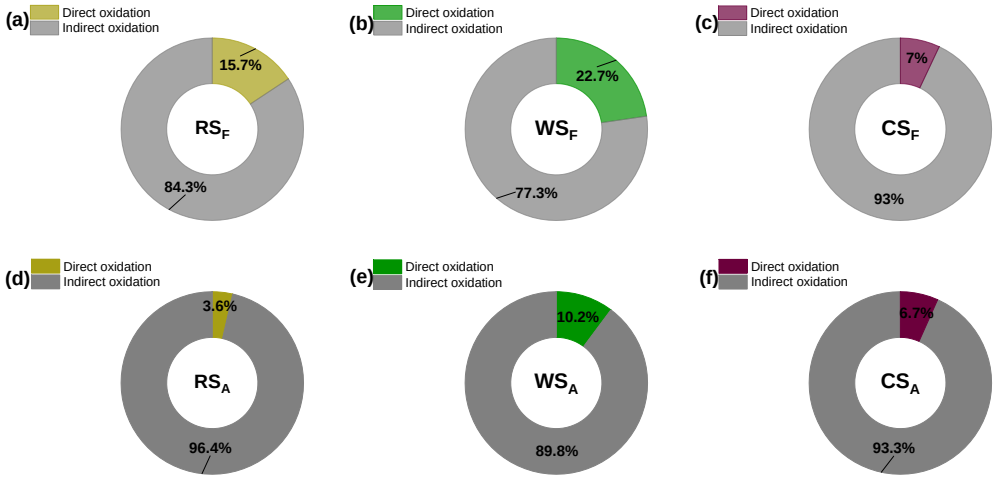
328 Figure 1. Sulfate production under different droplet compositions as a function of time by
329 droplet experiments: (a) fresh BB-NaCl droplets; (b) aged BB-NaCl droplets in air at 80% RH.
330 RS, WS, CS and IS represent rice straw, wheat straw, corn straw and incense burning,
331 respectively. The subscripts F and A represent fresh and aged, respectively.



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333 Figure 2 Contributions of direct and indirect PS* oxidation to sulfate in droplet experiments

334 Table 1. Sulfate formation rate constant ($k_{so_4^{2-}}$), reactive (γ_{SO_2}) and normalized SO_2 uptake
335 coefficient ($n\gamma_{SO_2}$) of various particle compositions at 80% RH. Sulfate formation rate ($k_{so_4^{2-}}$)
336 for aqueous phase reactions using different BB extracts and model compounds. 1, 10, 100 and
337 200 represent the concentration of different compounds (in ppm).

Particle Composition	$k_{so_4^{2-}}$	γ_{SO_2}	$n\gamma_{SO_2}$ [a]
	(μM min^{-1} ppmC^{-1})		ppmC^{-1}
RS$_F$-NaCl	9.4 ± 0.10	(2.2 ± 0.023)×10^{-6}	(6.2 ± 0.066)×10^{-8}
WS$_F$-NaCl	3.7 ± 0.048	(0.66 ± 0.0086)×10^{-6}	(2.0 ± 0.027)×10^{-8}
CS$_F$-NaCl	15.6 ± 0.11	(2.0 ± 0.015)×10^{-6}	(8.8 ± 0.065)×10^{-8}

IS_F-NaCl	0.83 ± 0.011	(1.7 ± 0.034)-×-10^{-6}	(0.61 ± 0.012)-×-10^{-8}
RS_A-NaCl	33.5 ± 0.38	(6.6 ± 0.074)-×-10^{-6}	(21.5 ± 0.24)-×-10^{-8}
WS_A-NaCl	6.2 ± 0.18	(0.92 ± 0.027)-×-10^{-6}	(3.5 ± 0.10)-×-10^{-8}
CS_A-NaCl	10.6 ± 0.23	(1.0 ± 0.023)-×-10^{-6}	(6.2 ± 0.13)-×-10^{-8}
IS_A-NaCl	0.72± 0.026	(1.3 ± 0.052)-×-10^{-6}	(0.46 ± 0.017)-×-10^{-8}

Aqueous Reactions	Concentration (ppm)	$k_{so_4^{2-}}$ (ppm min^{-1})	$k_{so_4^{2-}}$[a] (μM min^{-1})
RS_F	1	0.31	3.2
RS_F-NaCl	1-100	0.16	1.6
RS_F-NaCl	1-200	0.085	0.9
WS_F	1	0.19	2.0
CS_F	1	0.25	2.6
IS_F	1	0.19	2.0
RS_A	1	0.33	3.4
RS_A-NaCl	1-100	0.37	3.8
RS_A-NaCl	1-200	0.63	6.4
WS_A	1	0.26	2.7
CS_A	1	0.33	3.4
IS_A	1	0.080	0.82
NaCl	100	0.051	0.52
NaCl	200	0.079	0.81
SyrAld	1	0.15	1.5
SyrAld-Pyz	1-1	0.68	7.1
SyrAld-Pyz-NaCl	1-1-10	0.67	6.9
SyrAld-Pyz-NaCl	1-1-100	0.55	5.7
SyrAld-Pyz-NaCl	1-1-200	0.50	5.2
SyrAld-4-NC	1-1	0.11	1.1
SyrAld-4-NC-NaCl	1-1-10	0.13	1.4
SyrAld-4-NC-NaCl	1-1-100	0.13	1.4

SyrAld-4-NC-NaCl	1-1-200	0.15	1.5
SyrAld-NaCl	1-10	0.11	1.1
SyrAld-NaCl	1-100	0.17	1.8
SyrAld-NaCl	1-200	0.17	1.7
VL	1	0.26	2.7
VL-Pyz	1-10	0.61	6.4
VL-Pyz-NaCl	1-1-10	0.55	5.8
VL-Pyz-NaCl	1-1-100	0.43	4.5
VL-Pyz-NaCl	1-1-200	0.42	4.3
VL-4-NC	1-1	0.17	1.7
VL-4-NC-NaCl	1-1-10	0.22	2.3
VL-4-NC-NaCl	1-1-100	0.27	2.7
VL-4-NC-NaCl	1-1-200	0.23	2.4
VL-NaCl	1-10	0.25	2.6
VL-NaCl	1-100	0.26	2.7
VL-NaCl	1-200	0.28	2.9

[a]The $n\gamma_{SO_2}$ was calculated by normalizing the γ_{SO_2} with the TOC concentration in the BB extracts~~was normalized by the initial TOC concentration (ppmC)~~, i.e., $n\gamma_{SO_2} = \gamma_{SO_2}/TOC$

3.2 Aging effects on sulfate formation across various BB materials

To investigate the aging effects across various BB materials, we ~~aged~~ subjected the collected BB filters to OH radical aging by~~by~~ irradiating them with UV lights at wavelengths of ~~(~~185 nm and 254 nm~~)~~. This combination effectively generate OH radicals (Tang et al., 2023). Figure S4 exhibits the differences in sulfate formation rates of different fresh and aged BB materials. RS and WS show sulfate formation enhancement, while CS and IS show reduction after aging. Figure ~~2~~3(a) shows that the 18h sulfate enhancement factor ($Sulfate_A/Sulfate_F$) followed the trend of RS-NaCl (3.6) >WS-NaCl (1.4) > CS-NaCl (0.8) ≈ IS-NaCl (0.8), which is neither consistent with the trends of sulfate formation for BB_F-NaCl nor BB_A-NaCl, indicating that aging processes have different influence on sulfate formation towards BB materials. A similar trend was found for $n\gamma_{SO_2}$, showing the highest and lowest sulfate enhancement for RS-NaCl (3.5) and IS-NaCl (0.7), respectively.

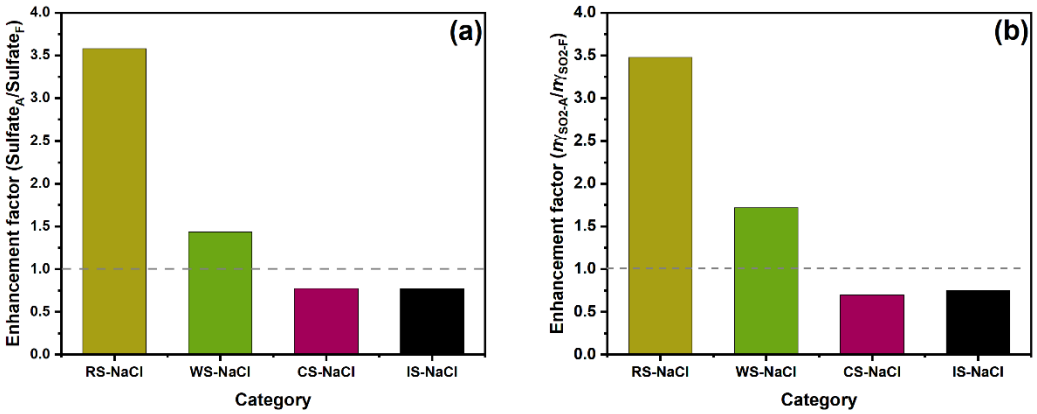


Figure ~~2~~3. Enhancement factor of (a) sulfate and (b) normalized SO_2 uptake coefficient $n\gamma_{SO2}$ between fresh and aged BB-NaCl droplets by droplet experiments.

~~We also performed aqueous reactions using fresh/aged BB extracts to investigate the aging effects on the sulfate formation (Figure S7). The sulfate formation rate ($k_{so_4^{2-}}$) for different BB extracts during initial photoinduced experiments ranged from 0.8 to 3.4 μM min^{-1}. The $k_{so_4^{2-}}$ obtained in bulk-phase reactions were a magnitude lower than that of the droplets (Table 1), which is consistent with previous studies (Wang et al., 2024c; Zhang and Chan, 2024). Wang et al. (2024c) discovered sulfate formation rate magnitudes higher at air-water interface (AWI) than conventional bulk-phase reactions. They attributed this to accelerated electron transfer process at AWI, where ^{3}PS* (^{3}HULIS* in their case) can accept electrons from HSO_3^- in a more efficient way due to their incomplete solvent cages. Zhang and Chan (2024) fitted a ~3 orders of magnitude higher rate constant of IC*+Cl$^-$ (~10^8 M^{-1}s^{-1}) in particle phase than bulk-phase rate constant (~10^5 M^{-1}s^{-1}) (Gemayel et al., 2021; Woods et al., 2020). They attributed the enhanced sulfate formation to the expedited reactions between ^{3}PS* and chloride ions to form reactive chlorine species, facilitated by the decreased solvation of chloride and ^{3}PS* at the AWI (Zhang and Chan, 2024). Many studies have demonstrated that chloride ions, bisulfite ions and surfactant-like PS have the propensity to reside at the AWI of droplets, primarily driven by polarization interactions. This promotes enlarged bond dipole moments and ordered alignment of reactant molecules, resulting in reduced entropy and heightened free energy of the initial state (Jungwirth and Tobias, 2002, 2006; Ruiz-Lopez et al., 2020; Tinel et al., 2016; Yan et al., 2016; Fu et al., 2015). Other factors, e.g., S(IV) concentration (8 ppm gaseous SO_2 in droplet experiment and 100 ppm HSO_3^- in aqueous reactions), and the addition of NaCl (1M NaCl addition in droplets and no NaCl addition in aqueous reactions) may also contribute to the high sulfate formation rate in droplet experiments. In this study, the more efficient sulfate formation in droplet experiments than bulk solutions can potentially be attributed to the accelerated reactions induced by photosensitizers at the AWI, intensity variance in droplets and aqueous solution, concentrations difference in S(IV) and the addition of NaCl. However, the detailed mechanisms of the accelerated sulfate formation in droplets than bulk are still uncertain and out of the scope of this paper, and more research should be performed in the future.~~

Aqueous reactions using fresh/aged BB extracts were performed to investigate the aging effects on the sulfate formation in cloud phase (Figure S5). As the experiment proceeded, sulfate

concentrations accumulated while bisulfite concentrations decreased. Concurrently, the pH of the aqueous solution decreased from approximately 5.0 to 3.0, reflecting enhanced acidity. In bulk experiments, all BB extracts have higher $k_{so_4^{2-}}$ after aging. The increased sulfate formation of BB extracts after aging may be due to changes in their chemical compositions. Compared to RS_F (28.3% for CHON- and 67.3% for CHN+ in total intensity), RS_A has higher CHON- (36.1%) and CHN+ (88.3%) percentages (Figs. S6-S7). Zhao et al. (2022) observed a slight increase in CHON percentage for RS from 53.4% to 56.2% after aging. Similar trend was observed for CS extracts, where CHON- and CHN+ percentage increases from 26.7% and 65.2% to 31.5% and 68.8%, respectively, after aging. Given the presence of chromophoric compounds in BrC~~As chromophoric compounds are present in brown carbon (BrC)~~ (Laskin et al., 2015), we constrained the DBE values to the range of ~~(~~0.~~5c~~5C≤DBE≤0.~~9c~~9C~~)~~ to semi-qualitatively distinguish BrC chromophores in the dissolved organic carbon ~~BrC~~ (Lin et al., 2018). $BB_{F/A}$ was defined as the water-soluble organic species while $BB_{F/A\text{-}BrC}$ represented the molecularly identified water-soluble brown carbon falling in the range of 0.5C⩽DBE⩽0.9C in BB extracts. These definitions will be consistently applied hereafter. Higher amounts of CHON- species were found in $RS_{A\text{-}BrC}$ (41.9%) and $CS_{A\text{-}BrC}$ (35.5%) than $RS_{F\text{-}BrC}$ (32.3%) and $CS_{F\text{-}BrC}$ (34.7%). One of the key categories of CHON- is nitrated aromatics, which have been widely identified in lab-generated BB smoke (Huang et al., 2022b; Wang et al., 2017a; Zhang et al., 2022; Xie et al., 2019) and field campaigns (Salvador et al., 2020; Mohr et al., 2013; Chen et al., 2022). A series of CHON- species, e.g., $C_6H_5NO_3$, $C_6H_5NO_4$, $C_7H_7NO_3$, and $C_8H_9NO_3$, which were tentatively identified as nitrophenol, nitrocatechol, methyl-nitrophenol, and dimethyl-nitrophenol, have been detected in our BB extracts. Nitrophenols photolysis has been found to be a potential source of OH radicals (Sangwan and Zhu, 2018; Guo and Li, 2023; Cheng et al., 2009; Sangwan and Zhu, 2016). Therefore, the increase in sulfate formation by RS_A and CS_A may partially be related to the more oxidants generated by nitrophenol photolysis.

Approximately 80% of the CHN+ species identified exhibited a diatomic nitrogen composition in their molecular formula. The precise determination of the molecular structures of these compounds solely based on elemental composition is challenging due to the presence of stable isomers. However, the N-bases, which contain two nitrogen atoms, can be attributed to various N-heterocyclic alkaloids (Figure S8). For example, homologs of $C_5H_6N_2(CH_2)_n$ were likely pyrazine, pyrimidine or amino pyridine, which were composed of six-membered heterocyclic rings with N atoms and alkyl side chains (Lin et al., 2012; Laskin et al., 2009). $C_5H_8N_2(CH_2)_n$ were likely alkyl-substituted imidazole compounds, featuring a five-membered heterocyclic ring with two nitrogen atoms as the core structure and alkyl side chains (Lin et al., 2012; Laskin et al., 2009). For $C_7H_6N_2(CH_2)_n$ homologs, the core skeleton was $C_7H_6N_2$, with an AI_{mod} of 0.8, indicating its distinctive characteristics of compounds containing fused five-membered and six-membered rings, such as benzimidazole or indazole (Wang et al., 2017b). Redox-inactive heterocyclic nitrogen-containing bases, e.g., pyridine, imidazole, and their derivatives, have been shown to enhance the redox activity of humic-like substances (HULIS) fraction by hydrogen-atom transfer, with the degree of enhancement directly correlated to their concentration (Dou et al., 2015; Kipp et al., 2004). Thus, the increased CHN+ percentage may also contribute to the enhanced sulfate formation of RS_A and CS_A by acting as a H-bond acceptor to facilitate the $^3PS^*$-mediated oxidation by generating more oxidants.

However, the CHON- and CHN+ percentages in WS_A were lower than WS_F, indicating that the sulfate enhancement in WS_A was not due to the CHON and CHN species. Instead, CHO- accounted for higher proportion in WS_A (68.5%) and $WS_{A\text{-}BrC}$ (68.9%) than WS_F (65.0%) and $WS_{F\text{-}BrC}$ (64.8%).This aligns with a prior AMS study, showing increased CHO proportions in aged wheat burning emissions (Fang et al., 2017). We suppose that CHO- compounds, particularly photosensitizing compounds with carbonyl groups, would explain the difference of sulfate formation in WS extracts (Gómez Alvarez et al., 2012; Mabato et al., 2023; Felber et al., 2020; Fu et al., 2015). Therefore, we filtered the chemical formula of CHO- species from UHPLC-Orbitrap-HRMS by applying the maximum carbonyl ratio (MCR) (Zhang et al., 2021b; Wang et al., 2024a; Calderon-Arrieta et al., 2024; Liu et al., 2023a), H/C, O/C as well as modified aromaticity index (AI_{mod}) to focus on potential ~~photosensitizers~~ PS (Zherebker et al., 2022; Koch and Dittmar, 2006). In short, molecular formula were classified into six groups, namely, condensed aromatics ($AI_{mod}\geq0.67$), polyphenolics ($0.50<AI_{mod}<0.67$), highly unsaturated and phenolic compounds ($AI_{mod}\leq0.5$, $H/C<1.5$), aliphatics ($H/C\geq1.5$, $O/C\leq0.9$, $N=0$), peptide-like compounds ($H/C\geq1.5$, $O/C\leq0.9$, $N>0$) and sugar-like compounds ($H/C\geq1.5$, $O/C>0.9$), details can be found in Text S1. As aliphatics, peptide-like compounds and sugar-like compounds are unlikely to be PS~~photosensitizers~~, we exclude them as potential PS. By applying a data filtration process involving CHO-, condensed aromatics, polyphenolics, highly unsaturated and phenolic compounds based on the aforementioned criteria ~~abovementioned~~, ~~and~~ as well as MCR≥0.9 (which includes oxidized unsaturated and highly unsaturated compounds such as PS like imidazole-carboxaldehyde and PAHs) (Zhang et al., 2021b), 52.6% and 49.7% of the compounds (by intensity) can be considered as potential PS in ~~were selected by~~ WS_A and WS_F, respectively. The main compositional difference lies in polyphenolics, comprising 26.3% and 21.8% of WS_A and WS_F respectively. Therefore, the higher sulfate formation in WS_A may be related to the higher contributions of the polyphenolics, e.g., $C_8H_8O_3$.

To summarize, we propose that the enhanced sulfate formation in CS_A and RS_A was likely due to the increased proportions (by intensity) of CHON and CHN species, potentially nitrophenols and N-heterocyclic compounds. Conversely, the increased sulfate formation in WS_A appears to be linked to a higher percentage of CHO species. However, the associations between detailed chemical characteristics and sulfate formation were not provided in this study due to the complexity of the interactions between different chemical categories and difficulties in the interpretation of the coefficients. Future studies are needed to elucidate the relationships between sulfate formation and the chemical characteristics.

3.3 Effects of Chloride and Nitrogen-containing Species on Sulfate Formation

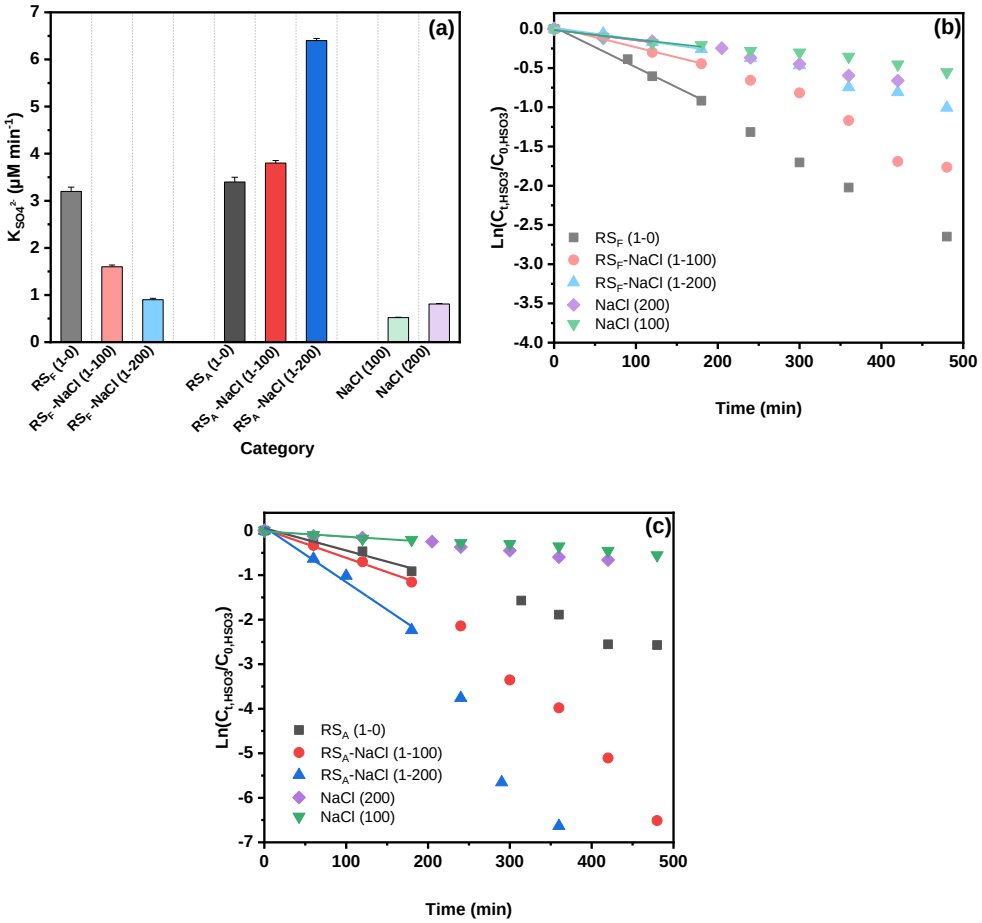
Unlike the droplet experiments where RS-NaCl has the highest sulfate enhancement factor after aging, aqueous reaction results (without NaCl) show a sulfate enhancement trend of WS>CS>RS>IS, suggesting that chloride may take effect in the droplet experiments, especially in RS-NaCl system. Therefore, bulk reaction experiments using ~~rice straw (~~RS~~)~~ extracts as an example were performed with 100-200 ppm NaCl additions, where the NaCl to TOC ratio ranged from 100:1 to 200:1 to match the 100:1 to 1000:1 range in droplet experiments, in order to evaluate the effects of chloride on sulfate formation. Interestingly, incorporating NaCl

yielded contrasting results for RS_F and RS_A (Figure ~~3~~4). While the addition of NaCl enhanced sulfate formation in RS_A, it showed the opposite trend in RS_F. The nature of the cations and ionic strength may affect the sulfate formation rate; however, previous studies have indicated that their effects are negligible (Zhang and Chan, 2024; Parker and Mitch, 2016). The opposite effect of the NaCl addition on RS_F and RS_A, to some extent, ~~explain~~explains the significantly higher sulfate and SO_2 uptake coefficient enhancement factor for RS-NaCl in Fig. 2. Compared to the RS-based system, NaCl control experiment showed minimum (but non-zero) sulfate formation (Table 1 and Figure ~~4~~3). On one hand, it ~~confirmed~~ supported the findings that chloride participated in the sulfate formation under light but no sulfate formation under dark ~~in bulk reactions, possibly by forming Cl and OH radicals in the presence of air and water~~ (Cao et al., 2024; Tang et al., 2023; Zhang and Chan, 2024). On the other hand, the opposite trend of Cl^- effects on RS_F and RS_A reflects its complex interactions with BB extracts under light and air. While direct reaction between S(IV) species and ~~triplet states of photosensitizers (~~^{3}PS*~~)~~ may occur (Wang et al., 2020b), other pathways, i.e., interactions among halide ions, ~~photosensitizers~~ PS and oxygen should also be considered. PS in BB extracts can absorb solar radiation and form ~~triplet state photosensitizer (~~^{3}PS*~~)~~, which can then react with molecular oxygen and form singlet-state oxygen $^1O_2$* through energy transfer. ^{3}PS* can also react with H-donor, typically organic acids (RH, e.g., vanillic acid, succinic acid, azelaic acid, glutaric acid, sorbic acid, salicylic acid, Table S3) through H transfer reactions, and form a ketyl radical ($PSH^{\bullet\bullet}$) and an alkyl or phenoxy radical ($R^{\bullet\bullet}$). $PSH^{\bullet}$ and $R^{\bullet\bullet}$ can then participate in a series of reactions to form $OH^{\bullet\bullet}$, $HO_2^{\bullet\bullet}$, H_2O_2 and $O_2^{\bullet\bullet-}$. In the presence of a large excess of Cl^-, Cl^- can act as an electron donor, and react with ^{3}PS*, forming a $Cl^{\bullet\bullet}$ and a deprotonated ketyl radical ($PS^{\bullet\bullet}$) (Jammoul et al., 2009). Further reactions are similar to the abovementioned reactions, including the formation of reactive chlorine species (RCS, i.e., $Cl^{\bullet}$, $Cl_2^{\bullet-}$ and $ClOH^{\bullet-}$) and reactive oxygen species (ROS, i.e., $OH^{\bullet\bullet}$, $HO_2^{\bullet\bullet}$, H_2O_2 and $O_2^{\bullet\bullet-}$). These RCS and ROS simultaneously contribute to S(IV) oxidation to S(VI) (Zhang and Chan, 2024).

Statistical analysis using the Pearson correlation coefficient revealed that the concentrations of CHO, CHON, and CHN species exhibited significant correlations (|R|>0.5) with the sulfate formation rate ($p < 0.05$, Figure S9). As PS can be the main CHO species contributing to sulfate formation, N-containing organic compounds (NOCs), i.e., CHN and CHON species, may affect the chloride contribution on sulfate formation rate. Therefore, we selected SyrAld and VL as model CHO (PS), pyrazine (Pyz) as a model CHN, and 4-nitrocatechol (4-NC) as a model CHON to elucidate how potential chemical compounds can alter the effects of chloride on sulfate formation rate by studying the CHO+Cl^-, CHO+CHN+Cl^-, and CHO+CHON+Cl^- systems. For SyrAld and VL, as the $[Cl^-]_0/[PS]_0$ increases, $k_{so_4^{2-}}$ initially decreases and then increases. The initial decrease of $k_{so_4^{2-}}$ may be attributed to the quenching of ^{3}PS* by electron transfer from Cl^- or loss of OH radials by forming $ClOH^{\bullet-}$ through reaction of $OH^{\bullet\bullet}$+Cl^- ↔$ClOH^{\bullet\bullet-}$(Anastasio and Newberg, 2007). Excessive chloride (e.g. 100 and 200 ppm) may generate Cl and OH radicals through photoexcitation in the presence of air and water and compensate for the loss of ^{3}PS* or OH radicals. Previous studies have shown controversial influence of halides on the photosensitized oxidation of organic compounds or bisulfite. Parker and Mitch (2016) and Zhang et al. (2023) attributed the significantly higher photodegradation of dienes, thioethers and acetaminophen to the formation of reactive halogen species generated by the reactions of PS and halides. Zhang and Chan (2024) reported that $[Cl^-/PS]_0$ in the range

of 1:2 to 4:1 did not lead to significant difference in sulfate formation, possibly due to the insufficient Cl^- concentration in triggering the interplay between PS and Cl^-. The differences between the current results and the aforementioned study might be attributed to the higher $[Cl^-/PS]_0$ (up to 1:200) which may have been sufficient to initiate the relevant reactions, as well as the difference in photosensitizing capacities of the PS studied (triplet quantum yield of 0.86 ± 0.05 for 2-IC and 0.21 ± 0.01 for VL) (Felber et al., 2021; 2020). Safiarian et al. (2023) reported that increasing chloride concentrations facilitated anthracene photosensitization by producing high-level reactive oxygen species (ROS). Wang et al. (2023a) found that the effects of chloride on sulfate formation depended on the specific PS: enhancing sulfate production for benzophenone (BP) and 3,4-dimethoxybenzaldehyde (DMB), but decreasing it for 1,4-naphthoquinone.

When incorporating CHN species, a 2-3-fold $k_{SO_4^{2-}}$ was observed, due to the enhanced H transfer by CHN acting as H-bond acceptor (Dou et al., 2015). With the addition of NaCl, the enhanced H-transfer effect by CHN was inhibited, possibly due to the consumption of $^3PS^*$ by Cl^-. The addition of model CHON species into PS decreased $k_{SO_4^{2-}}$, due to the consumption of $^3PS^*$ by CHON species, in agreement with Wang et al. (2023b) who reported increased effective quantum yield of 4-NC when co-photolysis with VL. Further addition of NaCl increased the $k_{SO_4^{2-}}$, possibly due to the consumption of 4-NC by RCS (Wang et al., 2024b), which, to some extent, reduced the loss of $^3PS^*$. Generally, the addition of chloride increased $k_{SO_4^{2-}}$ of PS-CHON but decreased $k_{SO_4^{2-}}$ of PS-CHN. However, the ambient air is characterized by the presence of tens of thousands of chemical compounds. As a result, the interplay among this diverse array of species may occur in ways that exceed current understanding, necessitating additional research to investigate the interactions between different organic compounds more thoroughly.


(a)
$K_{SO4^{2-}}$ (μM min^{-1})
RS$_F$ (1-0)
RS$_F$-NaCl (1-100)
RS$_F$-NaCl (1-200)
RS$_A$ (1-0)
RS$_A$-NaCl (1-100)
RS$_A$-NaCl (1-200)
NaCl (100)
NaCl (200)
Category
(b)
Ln(C$_{t,HSO3}$/C$_{0,HSO3}$)
RS$_F$ (1-0)
RS$_F$-NaCl (1-100)
RS$_F$-NaCl (1-200)
NaCl (200)
NaCl (100)
Time (min)
(c)
Ln(C$_{t,HSO3}$/C$_{0,HSO3}$)
RS$_A$ (1-0)
RS$_A$-NaCl (1-100)
RS$_A$-NaCl (1-200)
NaCl (200)
NaCl (100)
Time (min)

536

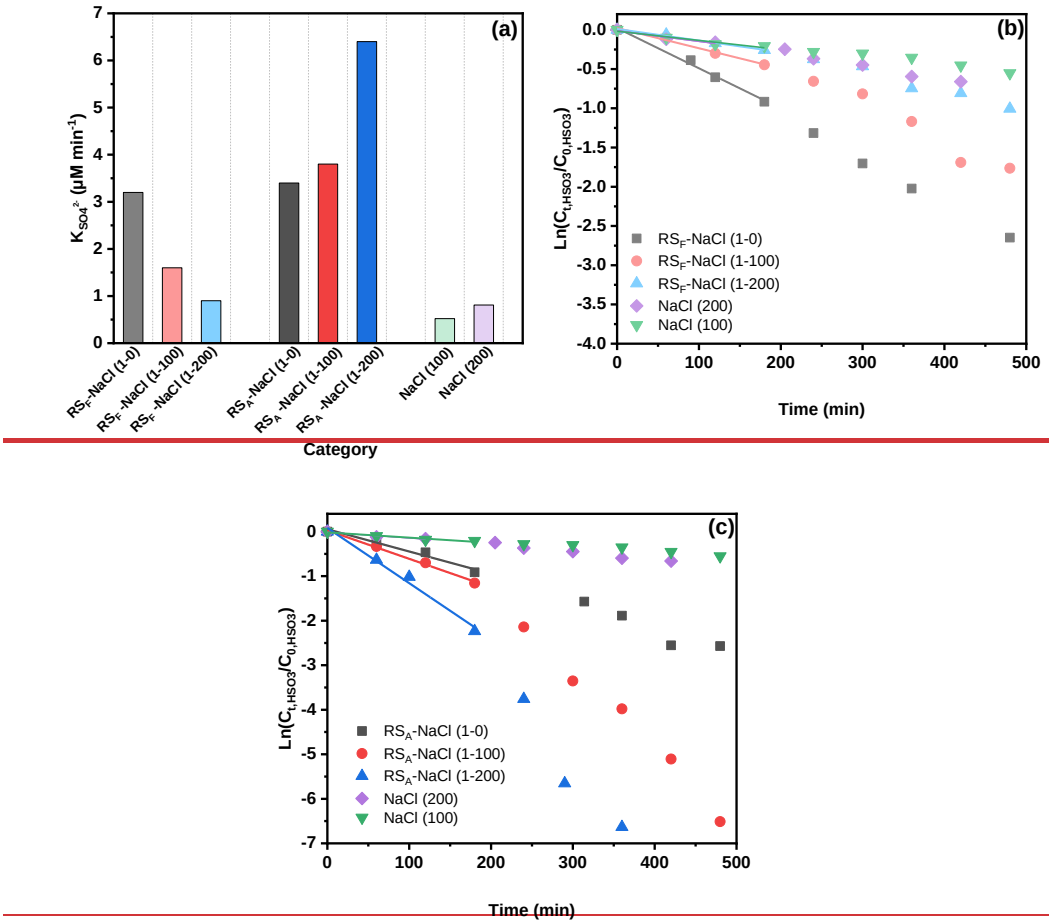


Figure ~~3~~4. (a) Sulfate formation rate and (b) (c) bisulfite decay in RS-NaCl aqueous ~~system~~reactions. 1-0, 1-100, and 1-200 refer to the concentration ratios of TOC_{RS} and NaCl, in which 1, 100, 200 represent 1 ppm, 100 ppm and 200 ppm, respectively.

3.4 Proposed mechanism for sulfate formation

A conceptual diagram of PS and chloride mediated ROS and RCS production in the oxidation of S (IV) to S (VI) was shown in Fig. 45. Initially, the ~~photosensitizers~~ PS (~~PS,~~ e.g., SyrAld and VL) absorb solar radiation and produce the singlet state ^{1}PS*, which then undergo a spin conversion through intersystem crossing, leading to the formation of the triplet state ^{3}PS*. The ^{3}PS* can react with molecular oxygen through energy transfer and generate singlet state $^1O_2$*, while the ^{3}PS* returns to ground state. The $^1O_2$* can then transform to $O_2^{\bullet-}$ via electron transfer. The ^{3}PS*can also react with an H donor (RH, e.g., organic acids, syringol, guaiacol, Table S3), leading to the formation of alkyl or phenoxy radical ($R^{\bullet}$) and a ketyl radical ($PSH^{\bullet}$). $R^{\bullet}$ can react with O_2 and form RO_2 radicals while $PSH^{\bullet}$ can transfer an H atom to O_2 and form $HO_2^{\bullet}$, returning to its ground state PS. Additionally, ^{3}PS* can react with an electron donor, e.g., Cl^-, and form chlorine radicals and $PS^{\bullet-}$. The formed $PS^{\bullet-}$ then reacts with O_2 and form $O_2^{\bullet-}$, which undergoes a series of reactions and form $HO_2^{\bullet}$, H_2O_2 and $OH^{\bullet}$. The above-mentioned reactions are the main processes in ROS pathway. Recently, Zhang and Chan(2024) have proposed that the reactive chlorine species (RCS) would contribute to sulfate formation. Cao et al. (2024)

proposed a mechanism of OH and Cl radicals formation by [Cl^--H_3O^+-O_2] under light irradiation through an electron transfer process. Our results also demonstrate that the addition of Cl^- will affect the oxidation process of S(VI) (Figures ~~3~~4, S10-S12). Combining the above, the RCS pathway was shown in yellow arrows in Figure 45. The $Cl^{\bullet}$ can be formed in two pathways, photoexcitation of the [Cl^--H_3O^+-O_2] complex that generates Cl radicals in deliquescent BB-NaCl droplets or aqueous BB-NaCl solution (Cao et al., 2024), and PS* mediated $Cl^{\bullet}$ formation via electron transfer by Cl^- (Corral Arroyo et al., 2019). The formed $Cl^{\bullet}$ can then react with each other through radical-radical reactions and produce molecular Cl_2. The $Cl^{\bullet-}$ can also react with Cl^- or $Cl_2^{\bullet-}$, forming $Cl_2^{\bullet-}$ or Cl_2. $Cl^{\bullet}$ and $Cl_2^{\bullet-}$ can also react with OH and form HOCl. ^{3}PS* itself can also oxidize the S(IV) (e.g., dissolved SO_2 or bisulfite) to S(VI). However, significantly lower sulfate formation was found in the presence of N_2 compared to air condition (Figure 2~~S3~~), highlighting the importance of secondary oxidants compared to direct PS* oxidation. As a consequence, these reactive species, e.g., $OH^{\bullet}$/$HO_2^{\bullet}$/$O_2^{\bullet-}$ and $Cl^{\bullet}$/$Cl_2^{\bullet-}$ may all participate in the oxidation of S(IV) to S(VI). In addition, the nitrogen-containing heterocyclic compounds such as pyrazine can act as H-bonding acceptor and facilitate the H transfer, which then generates more ROS (Dou et al., 2015). In light of the absence of substantial fluctuations in chloride concentration (Figure S13 and S14, insignificant chloride concentration change was found even in 10 ppm NaCl addition), it is postulated that chloride ions may function as a reactive medium rather than as direct reactants. In this proposed scenario, the Cl radicals and $Cl_2^{\bullet-}$ intermediates generated during the reaction subsequently undergo reversion back to Cl^- ions, thereby maintaining a relatively constant Cl^- concentration throughout the experimental observations. Note that although ROS and RCS pathways both contribute to the oxidation from S(IV) to S(IV), they may act as competitive relationships due to the co-consumption of PS*. Therefore, different Cl effects may occur regarding various combinations of reactants (Figure ~~3~~4, promoting effect in RS_A, inhibiting effects on RS_F).

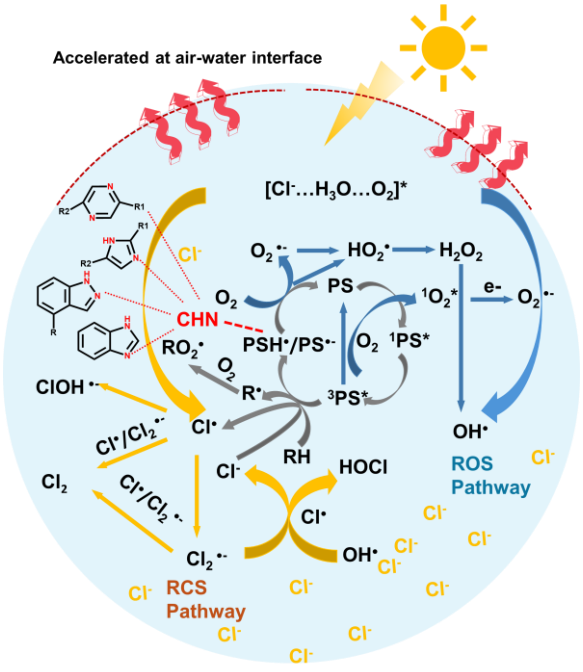


Figure 45. Conceptual diagram of PS and chloride mediated ROS and RCS production, which

participates in the oxidation processes from S(IV) to S(VI)

4 Atmospheric Implication

This study provided laboratory evidence that the ~~photosensitizers~~ PS in biomass burning extracts can enhance the sulfate formation in NaCl particles, primarily by triggering the formation of secondary oxidants under light and air, with less contribution of direct photosensitization via triplets (evidenced by N_2 atmosphere, Figure ~~S3~~2). The sulfate formation rate of BB_F-NaCl particles were ~10 folds higher that of IS_F-NaCl, following the trends of CS_F-NaCl>RS_F-NaCl>WS_F-NaCl>IS_F-NaCl. Upon UV exposure, the sulfate formation trends shifted to RS_A-NaCl>CS_A-NaCl>WS_A-NaCl>IS_A-NaCl, which might be explained by the effects of chloride (evidenced by aqueous reactions, Figure ~~3~~ 4 and Table 1). Interestingly, the incorporation of Cl^-into bulk solutions increased the sulfate formation rate in RS_A, while decreased it in RS_F. This seems to be different from our group's previous work where no significant sulfate formation rate was found with the addition of Cl^- (Zhang and Chan, 2024). The difference can be explained by the following reasons: 1) differences in PS/Cl^-, the prior study might use an insufficient PS/Cl^- ratio (2:1-1:4) while the current one significantly expands it to 1:200. 2) differences in photosensitizing capacity: the former study used a strong PS, while the current study focused on the real BB (using TOC as metric, with only a small portion of TOC considered as PS). 3) the complexity of the reaction system, the former study focused on mixing two individual species, while in real BB extracts, more complicated reactions may occur. Furthermore, our results using model PS show that although additional model CHN species would increase the sulfate formation by expedited H transfer via acting as H-bond acceptor, the addition of chloride could inhibit the sulfate formation rate, suggesting that the RCS pathway was less efficient in sulfate formation compared to ROS pathway in PS-CHN bulk system (Figure S10 and S11).

Previous studies have detected a significant proportion of NOCs, including nitroaromatics (CHON) and reduced nitrogen species (CHN) in biomass burning plumes, wildfires and ambient samples (Zhong et al., 2024; Wang et al., 2017b; Song et al., 2022; Cai et al., 2020). These NOCs are considered as ubiquitous contributor to BrC, and can affect global climate and human health. Moreover, recent research has discovered aerosol pollution in marine background regions, with high levels of NOCs when air masses are transported from wildfires or biomass burning events in nearby (Zhong et al., 2024; Qin et al., 2024). These NOCs, combined with reactive gases, may mix with sea-salt aerosols and impact regional air quality in coastal zones. While our prior study has examined the potential interplay between chloride and PS at limited mixing ratios (up to 4:1 in bulk solution) (Zhang and Chan, 2024), this work expanded the Cl^-/PS ratio to a broader range (200:1) and systematically identified the interactions among different organics, including PS, NOCs, and chloride, using sulfate formation as a compass. This highlights the importance to study secondary aerosol formation in mixed experimental system under air pollution complex. Our work suggests that in coastal regions heavily influenced by anthropogenic emissions like biomass burning, especially those near the rice-growing regions or affected by transported wildfire smoke, such as Guangdong, Fujian and Taiwan, the transported BB plumes together with the high RH (Cheung et al., 2015) and abundant reactive gases, would play an inevitable role in sulfate and potentially secondary

organic aerosol formation.

Data availability

Datasets are available upon request to the corresponding author, Chak K. Chan (chak.chan@kaust.edu.sa).

Author contributions

RT and CC conceptualized and designed the study. YQ and YC collected the samples. RT performed the experiments, data analysis and wrote the draft. JM provided assistance in data processing. All the authors reviewed, edited and contributed to the scientific discussions.

Competing interests

The authors declare no conflicts of interest.

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