Organosulfur Compounds Formed from Heterogeneous Reaction between SO2 and Particulate-Bound Unsaturated Fatty Acids in Ambient Air
Ming Zhu, Bin Jiang, Sheng Li, Qingqing Yu, Xu Yu, Yanli Zhang, Xinhui Bi, Jianzhen Yu, Christian George, Zhiqiang Yu, et al.

To cite this version:
Ming Zhu, Bin Jiang, Sheng Li, Qingqing Yu, Xu Yu, et al.. Organosulfur Compounds Formed from Heterogeneous Reaction between SO2 and Particulate-Bound Unsaturated Fatty Acids in Ambient Air. Environmental Science and Technology Letters, 2019, 6 (6), pp.318-322. 10.1021/acs.estlett.9b00218. hal-02167653

HAL Id: hal-02167653
https://hal.archives-ouvertes.fr/hal-02167653
Submitted on 28 May 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Distributed under a Creative Commons Attribution 4.0 International License
Organosulfur Compounds Formed from Heterogeneous Reaction between SO₂ and Particulate-Bound Unsaturated Fatty Acids in Ambient Air

Ming Zhu, † Bin Jiang, † Sheng Li, † Qingqing Yu, † Xu Yu, † Yanli Zhang, † Xinhui Bi, † Jianzhen Yu, † Christian George, ‡ Zhiqiang Yu, † and Xinming Wang *†‡§

† State Key Laboratory of Organic Geochemistry and Guangdong Key Laboratory of Environmental Protection and Resources Utilization, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
‡ University of Chinese Academy of Sciences, Beijing 100049, China
§ Center for Excellence in Urban Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China
⊥ Chemistry Department & Division of Environment, Hong Kong University of Science & Technology, Hong Kong, China
∥ Institut de Recherches sur la Catalyse et l’Environnement de Lyon (IRCELYON), CNRS, UMR5256, Villeurbanne F-69626, France

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 (PM₂.₅) 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 organosulfurs 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
Previous studies have been conducted at the site to characterize Guangzhou, Shenzhen, Dongguan, Foshan, and Zhuhai). These studies have located at the southernmost tip of Guangzhou in the central 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$^{-3}$.33-35 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 (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 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 m$^3$ 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 rebaked 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.16,29,33,34 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 m × 0.25 mm × 0.25 μm) was used. Splitless injection of a 1 μL 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 (Φ = 47 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 μm PTFE membrane (Φ = 25 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
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. In this study, OS were semiquantified with deuterated sodium dodecyl sulfate (C12D25SO4Na) 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, 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, C18H31O8S, C18H34O6S, C18H31O7S, C18H33O6S, and C18H32O5S, which can be formed through the reaction of SO2 with OLA according to laboratory studies, 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 study (Figure 2). As a matter of fact, as reported by Shang et al., apart from organosulfates, a larger amount of organics (CHONS) resolved by FT-ICR MS, the USFA-derived OS account for 7% sulfur of all the CHOS species and 13% sulfur of all the CHOS and CHONS species added together.

3.2. USFA-Derived OS. As listed in Table S1, USFA-derived OS 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 SO2 and unsaturated compounds based on laboratory studies.

This also indicates that this pathway from the reactions between SO2 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 C9H18O5S when reacted with SO2 (Table S2). This could be a probable explanation for the dominance of C9H18O5S 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. These results suggest that uptake of SO2 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 accounted 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 C19H34O6S, C18H33O6S, C19H33O8S, C18H32O7S, C19H34O8S, and C18H31O5S (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 SO2, 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 C8 products and other higher molecular weight peroxydic species can be formed from the ozonolysis of oleic acid. 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 2007–2013.21 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 nonorganosulfur 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−C16 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 (C9H17O5S−) (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)

■ AUTHOR INFORMATION

**Corresponding Author**

*Phone: +86-20-85290180. Fax: +86-20-85290706. E-mail: wangxm@gig.ac.cn.*

**ORCID**

Bin Jiang: 0000-0002-7453-828X
Yanli Zhang: 0000-0003-0614-2096
Jianzheng Yu: 0000-0002-6165-6500
Christian George: 0000-0003-1578-7056
Zhiqiang Yu: 0000-0002-8631-2704

**Notes**

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This study was supported by the National Key Research and Development Program (2016YFC0202204), the National Natural Science Foundation of China (Grant 41530641/41571130031), the Chinese Academy of Sciences (Grant QYZDJ-SSW-DQC032), the Guangzhou Science Technology and Innovation Commission (201607020002), Youth Innovation Promotion Association, CAS (2017406), and Hong Kong Scholars Awards (XJ2016036).

**REFERENCES**

(1) Liao, J.; Froyd, K. D.; Murphy, D. M.; Keutsch, F. N.; Yu, G.; Wennberg, P. O.; St. Clair, J. M.; Crounse, J. D.; Wisthaler, A.; Mikoviny, T.; Jimenez, J. L.; Campuzano-Jost, P.; Day, D. A.; Hu, W. W.; Ryerson, T. B.; Pollack, I. B.; Pfeiff, J.; Anderson, B. E.; Zioma, L. D.; Blake, D. R.; Meinardi, S.; Diskin, G. Airborne measurements of organosulfates over the continental US. J. Geophys. Res. Atmos. 2015, 120 (7), 2990–3005.
(2) Surratt, J. D.; Gomez-Gonzalez, Y.; Chan, A. W. H.; Vermeulen, R.; Shahgholi, M.; Kleindienst, T. E.; Edney, E. O.; Offenberg, J. H.; Lewandowski, M.; Jaoui, M.; Maenhaut, W.; Claey, M.; Flagan, R. C.; Seinfeld, J. H. Organosulfate formation in biogenic secondary organic aerosol. J. Phys. Chem. A 2008, 112 (36), 8345–8378.
(3) Frossard, A. A.; Shaw, P. M.; Russell, L. M.; Kroll, J. H.; Canagaratna, M. R.; Worsnop, D. R.; Quinn, P. K.; Bates, T. S. Springtime Arctic haze contributions of submicron organic particles from European and Asian combustion sources. J. Geophys. Res. Atmos. 2011, 116, 116.
(4) Tolocka, M. P.; Turpin, B. Contribution of organosulfur compounds to organic aerosol mass. Environ. Sci. Technol. 2012, 46 (15), 7978–7983.
(5) Lin, Y.-H.; Arashiro, M.; Martin, E.; Chen, Y.; Zhang, Z.; Sexton, K. G.; Gold, A.; Jaspers, I.; Fry, R. C.; Surratt, J. D. Isoprene-derived secondary organic aerosol induces the expression of oxidative stress response genes in human lung cells. Environ. Sci. Technol. Lett. 2016, 3 (6), 250–254.
(6) Nguyen, T. B.; Lee, P. B.; Udipye, K. M.; Bones, D. L.; Laskin, J.; Laskin, A.; Nizkorodov, S. A. Formation of nitrogen- and sulfur-containing light-absorbing compounds accelerated by evaporation of water from secondary organic aerosols. J. Geophys. Res. Atmos. 2012, 117, 117.
(7) Noziere, B.; Ekstrom, S.; Alberg, T.; Holstrom, S. Radical-initiated formation of organosulfurates and surfactants in atmospheric aerosols. Geophys. Res. Lett. 2010, 37, 37.
(8) Charlson, R. J.; Schwartz, S. E.; Hales, J. M.; Cess, R. D.; Coakley, J. A.; Hansen, J. E.; Hofmann, D. J. Climate forcing by anthropogenic aerosols. Science 1992, 255 (5045), 423–430.
(9) Riipinen, I.; Yi-Juutti, T.; Pierce, J. R.; Petaja, T.; Worsnop, D. R.; Kulmala, M.; Donahue, N. M. The contribution of organics to atmospheric nanoparticle growth. Nat. Geosci. 2012, 5 (7), 453–458.
(10) Smith, J. N.; Dunn, M. J.; VanReken, T. M.; Iida, K.; Stolzenburg, M. R.; McMurry, P. H.; Huey, L. G. Chemical composition of atmospheric nanoparticles formed from nucleation in Tecamac, Mexico: Evidence for an important role for organic species in nanoparticle growth. Geophys. Res. Lett. 2008, 35 (4), L04808.
(11) Wang, L.; Khalizov, A. F.; Zheng, J.; Xu, W.; Ma, Y.; Lal, V.; Zhang, R. Y. Atmospheric nanoparticles formed from heterogeneous reactions of organics. Nat. Geosci. 2010, 3 (4), 238–242.
(12) Surratt, J. D.; Chan, A. W. H.; Eddingsaas, N. C.; Chan, M. N.; Loza, C. L.; Kwan, A. J.; Hersey, S. P.; Flagan, R. C.; Wennberg, P. O.; Seinfeld, J. H. Reactive intermediates revealed in secondary organic aerosol formation from isoprene. Proc. Natl. Acad. Sci. U. S. A. 2010, 107 (15), 6640–6645.
(13) Froyd, K. D.; Murphy, S. M.; Murphy, D. M.; De Gouw, J. A.; Eddingsaas, N. C.; Wennberg, P. O. Contribution of isoprene-derived organosulfates to free tropospheric aerosol mass. *Proc. Natl. Acad. Sci. U. S. A.* 2010, 107 (50), 21360–21365.

(14) Inuma, Y.; Boge, O.; Kahnt, A.; Herrmann, H. Laboratory chamber studies on the formation of organosulfates from reactive uptake of monoterpenes. *Phys. Chem. Chem. Phys.* 2009, 11 (36), 7958–7997.

(15) Drozd, G. T.; Woo, J. L.; McNeill, V. F. Self-limited uptake of α-pinen oxide to acidic aerosol: the effects of liquid-liquid phase separation and implications for the formation of secondary organic aerosol and organosulfates from epoxides. *Atmos. Chem. Phys.* 2013, 13 (16), 8255–8263.

(16) Riva, M.; Da Silva Barbosa, T.; Lin, Y.; Stone, E. A.; Gold, A.; Suratt, J. D. Chemical characterization of organosulfates in secondary organic aerosol derived from the photooxidation of alkanes. *Atmos. Chem. Phys.* 2016, 16 (17), 11001–11018.

(17) Riva, M.; Tomaz, S.; Cui, T. Q.; Lin, Y. H.; Perraudin, E.; Gold, A.; Stone, E. A.; Villenave, E.; Suratt, J. D. Evidence for an unrecognized secondary anthropogenic source of organosulfates and sulfonates: gas-phase oxidation of polycyclic aromatic hydrocarbons in the presence of sulfate aerosol. *Environ. Sci. Technol.* 2015, 49 (11), 6654–6664.

(18) Kundu, S.; Quraishi, T. A.; Yu, G.; Suarez, C.; Keutsch, F. N.; Stone, E. A. Evidence and quantitation of aromatic organosulfates in ambient aerosols in Lahore, Pakistan. *Atmos. Chem. Phys.* 2013, 13 (9), 4865–4875.

(19) Staudt, S.; Kundu, S.; Lehmler, H.-J.; He, X.; Cui, T.; Lin, Y.-H.; Kristensen, K.; Glasius, M.; Zhang, X.; Weber, R. J.; Suratt, J. D.; Stone, E. A. Aromatic organosulfates in atmospheric aerosols: Synthesis, characterization, and abundance. *Atmos. Environ.* 2014, 94, 366–373.

(20) Wang, X. K.; Rossignol, S.; Ma, Y.; Yao, L.; Wang, M. Y.; Chen, J. M.; George, C.; Wang, L. Molecular characterization of atmospheric particulate organosulfates in three megacities at the middle and lower reaches of the Yangtze River. *Atmos. Chem. Phys.* 2016, 16 (4), 2285–2298.

(21) Ma, Y.; Xu, X.; Song, W.; Geng, F.; Wang, L. Seasonal and diurnal variations of particulate organosulfates in urban Shanghai, China. *Atmos. Environ.* 2014, 85, 152–160.

(22) Shang, J.; Passantani, M.; Dupart, Y.; Ciuraru, R.; Tinel, L.; Rossignol, S.; Perrier, S.; Zhu, T.; George, C. SO4 uptake on oleic acid: a new formation pathway of organosulfur compounds in the atmosphere. *Environ. Sci. Technol. Lett.* 2016, 3 (2), 67–72.

(23) Passantani, M.; Kong, L. D.; Shang, J.; Dupart, Y.; Perrier, S.; Chen, J. M.; Donaldson, D. J.; George, C. Organosulfate formation through the heterogeneous reaction of sulfur dioxide with unsaturated fatty acids and long-chain alkenes. *Angew. Chem., Int. Ed.* 2016, 55 (35), 10336–10339.

(24) Zhao, X. Y.; Hu, Q. H.; Wang, X. M.; Ding, X.; He, Q. F.; Zhang, Z.; Shen, R. Q.; Lu, S. J.; Liu, T. Y.; Fu, X. X.; Chen, L. G. Formation profiles of organic aerosols from Chinese residential cooking: case study in urban Guangzhou, south China. *J. Atmos. Chem.* 2015, 72 (1), 1–18.

(25) Rogge, W. F.; Hildemann, L. M.; Mazurek, M. A.; Cass, G. R.; Simoneit, B. R. T. Sources of fine organic aerosol. 1. Charbroilers and meat cooking operations. *Environ. Sci. Technol.* 1991, 25 (6), 1112–1125.

(26) Robinson, A. L.; Subramanian, R.; Donahue, N. M.; Bernardo-Bricker, A.; Rogge, W. F. Source apportionment of molecular markers and organic aerosol. 2. Biomass smoke. *Environ. Sci. Technol.* 2006, 40 (24), 7811–7819.

(27) Chan, C. K.; Yao, X. Air pollution in mega cities in China. *Atmos. Environ.* 2008, 42 (1), 1–42.

(28) Ho, K. F.; Ho, S. S. H.; Lee, S. C.; Kawamura, K.; Zou, S. C.; Cao, J. J.; Xu, H. M. Summer and winter variations of dicarboxylic acids, fatty acids and benzoic acid in PM2.5 in Pearl River Delta Region, China. *Atmos. Chem. Phys.* 2011, 11 (5), 2197–2208.

(29) Zhao, X. Y.; Wang, X. M.; Ding, X.; He, Q. F.; Zhang, Z.; Liu, T. Y.; Fu, X. X.; Gao, B.; Wang, Y. P.; Zhang, Y. L.; Deng, X. J.; Wu, D. Compositions and sources of organic acids in fine particles (PM_{2.5}) over the Pearl River Delta region, south China. *J. Environ. Sci.* 2014, 26 (1), 110–121.

(30) Lu, Z.; Streets, D. G.; Zhang, Q.; Wang, S.; Carmichael, G. R.; Cheng, Y. F.; Wei, C.; Chin, M.; Diehl, T.; Tan, Q. Sulfur dioxide emissions in China and sulfur trends in East Asia since 2000. *Atmos. Chem. Phys.* 2010, 10 (13), 6311–6331.

(31) Jia, Z.; Zhang, Q.; Shi, Q.; Sulfur dioxide and primary carbonaceous aerosol emissions in China and India, 1996–2010. *Atmos. Chem. Phys.* 2011, 11 (18), 9839–9864.

(32) Report on the State of the Environment of China: 2013. Ministry of Environmental Protection the People’s Republic of China. http://www.mee.gov.cn/gkml/sthjbgw/qt/201407/W02014070705048054125.pdf (accessed May 2019).

(33) Ding, X.; Wang, X. M.; Gao, B.; Fu, X. X.; He, Q. F.; Zhao, X. Y.; Yu, J. Z.; Zheng, M. Tracer-based estimation of secondary organic carbon in the Pearl River Delta, south China. *J. Geophys. Res. Atm. 2012, 117*, na.

(34) Yu, Q. Q.; Gao, B.; Li, G. H.; Zhang, Y. L.; He, Q. F.; Deng, W.; Huang, Z. H.; Ding, X.; Hu, Q. H.; Huang, Z. Z.; Wang, Y. J.; Bi, X. H.; Wang, X. M. Attributing risk burden of PM2.5-bound polycyclic aromatic hydrocarbons to major emission sources: Case study in Guangzhou, south China. *Atmos. Environ.* 2016, 142, 313–323.

(35) He, Q. F.; Ding, X.; Wang, X. M.; Yu, J. Z.; Fu, X. X.; Liu, T. Y.; Zhang, Z.; Xue, J.; Chen, D. H.; Zhong, L.; Donahue, N. M. Organosulfates from pinene and isoprene over the Pearl River Delta, south China: seasonal variation and implication in formation mechanisms. *Environ. Sci. Technol.* 2014, 48 (16), 9236–9245.

(36) Jia, Z.; Liu, Z.; Xie, J.; Shen, R.; Bi, X.; Lu, S. J.; Liu, T. Y.; Zhang, Z.; Fu, X.; Xie, J.; Chen, D. H.; Zhong, L.; Donahue, N. M. Polycyclic aromatic hydrocarbons (PAHs) in ambient aerosols from Beijing: Characterization of low volatile PAHs by positive-ion atmospheric pressure photoionization (APPI) coupled with Fourier Transform Ion Cyclotron Resonance. *Environ. Sci. Technol.* 2014, 48 (9), 4716–4723.

(37) Jiang, B.; Lu, Z.; Liang, B. Y.; Huang, Z. Y.; Huang, X. H.; Xu, C. M.; Yu, J. Z.; Shi, Q. Molecular composition of urban organic aerosols on clear and hazy days in Beijing: a comparative study using FT-ICR MS. *Environ. Chem.* 2016, 13 (5), 888–901.

(38) Huang, H. M.; Ariya, P. Oxidation of oleic acid and oleic acid/ sodium chloride (aq) mixture droplets with ozone: Changes of hygroscopicity and role of secondary reactions. *J. Phys. Chem. A* 2007, 111 (4), 620–632.

(39) Zahardis, J.; LaFranchi, B. W.; Petrucci, G. A. Photoelectron resonance capture ionization-aerosol mass spectrometry of the ozonolysis products of oleic acid particles: Direct measure of higher molecular weight oxygenates. *J. Geophys. Res. Atmos.* 2005, 110, D8.

(40) Zahardis, J.; Petrucci, G. A. The oleic acid-ozone heterogeneous reaction system: products, kinetics, secondary chemistry, and atmospheric implications of a model system - a review. *Atmos. Chem. Phys.* 2007, 7, 1237–1274.

(41) Fu, X.; Wang, X.; Hu, Q.; Li, G.; Ding, X.; Zhang, Y.; He, Q. F.; Liu, T.; Zhang, Z.; Yu, Q. Q.; Shen, R.; Bi, X. Changes in visibility with PM_{2.5} composition and relative humidity at a background site in the Pearl River Delta region. *J. Environ. Sci.* 2016, 40, 10–19.