

# Aerosol size distribution characteristics of organosulfates in the Pearl River Delta region, China



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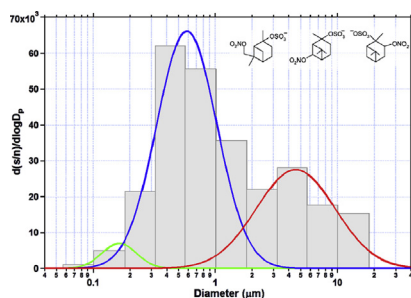
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## HIGHLIGHTS

- BVOC-derived organosulfates are characterized with a dominant droplet mode.
- A minor coarse mode of OS is likely from coagulation with small particles.
- Nitrooxy OS has a larger coarse mode due to slower hydrolysis on alkaline particles.
- Low unsaturated alkyl organosulfates are abundant and likely secondary in origin.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Organosulfates (OSs) have been detected in various atmospheric environments, but their particle size distribution characteristics are unknown. In this work, we examined their size distributions in ambient aerosols to gain insights into the formation processes. Size-segregated aerosol samples in the range of 0.056–18 μm were collected using a ten-stage impactor at a receptor site in Hong Kong in both summer and winter and in Nansha in the Pearl River Delta in winter. The humic-like substances fraction in the size-segregated samples was isolated and analyzed using electrospray ionization coupled with an Orbitrap Ultra High Resolution Mass Spectrometer. Through accurate mass measurements, ~190 CHOS and ~90 CHONS formulas were tentatively identified to be OS compounds. Among them, OS compounds derived from isoprene,  $\alpha$ - $\beta$ -pinene, and limonene and alkyl OSs having low double bond equivalents (DBE = 0,1) and 0–2 extra O beyond those in  $-\text{OSO}_3$  were found with high intensity. The biogenic volatile organic compounds-derived OS formulas share a common characteristic with sulfate in that the droplet mode dominated, peaking in either 0.56–1.0 or 1.0–1.8 μm size bin, reflecting sulfate as their common precursor. Most of these OSs have a minor coarse mode, accounting for 0–45%. The presence of OSs on the coarse particles is hypothesized to be a result of OSs on small particle (<0.32 μm) coagulating with coarse particles, as the abundance ratios of OS to non-sea-salt sulfate present on the coarse particles were similar to those on particles <0.32 μm. Among a few pairs of CHONS and CHOS that could be linked up through hydrolysis of a nitrooxy group in the CHONS form (e.g.,  $m/z$  294:  $\text{C}_{10}\text{H}_{16}\text{O}_7\text{NS}^-$  vs.  $m/z$  249  $\text{C}_{10}\text{H}_{17}\text{O}_5\text{S}^-$  from  $\alpha/\beta$ -pinene, differing by  $(+\text{H}_2\text{O}-\text{HNO}_3)$ ), the CHONS compounds had an enhanced

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coarse mode presence. This could be interpreted as a result of slower hydrolysis of the CHONS compounds on the alkali coarse particles. The low DBE alkyl OS compounds have a dominant droplet mode at the Hong Kong site, but a more significant coarse mode presence was observed for  $C_nH_{2n+1}O_4S^-$ ,  $C_nH_{2n-1}O_4S^-$ , and  $C_nH_{2n-1}O_5S^-$  formulas in the Nansha site, possibly suggesting site-specific mixed secondary and primary sources for these formulas.

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## 1. Introduction

Organosulfates (OSs) have been detected in various atmospheric environments, ranging from the Arctic, marine, rural, suburban, to urban settings (e.g., Surratt et al., 2008; Lin et al., 2012a; Hansen et al., 2014; Willoughby et al., 2014; Ma et al., 2014). A few studies estimated the total contribution of OS in bulk  $PM_{2.5}$  or  $PM_{10}$  indirectly from the difference between total S and inorganic sulfate-S by assuming all non-sulfate-S exists as OSs (e.g., Maenhaut et al., 2011; Tolocka and Turpin, 2012; Shakya and Peltier, 2013). Maenhaut et al. (2011) and Surratt et al. (2008) examined total S and inorganic sulfate-S data for 63  $PM_{10}$  samples collected at a location (K-puszta, Hungary) representing Central European regional air in a 2003 summer campaign. They estimated that the average OS amount was  $0.33 \mu\text{gS}/\text{m}^3$  and this roughly accounted for 30% of the total  $PM_{10}$  organic matter (OM) at K-puszta. Tolocka and Turpin (2012) analyzed a data set of over 150,000 measurements from the IMPROVE  $PM_{2.5}$  database in the US. They estimated the contribution of OS to  $PM_{2.5}$  OM in the range of 3.3–14% (assuming an average OS molecular weight of 334) at twelve different sampling sites. These studies indicate the importance of this compound class on a global scale.

The application of ultra-high resolution mass spectrometry (UHRMS) (such as Fourier Transform Ion Cyclotron Resonance mass spectrometer (FT-ICR MS), Orbitrap mass spectrometer) coupled with soft ionization techniques such as electrospray ionization (ESI) to the study of atmospheric aerosols have provided qualitative surveys of possible OS compounds present in ambient PM. Due to their facile ionization forming  $[M-H]^-$  ions under ESI conditions, OS compounds are detected as an abundant class of organic formulas in the UHRMS studies (e.g., Reemtsma et al., 2006; Schmitt-Kopplin et al., 2010; Mazzoleni et al., 2010; Lin et al., 2012a, 2012b; Zhao et al., 2013). The extreme resolving power and mass accuracy of UHRMS allows identification of hundreds of individual OS molecular formulas in the complex mixture of organic aerosol. In our previous UHRMS (LTQ Orbitrap) study of the water-soluble humic-like substances (HULIS) fraction isolated from aerosols at seven locations in East Asia, hundreds (~140–300) of formulas were assigned to OSs (Lin et al., 2012a). Using FT-ICR MS, Willoughby et al. (2014) examined the water-soluble fraction of an ambient aerosol sample collected in a rural location in Virginia in eastern USA influenced by both natural and anthropogenic emissions and reported the detection of 868 CHOS formulas and 214 CHONS formulas, a large majority of which were OS formulas.

The more commonly adopted analytical approach for quantitative or semi-quantitative OS studies is liquid chromatography (LC) coupled with lower resolution mass spectrometer, which has been used since the discovery of this class of organic compounds in atmospheric aerosols (e.g., Romero and Oehme, 2005; Iinuma et al., 2007b; Surratt et al., 2007; Surratt et al., 2008; Gomez-Gonzalez et al., 2008; Claeys et al., 2010; Chan et al., 2010; Kristensen and Glasius, 2011; Gomez-Gonzalez et al., 2012; Ma et al., 2014; He et al., 2014). The LC-MS methods require some prior knowledge of OS chemical structures for the selection of an appropriate column for separation and suitable target ions for quantification. As such,

these studies mainly centered on OS compounds associated with biogenic volatile organic compounds (BVOCs), the identification of which was previously established through comparing smog chamber experiments with field studies (e.g., Surratt et al., 2006; Iinuma et al., 2007a; Surratt et al., 2008; Iinuma et al., 2009; Chan et al., 2011). The list of these known BVOC-derived OSs only account for a small number of OS compounds detected using UHRMS.

In this work we explore the unique advantages of UHRMS offering ultrahigh mass resolution and high sensitivities for compounds of facile ESI for comparison of OS abundance in size-segregated aerosol samples. The intense OS peaks detected across the size range of  $0.056\text{--}18 \mu\text{m}$ , which include some known BVOC-derived OSs, recently identified polycyclic aromatic hydrocarbons (PAHs) derived organosulfur species, and previously little known alkyl OSs of low oxidation degree, are selected for investigation of size distribution characteristics. The size-specific information could provide insights into sources and formation mechanisms of OS as particles of different sizes are associated with different sources, formation and growth mechanisms (Hinds, 1999; Seinfeld and Pandis, 2006). As far as we know, only one study in the literature (Lukács et al., 2009) reported limited size distribution characteristics. They used an 8-stage Berner impactor to measure size distribution of total water-soluble OS aerosol samples collected in May and June 2006 at K-puszta, Hungary, however, they confined the chemical analysis to the stages encompassing the size range of  $0.065\text{--}2 \mu\text{m}$ , leaving OS on coarse particle unexplored. The objective of this study is to investigate the size distribution characteristics of abundant OS compounds in the Pearl River Delta, China, a subtropical region with an active biosphere and intensive anthropogenic emissions. Through size distribution analysis, the formation processes and potential sources of OSs are discussed.

## 2. Methodology

### 2.1. Aerosol samples

Ambient aerosol samples were collected at two suburban sites in the Pearl River Delta (PRD) region. One site is the Hong Kong University of Science and Technology (UST,  $22^\circ20'15.72''$  N,  $114^\circ16'03.23''$  E), a coastal site with little residential and commercial activities on the east coast of Hong Kong (Bian et al., 2014). The other site is Nansha (NS,  $22^\circ45'08.90''$  N,  $113^\circ36'09.17''$  E), a suburban district of Guangzhou city and located in the middle of the Pearl River estuary (Lin et al., 2010b). Samples were collected in 2011 summer and in 2011–12 winter at the UST site while only in winter 2008 at the NS site. A Micro-Orifice Uniform Deposit Impactor (MOUDI) aerosol sampler (nonrotating version, MSP Corp., Shoreview, MN) was used to collect size-segregated samples on quartz fiber filters pre-baked at  $550^\circ\text{C}$  for at least 8 h, each sample collected for 24 h from 0:00 to 24:00 (Bian et al., 2014). Operated at a flow rate of  $30 \text{ L min}^{-1}$ , MOUDI provides the following nominal cut sizes: 18 (inlet), 10.0, 5.6, 3.2, 1.8, 1.00, 0.56, 0.32, 0.18, 0.100, and  $0.056 \mu\text{m}$ . The filter substrates were stored in freezer at  $-18^\circ\text{C}$  until analysis.

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