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Organosulfur Compounds Formed from Heterogeneous Reaction between SO₂ and Particulate-Bound Unsaturated Fatty Acids in Ambient Air

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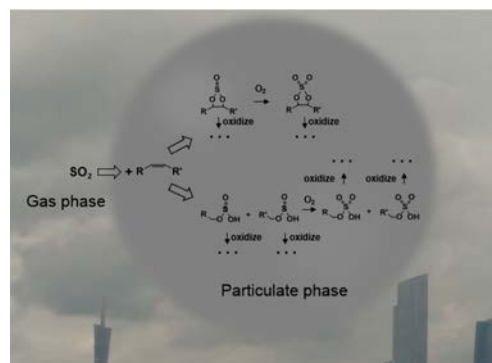
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ABSTRACT: Laboratory studies have demonstrated that uptake of SO₂ on oleic acid (OLA) could directly produce organosulfates (OS); yet, it is unknown whether this pathway is significant in secondary organosulfur production in ambient air. Here, we collected filter-based samples of ambient fine particles (PM_{2.5}) in the Pearl River Delta region in southern China and determined organosulfur compounds with Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS). The results are in agreement with the occurrence of organosulfur formed from the reactive uptake of SO₂ by OLA and a wider range of C₁₄–C₂₄ unsaturated fatty acids in ambient air as reported by laboratory studies, as well as additional species that are likely oxidation products of the primary products previously identified. OS formed from the heterogeneous reaction between SO₂ and unsaturated fatty acids accounted for 7%–13% sulfur of the CHOS species and 5%–7% sulfur of all the CHOS and CHONS species. They contributed about 0.3‰–0.9‰ of the total organic mass of the fine particle samples collected.



1. INTRODUCTION

As representative secondary organic aerosols (SOA) formed from complex atmospheric reactions between organic and inorganic compounds, organosulfates (OS) are relatively stable and long-lived organic components of submicron particulate matter in the atmosphere and can contribute up to 30% of the organic aerosols.^{1–4} A recent study showed that OS has potential toxicity on lung cells.⁵ Although their human health impacts are still largely unknown, as hydrophilic, lipophilic, and low-volatile organic species, OS can form a film on particle surface, changing the hygroscopicity of particles.⁵ Studies also suggest that OS may promote nanoparticle growth and affect cloud condensation nuclei (CCN) or ice nuclei (IN) activities, and as a potentially important source of light-absorbing compounds, OS may play a role in aerosol climate forcing.^{6–11} Therefore, investigating precursors, formation mechanisms, and fates of OS is essential to improve our knowledge about SOA.

Previous studies on the formation mechanisms of OS were focused on those derived from biogenic volatile organic compounds (BVOCs), including isoprene, monoterpenes, and

sesquiterpenes.^{12–15} An aircraft survey revealed that OS derived from isoprene epoxydiols (IEPOX) contributed 0.2%–1.4% of the total organic aerosol mass over the continental U.S.¹ Recently, there have been concerns about the formation of OS from anthropogenic precursors such as alkanes and polycyclic aromatic hydrocarbons (PAH).^{16–19} Field studies revealed that alkanes and aromatics could be major unrecognized OS precursors, and up to two-thirds of the OS identified could be derived from aromatics.^{16,20,21} This formation pathway of OS from anthropogenic precursors is of greater importance in urban areas where many pollutants from human activities occur in higher levels in the ambient air.

Very recently, laboratory studies have demonstrated that uptake of SO₂ on oleic acid (OLA) and other unsaturated fatty acids (USFA) can directly lead to the production of OS.^{22,23}

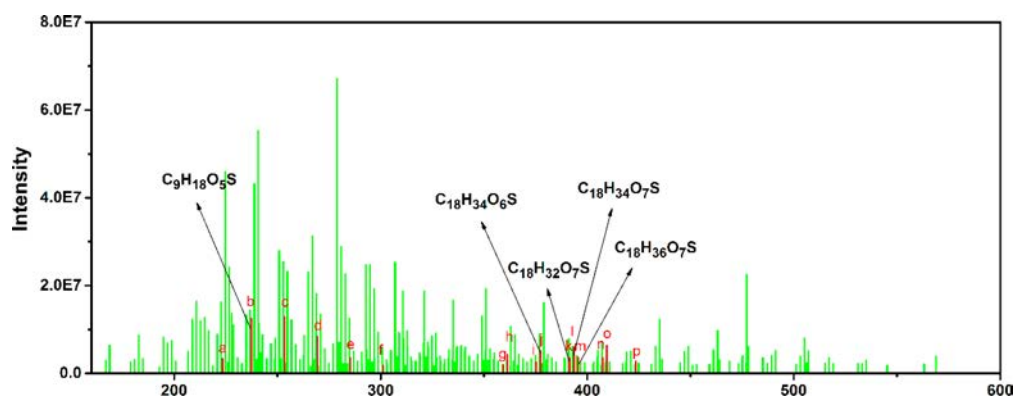


Figure 1. Typical diagram showing OLA-derived OS (peaks a to p) in the sample collected on December 7, 2013, at WQS. Detailed information is presented in Table S2. Peaks b, j, k, l, and m with the molecular formulas shown above them are OS reported by Shang et al. in the laboratory study.²²

These OS are proposed to be formed via the direct addition of SO_2 to a double bond or the separate addition of SO_2 to the cleavage of a double bond (Figure S1). This formation pathway of OS by heterogeneous reactions between SO_2 and unsaturated fatty acids, however, needs to be verified by field measurements to recognize its importance relative to other pathways in ambient air.

Large amounts of saturated and unsaturated fatty acids (USFA) have been observed in the emissions of high temperature cooking, especially the Chinese-style cooking with more frying,²⁴ and OLA is often used as a molecular tracer for cooking emissions since it is mainly present in animal and vegetable oils in the form of glycerides.^{25,26} In urban areas, cooking emission is among the important emission sources; yet in China, no regulations or guidelines are targeted on residential cooking emissions. According to field studies in the Pearl River Delta (PRD) region, one of China's most urbanized and industrialized regions and the world's largest megacity, the average concentration of OLA reached near 5 ng m^{-3} .^{27–29} Also, China is a large contributor to the global SO_2 burden due to its heavy dependence on coal burning for energy supply.^{30,31} Consequently, OS formed by the heterogeneous reactions between SO_2 and USFA, if possible in ambient air, would be comparatively more abundant over China's urban areas, considering the presence of precursors USFA (like OLA) and SO_2 .^{29,32}

In this study, 24-h filter-based fine particle ($\text{PM}_{2.5}$) samples were collected in Guangzhou, a central city in the PRD region. Organosulfur compounds from aerosol samples were characterized by negative electrospray ionization (ESI) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS). The main objectives are (1) to verify whether OS formation by the uptake of SO_2 on OLA and other USFA really takes place in ambient air and (2) to assess if it is a significant pathway of forming organosulfur compounds in ambient air.

2. MATERIALS AND METHODS

2.1. Field Sampling. The 24-h filter-based $\text{PM}_{2.5}$ samples were collected in December 2013 at a regional background site, Wanqingsha (WQS, 22.42°N , 113.32°E), using a high volume sampler (Tisch Environmental, Inc., Ohio, USA) with a constant flow rate of $1.1 \text{ m}^3 \text{ min}^{-1}$. As showed in Figure S2, WQS is located at the southernmost tip of Guangzhou in the central PRD region and is surrounded by city clusters (e.g., Hong Kong, Guangzhou, Shenzhen, Dongguan, Foshan, and Zhuhai). Previous studies have been conducted at the site to characterize

SOA, biogenic OS, and other air pollutants.^{33–35} All the filters (Whatman, Mainstone, U.K.) were prebaked at 450°C for 6 h, wrapped with aluminum foil, and stored at 4°C before and -20°C after collection. A field blank was also collected during the campaign. Sulfur dioxide (SO_2) was measured online by a Thermo Scientific model 43i SO_2 analyzer during the whole sampling period. The meteorological parameters including wind speed/direction, temperature, and relative humidity (RH) were measured by a mini-weather station (Vantage Pro2, Davis Instruments Corp., USA).

2.2. Laboratory Analysis. **2.2.1. Unsaturated Fatty Acids by GC-MSD.** Detailed extraction procedures of filter samples were described elsewhere.^{24,29,33,34} After extraction, concentrating, and methylation steps, unsaturated fatty acids in extracts were analyzed by an Agilent model 7890 gas chromatography coupled to an Agilent model 5975C mass spectrometer detector. An HP-5 MS capillary column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$) was used. Splitless injection of a $1 \mu\text{L}$ sample was performed. The GC temperature was initially set at 65°C (held for 2 min) and raised at a rate of 5°C min^{-1} to 290°C (held for 20 min). USFA were identified according to their mass spectra and retention times, calibrated with their authentic standard solutions.

2.2.2. Organosulfur Compounds by FT-ICR-MS. A punch ($\Phi = 47 \text{ mm}$) of each filter sample collected from December 1 to December 10 was taken and extracted twice for 20 min in 20 mL of methanol by ultrasonication. Before extraction, hexadecanoic acid-D31 was spiked onto the filters as an internal standard. The extracts for each filter punch were combined, filtered through a glass syringe on a $0.45 \mu\text{m}$ PTFE membrane ($\Phi = 25 \text{ mm}$; Pall Corporation, USA), blown almost to dryness under a gentle stream of nitrogen, and dissolved in 1 mL of methanol. The samples were then analyzed using a solariX XR Fourier transform-ion cyclotron resonance mass spectrometry (FT-ICR MS; Bruker Daltonik GmbH, Bremen, Germany) equipped with a 9.4 T refrigerated actively shielded superconducting magnet (Bruker Biospin, Wissembourg, France) and a Paracell analyzer cell located at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. The samples were ionized in negative ion mode using the ESI ion source. The detection mass range was set to m/z 150–1000. Ion accumulation time was set to 0.65 s. A total of 100 continuous 4M data FT-ICR transients were co-added to enhance the signal-to-noise ratio and dynamic range. The mass spectra were calibrated externally with arginine clusters in negative ion mode using a linear calibration. The final spectrum was internally recalibrated with typical O_3 class species peaks using quadratic

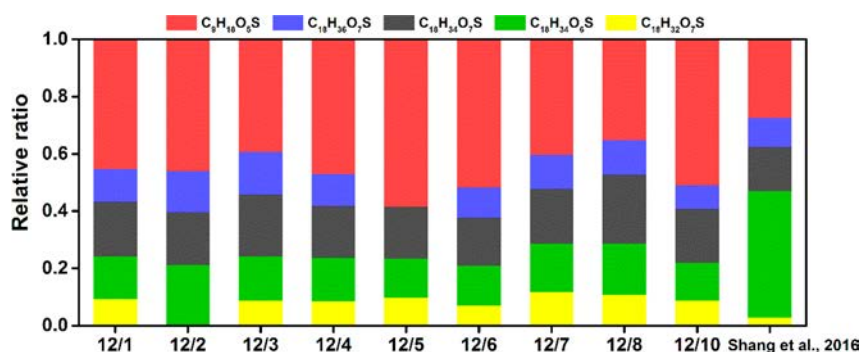


Figure 2. Comparisons of compositions of OLA-derived OSs in the ambient air samples with that from the laboratory study by Shang et al.²² Bar charts are intensity-weighted elemental composition percentages in each sample.

calibration in DataAnalysis 4.4 (Bruker Daltonics). A typical mass-resolving power $>450,000$ at m/z 319 with <0.2 ppm absolute mass error was achieved. During data analysis, mass tolerance of ± 1.5 ppm was used to calculate all mathematically possible formulas for all ions with a signal-to-noise ratio above 10. Detailed information about data processing was presented previously.^{36,37} In this study, OS were semiquantified with deuterated sodium dodecyl sulfate ($C_{12}D_{25}SO_4Na$) as an alternative standard due to the lack of authentic standards. Field and laboratory blanks were analyzed in the same way as field samples; detailed information on the blanks is in the SI. Both OSs and USFA were not found in the blanks. To confirm the identical formula observed in our ambient samples with those from the laboratory studies,^{22,23} an Orbitrap Fusion Tribrid mass spectrometer (Orbitrap Fusion TMS, Thermo Fisher Scientific, USA) was also used to analyze selected samples following the analytical procedures as described in the laboratory studies.

3. RESULTS AND DISCUSSION

3.1. OLA-Derived OS. Five OS products, namely, $C_{18}H_{32}O_7S$, $C_{18}H_{34}O_6S$, $C_{18}H_{34}O_7S$, $C_{18}H_{36}O_7S$, and $C_9H_{18}O_5S$, which can be formed through the reaction of SO_2 with OLA according to laboratory studies,^{22,23} were all detected by FT-ICR-MS in the collected $PM_{2.5}$ samples (Figure 1). This indicated that the formation pathway exists in the real atmosphere, although the compositions of OLA-derived OS detected in the ambient air samples were different from those in the laboratory study²² (Figure 2). As a matter of fact, as reported by Shang et al., apart from organosulfates, a larger amount of oxygenated hydrocarbons were formed from the $SO_2 + OLA$ reaction; these oxygenated hydrocarbons were also observed in the ambient samples.²² However, like organosulfates, they were also quite different in their compositions when compared to that from the laboratory study (Figure S3). While $C_{18}H_{34}O_6S$ ($C_{18}H_{33}O_6S^-$, m/z 377.201) was the most abundant (44%) OLA-derived OS from the laboratory study,²² $C_9H_{18}O_5S$ ($C_9H_{17}O_5S^-$, m/z 237.080) instead was the most abundant (46%) OLA-derived OS in the ambient air. As shown in Figure S4, both OLA and its *trans* isomer elaidic acid (EA) were detected in ambient air, with the mass ratios of OLA to EA ranging from 5.1 to 20.0. At room temperature, OLA is a liquid while EA is a solid, and the SO_2 uptake coefficients of OLA and EA are 5×10^{-6} and 1×10^{-5} in a laboratory study, respectively.²³ It is not clear whether the presence of both the *cis/trans* isomers was one reason for the difference in OLA-derived OS observed in the laboratory studies versus that

detected in the ambient air. However, due to much lower abundance of EA, its presence should be not be the main reason for the dominance of $C_9H_{18}O_5S$ as a product from the cleavage of a double bond.

3.2. USFA-Derived OS. As listed in Table S1, 17 C_{14} – C_{24} USFA were detected with C18:1 acids (OLA and EA) accounting for 14.3%–51.2% of the total USFA in the field samples (Figure S4). Table S2 shows the main organosulfur compounds identified in the field samples following the proposed mechanisms for reactions between SO_2 and unsaturated compounds based on laboratory studies.²³ This also indicates that this pathway from the reactions between SO_2 and USFA take place in the ambient air. It worth noting that apart from OLA, other unsaturated fatty acids, such as myristoleic acid (C14:1), *cis*-9-hexadecenoic acid (C16:1), linoleic acid (C18:2 *cis*-9,12), and linolenic acid (C18:3) could also produce $C_9H_{18}O_5S$ when reacted with SO_2 (Table S2). This could be a probable explanation for the dominance of $C_9H_{18}O_5S$ in the USFA-derived OS in ambient air as mentioned above.

As shown in Figure S5, USFA-derived OS in the samples seemed to increase with rising USFA concentrations. The semiquantitatively calculated concentration of USFA-derived OS ranged from 13.7 to 56.0 $ng\ m^{-3}$, accounting for 0.3%–0.9% of the total particulate organic aerosol mass. Our previous studies at the same site revealed that isoprene-derived OS represented 0.04% of organic aerosols in summer and 0.03% in fall.³⁵ These results suggest that uptake of SO_2 by USFA should be a significant pathway in forming OS. As for the sulfur-containing organics (CHOS) and nitrogen/sulfur-containing organics (CHONS) resolved by FT-ICR MS, the USFA-derived OS account for 7%–13% sulfur of all the CHOS species and 5%–7% sulfur of all the CHOS and CHONS species added together.

3.3. Complex USFA-Derived OS in Ambient Air. Table S2 lists the potential USFA-derived OS in the ambient $PM_{2.5}$ samples. Quite a few OS, such as $C_9H_{18}O_6S$, $C_9H_{18}O_7S$, $C_9H_{18}O_8S$, $C_{18}H_{33}O_7S$, $C_{18}H_{31}O_8S$, and $C_{18}H_{31}O_9S$ (Figure 1; Table S2), which have the same double bond equivalents (DBE) with OLA-derived OS, might also originate from the heterogeneous reaction between USFA and SO_2 , but they have not been reported in laboratory studies. These USFA-derived OS in the ambient air showed higher oxygen-to-carbon ratios than the OS formed under laboratory conditions. Formation of these highly oxidized OS might involve other oxidants, such as the OH radical and ozone, in ambient air. For example, low molecular weight C_9 products and other higher molecular weight peroxidic species can be formed from the ozonolysis of oleic acid.^{38–40} USFA-derived OS could also be

further oxidized by other oxidants, or oxidation products of USFA could further react with SO₂ to form OS (Figure S1). That could be one probable reason for more highly oxidized USFA-derived OS species observed in the ambient air than in the laboratory. Hitherto, these complex oxidation processes that resulted in formation of OS in ambient air are not yet fully understood, and more investigations, especially chamber simulation studies, are needed for more detailed study of mechanisms and kinetics.

Although the number of samples are quite limited, a good positive correlation between relative humidity and concentration of USFA-derived OS (Figure S6) is observed. This dependency on relative humidity is consistent with that from the laboratory study.²² The uptake coefficient of SO₂ would increase under higher relative humidity, which indicates that increasing humidity would accelerate SO₂ uptake and thereby OS formation.²² In the PRD region, the average relative humidity was near 70% during 2007–2013.⁴¹ This high relative humidity would facilitate the reactive uptake of SO₂ for OS formation. In particular, haze episodes mostly occur with comparatively much higher relative humidity and accumulated pollutant levels in the boundary layer. This suggests that much more OS, including those from USFA-derived ones, would be produced during the haze episodes. In this study (Figure S5), more USFA-derived organosulfur compounds were observed in samples collected on two haze days (December 3 and 7). Nonetheless, for in-depth understanding of a large number of organosulfur compounds, more laboratory and field works are needed in the future.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free at DOI: 10.1021/acs.estlett.9b00218.

Detailed information on field sampling. Proposed mechanism for the uptake of SO₂ on unsaturated fatty acid (Figure S1). Location of the sampling site WQS in the Pearl River Delta region (Figure S2). Comparison of compositions of the nonorganosulfate species in the ambient air samples with that from the laboratory study (Figure S3). C18:1 acids and the shares of C18:1 acids (%) in the detected C₁₄–C₂₄ unsaturated fatty acids during the sampling period (Figure S4). Time series of USFA, USFA-derived OS, and SO₂ at WQS during the sampling period (Figure S5). Correlation between relative humidity and USFA-derived OS (Figure S6). MS² spectrum of parent ion at *m/z* 237.0802 (C₉H₁₇O₃S⁻) (Figure S7). Unsaturated fatty acids in samples collected at WQS (Table S1). Detected main organosulfur compounds and their possible precursors in the ambient air samples (Table S2). (PDF)

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Notes

The authors declare no competing financial interest.

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