



Molecular Characterization of Organosulfates in Arctic Ocean and Antarctic atmospheric aerosols

Yuqing Ye¹, Zhouqing Xie^{1,2*}, Ming Zhu³, Xinming Wang³

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¹ Institute of Polar Environment & Anhui Key Laboratory of Polar Environment and Global Change, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China

² Center for Excellence in Urban Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, Fujian 361021, China.

10 ³ State Key Laboratory of Organic Geochemistry and Guangdong Key Laboratory of Environmental Protection and Resources Utilization, Guangzhou, 510640, China

Correspondence to: Zhouqing Xie (zqxie@ustc.edu.cn)

Abstract. Organic aerosols are ubiquitous components of atmospheric aerosols. Organosulfate aerosols have been detected
15 in the Arctic Ocean atmosphere and may play an important role in the radiative balance in Polar Regions. Aerosol samples
from the Arctic Ocean and Antarctic atmosphere during 2014/2015 CHINARE were analysed by ultrahigh resolution mass
spectrometry coupled with negative ion mode electrospray ionization (ESI(-)-UHRMS). Hundreds of organic compounds
were detected and tentatively determined by their formulas, including organosulfates (OSs), nitrooxy-organosulfates (NOSs),
organonitrates (ONs) and oxygenated hydrocarbons (OxyCs). The number of OSs/NOSs accounted for 28–32% of the total
20 number of detected molecules at polar sites and ONs were 28–40%. Organic compounds of Arctic Ocean and Antarctic
aerosols had high oxidation states for carbon and a large percentage of high molecular weight formulas; this indicated that
“aged” organic aerosols likely comprise a significant part of the polar atmosphere. We hypothesized that highly oxidized
HMW compounds tend to be transported to the polar area from stratospheric reservoirs. Dramatic differences of the
molecular characteristics were observed when we compared aerosol samples between polar sites and Guangzhou sites,
25 reflecting the different oxidation mechanisms and atmospheric transmission. The polar sites contained higher fractions of
OSs/NOSs and lower fractions of ONs than the Guangzhou sites did; this indicated that the oxidation of NO_x was weaker in
the polar region. Observing that the fraction and oxidation states of polycyclic aromatic OSs/NOSs polar regions were
similar to the Guangzhou urban area but not the rural area implied an anthropogenic influence on OSs/NOSs in remote polar
areas. In addition, the contribution of potential precursors (anthropogenic and biogenic volatile organic compounds) to OS
30 and NOS formation as well as the effects of nss-SO₄ aerosols, pH and RH on OS formation in polar areas were discussed.



Our study presents the first overview of OSs and ONs in the Arctic Ocean and Antarctic atmosphere and promotes the understanding of their characteristics and sources.

1 Introduction

Atmospheric aerosols directly affect radiation by absorbing and scattering radiation (Brimblecombe, 1996; Seinfeld et al., 1998; Jacobson et al., 2000). They also serve as cloud condensation nuclei (CCN) and provide indirect radiation forcing (Seinfeld et al., 1998; Novakov and Penner, 1993). Exposure to aerosols causes respiratory and cardiovascular disease which increases mortality rates (Elder and Oberdörster, 2006; Pope Iii et al., 2002; Hallquist et al., 2009). Hence, aerosols play a key role in climate change, air quality and have an adverse effect on human health.

Organic aerosols (OAs) comprise 20–90% of the submicron atmospheric particulate mass (Kroll and Seinfeld, 2008; Hallquist et al., 2009; Jimenez et al., 2009). The complexity of OAs inhibits our understanding, as only 10–30% of OAs have thus far been identified (Hoffmann et al., 2011). Secondary organic aerosols (SOAs) are a substantial component of OAs. Researches have been verified SOAs are ubiquitous in the Arctic and Antarctic atmosphere, and biogenic volatile organic compounds (BVOCs) are important precursors of SOA, such as isoprene, α -pinene, monoterpene and sesquiterpene; these BVOCs-derived SOA can used as tracers and their contribution to total organic carbon (OC) varied from 0.01–56 ng m⁻³ (Kawamura et al., 1996; Fu et al., 2009; Fu et al., 2013; Hu et al., 2013). They are formed through photooxidation, heterogeneous and multiphase processes of organic matter in the atmosphere, as well as participate in multiple reactions (Ravishankara, 1997; Goldstein and Galbally, 2007; Kroll and Seinfeld, 2008; Jimenez et al., 2009).

Organosulfate (OS) aerosols, as a newly-identified but important class of SOA, contribute ~4–30% of ambient submicron OAs in a variety of field studies, ranging from Arctic, marine, forest, rural to urban areas (Surratt et al., 2008; Lukács et al., 2009; Hawkins et al., 2010; Stone et al., 2012; Tolocka and Turpin, 2012; Hansen et al., 2014; Frossard et al., 2011) and can act as tracers of SOA information (Zhang and Worton, 2012; Nozière et al., 2010; Nozière et al., 2015; Hettiyadura et al., 2018). Because OS molecules contain both hydrophilic and hydrophobic functional groups and relates to the optical properties of aerosols, it changes the potential impact on climate by affecting the aerosol hygroscopicity (Pang et al., 2006) and light absorption (Song et al., 2013; Jacobson, 1999; Lu et al., 2011; Laskin et al., 2015).

Formation mechanisms and molecular-level characterization of OSs need further investigation to improve our knowledge of OA sources, evolution and properties. Many studies have shown that biogenic volatile organic compounds (BVOCs) such as isoprene, monoterpenes, sesquiterpenes, oxygenated derivatives and some green leaf alcohols play an important role in producing OSs (Surratt et al., 2007; Iinuma et al., 2007; Surratt et al., 2008; N. L. Ng, 2008; Riva et al., 2016a; Zhang and Worton, 2012; Mael et al., 2015; Schindelka et al., 2013; Shalamzari et al., 2014; Shalamzari et al., 2016; Liggio and Li, 2006; Iinuma et al., 2009; Perri et al., 2010; Chan et al., 2011; Darer et al., 2011; Chen and Jang, 2012; Barbosa et al., 2017; Szmigielski, 2016; Nozière et al., 2010; McNeill et al., 2012). However, recent studies have focused on anthropogenic emissions (e.g. alkanes, polycyclic aromatic hydrocarbons (PAHs), unsaturated fatty acids and diesel fuel) as OS precursors



to try and explain a large number of unidentified OSs with aliphatic or aromatic carbon skeletons; their results showed the human effect on OS formation is underestimated and potentially enormous (Tao et al., 2014; Wang et al., 2016; Kuang et al., 2016; Riva et al., 2015; Riva et al., 2016c; Passananti et al., 2016; Shang et al., 2016; Blair et al., 2017). These organic precursors are further oxidized and react with sulfur-containing nucleophiles – SO₂/SO₃ gas, dimethyl sulfide, sulfate acids and SO₃/SO₄ radicals – involving heterogeneous and multiphase reactions.

The polar environment is well known to be sensitive to perturbations of the radiative budget. The Arctic and the Antarctic are warming at a rate of twice the global average with the atmospheric temperature increasing by 2~3 °C (ACIA, 2004; IPCC, 2013; Bromwich et al., 2012; Cohen et al., 2012). Atmospheric aerosols are pivotal factors changing the polar radiative balance. Since Mitchell first observed an Arctic haze in 1956 (Mitchell, 1957), concerns about polar atmospheric aerosols and the influence of humans has increased. These polar aerosols primarily consist of sulfate and organic aerosols and indicate their anthropogenic sources (Minikin et al., 1998; Mazzera et al., 2001; Mishra et al., 2004; Quinn et al., 2007; Tunved et al., 2013; Nguyen et al., 2016). Frossard et al. analysed the composition of Arctic organic aerosols during a haze period and detected organic sulfate functional groups in aerosol samples using FTIR spectroscopy (Frossard et al., 2011). Hansen et al. examined the speciation of secondary organic aerosols using HPLC with a quadrupole Time-of-Flight mass spectrometer and reported the occurrence of 12 organosulfates and one nitrooxy organosulfate in Arctic aerosols at Zeppelin Mountain and Station Nord, contributing 7~20% of the total organic aerosols (Hansen et al., 2014). However, the investigation of OS aerosols in the polar region is still rare.

This study presents the molecular characteristics of organosulfates (OSs), nitrooxy organosulfates (NOSs), organonitrates (ONs) and certain oxygenated hydrocarbons (OxyCs) found in aerosol samples collected in the Arctic and Antarctic during the 2014/2015 Chinese National Arctic/Antarctic Research Expedition (CHINARE). We utilized an Orbitrap mass spectrometer with high mass resolution and accuracy as well as electrospray ionization (ESI) as a soft ionization source in the negative ion mode. The differences in the molecular levels, oxidation state and aromaticity among the detected aerosols of Arctic, Antarctic and Guangzhou sites were discussed.

2 Experimental

2.1 Sample Collection

For the polar samples, total suspended particles (TSP) samples as well as field blank samples were collected aboard the CHINARE 14 cruise from the East China Sea (35 °N, 130 °E) to the Arctic Ocean (81 °N, 157 °W) from July 2014 to September 2014. TSP samples were also collected at Zhongshan Station (70 °S, 76 °E) and Kunlun Station (80 °S, 77 °E) in Antarctica from January to February 2015. In the expedition cruise to the Arctic Ocean, TSP samples were collected by a high-volume air sampler on the uppermost front deck of the icebreaker Xuelong with a sampling flow rate of 1.05 m³ min⁻¹ through a quartz fibre filter (QFF) (Whatman QM-A, 20.3×25.4 cm, UK). The high-volume air sampler was placed windward to reduce the impact of ship exhaust. Each sampling lasted for a day and the air volume ranged from 1360 to 1514



m³ (at 0 °C and 1 atm). In Antarctica, medium-volume air samplers were placed at the two stations to collect TSP samples through 82-mm QFFs. Each sampling lasted for 12–24 h and the air volume ranged from 52.6 to 105.1 m³ (at 0 °C and 1 atm). The QFFs were prebaked at 450 °C for 4 h to remove potential organic contamination. QFFs were then wrapped with aluminium foil, zipped in plastic bags and stored in freezers at –20 °C before further analysis.

5 For the Guangzhou samples, 24-hours filter-based PM_{2.5} samples were collected in an urban site (23 °N, 113 °E) and a rural site (22 °N, 113 °E) using a high-volume air sampler (Tisch Environmental, Inc. Ohio, USA) with a constant flow rate of 1.1 m³ min⁻¹. The procedures for prebaking the filters (Whatman QM-A, 20.3×25.4 cm, UK) and preserving samples were identical with the polar samples.

2.2 Sample Analysis

10 2.2.1 ESI-UHRMS Analysis

Considering the low concentrations of Arctic and Antarctic atmospheric aerosols, two Arctic samples and four Antarctic samples from the same location were combined for pre-processing and analysis. Portions of the filters (~25 cm², representing approximately 68 m³ and 36 m³ of sampled air in the Arctic and the Antarctic, respectively) were extracted with 10 mL of a 1:1 v:v mixture of methanol and MQ water in an ultrasonic bath for 1h. The extract was then filtered with a glass springe
15 equipped with a 0.25 µm PTFE membrane to remove insoluble materials. These extraction and filtration steps were performed twice; the extracts were combined and evaporated to dryness under a gentle N₂ steam. The extracts were immediately redissolved in 400 µL of 1:1 v:v mixture of MQ water and acetonitrile.

Sample aliquots (70 µL) of the extracts were directly injected by an autosampler and travelled through a steel capillary column for 3 min. In this study, we chose direct injection rather than liquid chromatography (LC) injection because our
20 objective was to obtain an overall picture of the molecular characteristics of OS/NOS aerosols from the Polar Regions. The extracts from the polar samples were analysed using an LTQ-Orbitrap XL mass spectrometer (Thermo Fisher Scientific, USA) coupled with a heated ESI source, with the spray voltage set at 3 kV. The system was operated under negative ESI mode with a resolving power of 100,000 at m/z 400 and absolute mass error <0.02 ppm; and signals of 50–800 m/z range were recorded for data processing. The extracts from the Guangzhou samples (one sample from urban site, one sample from
25 rural site) were analysed using a solariX XR FT-ICR MS (Bruker Daltonik GmbH, Bremen, Germany) (equipped with a 9.4 T refrigerated actively shielded superconducting magnet (Bruker Biospin, Wissembourg, France) and the Paracell analyzer cell) in 3 kV negative ESI mode. A mass-resolving power > 450,000 at m/z 319 with absolute mass error <0.02 ppm was achieved; signals of 150–1000 m/z range were recorded. The same pre-treatments were applied for field blank samples.

2.2.2 Inorganic Ion Analysis

30 Soluble inorganic ions were analysed by ion chromatography (Dionex DX-120, Osaka, Japan). A round, 1-inch diameter filter was cut off to rinse with 10 mL of MQ water in an ultrasonic bath for ~40 min. After centrifuging for 10 min, the



supernatant was extracted and the remained filter was treated again following the same procedure. The extracts were combined and filtered through a 0.25 μm PTFE membrane before injection into the IC system. The cations were analysed using a CS12A analytical column with a CDRS600 guard column. Anions were analysed using an AS19 analytical column with a CDRS500 guard column.

5 2.3 Data Processing

The mass spectra from Orbitrap MS were obtained and analysed by Xcalibur software (V2.1, Thermo Fisher Scientific, USA) and the mass spectra from FT-ICR MS were initially retrieved in DataAnalysis software (V4.4, Bruker Daltonics). All ions within the 50–800 m/z range (Orbitrap MS) or 150–1000 m/z range (FT-ICR MS) with a signal-to-noise ratios (s/n) ≥ 10 were selected to elucidate possible formulas with mass tolerances of ± 2 ppm. These formulas are expressed as $C_cH_hO_oN_nS_s$, with the constraints of 1–80 of c , 2–200 of h , 0–50 of o , 0–5 of n and 0–2 of s . Further limitations were applied to ensure the retrieved compounds did exist in nature: H/C, O/C/, N/C, S/C and double bond equivalent to carbon number ratios (DBE/C) were restricted in the range of 0.3–30, 0–3, 0–0.5, 0–0.2 and 0–1, respectively; the formulas which broke the nitrogen rule for even electron ions were excluded. Compounds with carbon, nitrogen and sulfur numbers satisfying $4s+3n \leq o$ were tentatively regarded as organosulfates, organonitrates and nitroxy organosulfates. The raw data of blank filters were processed the same way and the formulas exported from blank filters were subtracted from sample-derived formulas, regardless of the intensity (Lin et al., 2012a; Lin et al., 2012b).

The DBE value (calculated using Eq. 1) provides the degree of molecular unsaturation without inclusion of the double bonds from sulfate groups (2 S=O) (Wang et al., 2016).

$$\text{DBE} = \frac{2c+2+n-h}{2} \quad (1)$$

The aromaticity equivalent (X_c) identified potential monocyclic and polycyclic aromatic compounds (Yassine et al., 2014; Tong et al., 2016; Wang et al., 2017b). A general equation for X_c containing only carbon, hydrogen, nitrogen, sulfur and phosphorus is given in Eq. (2):

$$X_c = \frac{3[\text{DBE}-(m \times o + n \times s)]-2}{\text{DBE}-(m \times o + n \times s)} \quad (2)$$

where o , and s refer to the number of oxygen and sulfur atoms, respectively while m , and n correspond to the fraction of oxygen and sulfur involved in the π -bond structure of the compound. If $\text{DBE} \leq (m \times o + n \times s)$, then $X_c = 0$. In this study, $m=n=0.5$ was used for the assigned formulas since they were detected in negative ESI mode as ESI^- is sensitive to carboxylic groups and carboxylic acids are characterized as $m=n=0.5$. If either o or n is an odd number, $(m \times o + n \times s)$ is rounded to the next lower integer. A value of $X_c \geq 2.5000$ was proposed as unambiguous minimum criteria for the presence of an aromatic structure; $X_c \geq 2.7143, 2.8000, 2.8333, 2.9231$ were considered as the thresholds for molecules containing cores of naphthalene, anthracene, pyrene and ovalene, respectively.

Carbon oxidation state (OSc) has been used as a metric for the degree of oxidation of atmospheric organic aerosols (Kroll et al., 2011). For organic compounds consisting of carbon, hydrogen and oxygen, OSc can be calculated using Eq. (3):



$$OSc \approx 2O/C - H/C \quad (3)$$

Where O/C and H/C are the elemental ratios of oxygen-to-carbon and hydrogen-to-carbon. Eq. (3) can be applied to organosulfates and organonitrates because most of the ESI-MS detected heteroatom-containing compounds have only minor deviations in their oxidation states.

- 5 In this study, OS, NOS, ON and OxyC refer to organosulfate, nitrooxy-organosulfate, organonitrate and oxygenated hydroxycarbon.

2.4 Back-trajectory calculations

- Back-trajectories for Arctic Centre Sea (81.05 °N, 157.4 °W), Arctic Pack Ice (71.5 °N, 168.05 °W), Antarctic Kunlun Station (80.42 °S, 77.12 °E) and Antarctic Zhongshan Station (70.13 °S, 76.58 °E) were computed using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPPLIT) model from the NOAA Air Resources Laboratory (Draxler and Rolph, 2003). BTs were back-traced for 120 h with 6 h steps at elevations of 100, 500 and 1000 m above ground level.

2.5 Aerosol pH calculation

- A thermodynamic equilibrium model (ISORROPIA II) were used to predict the pH of the polar aerosol samples for the $K^+ - Ca^{2+} - Mg^{2+} - NH_4^+ - Na^+ - SO_4^{2-} - NO_3^- - Cl^- - H_2O$ system (Fountoukis and Nenes, 2007). The model was set up in the forward mode with a metastable state. The concentrations of inorganic ions, the relative humidity and temperature were input into the model together to calculate the pH of aerosol bulk.

3 Results and Discussion

3.1 General Characterizations

- The main purpose of this study was to tentatively identify organosulfate and other organic aerosols in the polar atmosphere and compare them with those of Guangzhou, whose atmosphere is affected by anthropogenic pollution, plant emissions and ocean aerosols.

- Using HR-MS (Orbitrap for Arctic and Antarctic, FT-ICP for Guangzhou) equipped with an ESI- mode, assigned formulas of organic aerosols were detected in Arctic Centre Sea, Arctic Pack Ice, Antarctic Kunlun Station, Antarctic Zhongshan Station, Rural and Urban Guangzhou; these formulas were classified into four groups by their elemental composition: oxygenated hydrocarbons (CHO), organosulfate (CHOS), organonitrate (CHON) and nitrooxy-organosulfate (CHONS). In total, there were 330, 215 and 1777 (1069 in common) different OS and ON molecular formulas found in atmospheric particles from the Arctic, Antarctic and Guangzhou, respectively.

- Table 1 summarizes the elemental formulas obtained from the six sampling sites, including the numbers and the fractional percentages of the identified formulas, carbon number range, average molecular weight values (intensity-weighted average \pm standard deviation), DBE, O/C and OSc, and the numbers of aliphatic and aromatic compounds. Among the six sites,



approximately 21–32% of formulas were OSs and NOSs (i.e. CHOS (blue) and CHONS (light blue) in Fig. 1). Obviously, samples collected in Guangzhou had the greatest number of total formulas (2270 in urban areas, 1918 in the rural areas) as well as formulas in each category, far more than the polar areas (25 in the Arctic Center Sea, 487 in the Arctic Pack ice, 124 in the Antarctic Kunlun Station and 247 in the Zhongshan Station). The Arctic Centre Sea was at the highest latitude (81.07 °N); the fewest number of formulas were found there, just 1% of the number of formulas found in Guangzhou aerosols. However, OSs and NOSs in the polar areas accounted for a larger fraction (up to ~30%) of the total assigned formulas than those from Guangzhou (~20%, see Table 1 and Fig. 1 pie charts). But Guangzhou had the most abundant ON components among the three regions, accounting for nearly 50% of the total formulas; while ONs in Arctic and Antarctic aerosols accounted for ~30%. Because Arctic and Antarctic samples were collected during the summertime at each location, there was no nocturnal oxidation of NO₃ taking place. This may partially explain the smaller ON fractions in the polar atmosphere relative to Guangzhou samples. In addition, the Guangzhou NO_x concentrations far exceeded those in the Polar Regions (Shao et al., 2009; Seppälä et al., 2007). It should be noted that in the same polar area, higher-latitude sites (i.e. Arctic Center Sea and Antarctic Kunlun Station) had fewer aerosol formula types than the lower-latitude sites (i.e. Arctic Pack Ice and Zhongshan Station). One possible reason for this observation stems from the effect other continents have on lower latitude sites, with additional pollutants from natural and anthropogenic sources, as shown in the backward trajectories from sampling sites in Fig. S1.

Mass spectra of compounds detected by Orbitrap with ESI⁻ were reconstructed as seen in Fig. 1, displaying the assigned formulas by setting the most abundant peak (CHO, CHON, CHOS and CHONS) as 100%. Considering the different signal responses from various species, we did not discuss the absolute abundance in this study. The total identified formulas covered a wide range of molecular weights (90–800 Da) among the six sites. Polar atmospheric aerosol compounds displayed more dispersive molecular weight ranges, composed mostly of MWs from 250–500 Da; MW ranges from Guangzhou samples were from 200–400 Da (Fig. 2). Moreover, half of the OSs and NOSs in polar aerosols had MW values between 400–600 Da as compared to Guangzhou values of 300–400 Da. The highest peaks in the mass spectra varied among different sites – the peaks centred ~100–200 Da in samples from the Arctic Pack Ice zone and Antarctic Zhongshan Station; peaks from Guangzhou samples were centred from 250–400 Da. There was no clear distribution in samples from the Arctic Centre Sea zone and Antarctic Kunlun Station due to the relatively few number of formulas detected. These discrepancies in MW distributions between polar sites and Guangzhou sites showed a larger fraction of high-molecular-weight (HMW) compounds in the Arctic and Antarctic areas which are possibly due to the preservation of HMW molecules in the stratosphere and subsequent transportation to remote areas instead of reacting with atmospheric oxidants (as LMW molecules tend to do), underlying that aerosols in polar regions and the Guangzhou area undergo different transportation and formation mechanisms. Within a particular sampling site, the OSs and NOSs shows a much higher molecular weight distribution than ONs, partly due to an increase in nitrogen and sulfur atoms which require additional C and O atoms.



3.2 Aromaticity and Oxidation state

Aliphatic compounds, with formulas $(DBE-n) < 4$, made up ~20%–30% of compounds found in Arctic and Antarctic sites, but > 40 % at Guangzhou sites. $X_c \geq 2.5$ was used for confirmation of aromatics in this study (Wang et al., 2017a) and aromatic compounds accounted for a large number of formulas (>40%) at these sampling sites. OSs and NOSs displayed an enormous difference in compositions between polar sites and Guangzhou sites (Fig. S2); Figure S2 shows the fractions of aliphatic and aromatic compounds at each sampling site. Nearly 80% of total OS and NOS molecules were aliphatic and less than 10% were aromatic with a DBE average of 2.2 in the Guangzhou samples. This was consistent with previous urban area studies (Kuang et al., 2016; Wang et al., 2016; Wang et al., 2017a; Stone et al., 2012; Ma et al., 2014). Compared to the polar regions in this study, aliphatic molecules comprised 0%, 32%, 19% and 41% and aromatic molecules comprised 29%, 39%, 24% and 30% of all total detected OSs and NOSs at the Arctic Centre Sea, Arctic Pack Ice, Antarctic Kunlun Station and Antarctic Zhongshan Station, respectively. As stressed in previous chamber studies of PAH-derived OSs (Riva et al., 2015), the greater percentage of aromatic OSs and NOSs in the Polar Regions relative to Guangzhou sites suggested that anthropogenic sources contributed more significantly to OS aerosols than the biogenic sources in the Polar Regions.

Van Krevelen (VK) diagrams are usually employed to describe the compositional characteristics of complex organic mixtures, providing the overall oxidation and unsaturation conditions. The H/C ratio of each compound found in the MS is plotted versus its O/C ratio, color-coded by X_c value (Wu et al., 2004; Kim et al., 2003), as shown in Fig. 3 (OSs and NOSs), Fig. S3 (ONs) and Fig. S4 (OxyCs). It should be stressed that we used $(o-2n-3s)/c$ to replace o/c here, due to nitrate and sulfate groups containing more oxygen atoms than common oxygen-containing functional groups (Wang et al., 2016). Figure 4, Figure S5 and Figure S6 present the OSc as a function of carbon number and color-coded by X_c value of OSs and NOSs, ONs, and OxyCs. Detected OS and NOS compounds in the polar regions and the Guangzhou sites showed clearly different VK diagram patterns and oxidation state diagrams. The majority of OSs and NOSs plotted in 0 to 1.0 of O/C and between (–1)–(+2) of OSc for polar samples, while the Guangzhou samples mainly plotted in 0 to 0.8 of O/C values and between (–2)–(+1) of OSc values. In Fig.3 and Fig. 4, organosulfate compounds in the light green oval all featured low O/C (0–(+0.3)), low H/C (0–(+1.0)) and high OSc ((–1)–(+1)) with ≥ 20 carbon number and were considered as polycyclic aromatic OSs; they were all present at all four polar sites and urban Guangzhou site but absent from rural Guangzhou site (where the biogenic influences dominated). The similarity of polycyclic aromatic OSs in high oxidation states between the polar sites and the Guangzhou urban sites were consistent with previously reported PAH-derived OSs (Staudt et al., 2014; Riva et al., 2015) and suggested that the polar regions were more affected by long-transported or in-situ pollutants from human activities. Nevertheless, OS and NOS molecules plotted in the dark green oval in the VK diagrams and the OSc plots were unique to polar sites, except the Arctic Centre Sea site. These aliphatic OSs and NOSs with 10–20 carbons had O/C ratios of 0.8–1.0 and OSc of 1–2. The high oxidation state indicated that there were more “aged” oxidized organic aerosols in the polar atmosphere, partly due to the longer resistant time of aerosols and more light exposure in the summertime polar atmosphere. This corresponds to the inference from high concentration of HMW molecules in polar sites as mentioned above. Previous



studies have observed that photochemical activity is promoted in the polar atmosphere where oxygenated organic aerosols are a mix of primary marine aerosols and transported SOA from other continents (Mochida et al., 2002; Hawkins et al., 2010; Russell et al., 2010).

The aromaticity and oxidation states of ONs and OxyCs were quite different than OSs. Comparing the three species
5 (OxyCs, ONs, OSs and NOSs) measured at a single Polar Region site, OxyCs had the largest percentage of aromatic molecules and the smallest percentage of aliphatic molecules, yet ONs contained the most abundant aliphatic components (Fig. S6).

3.3 Potential Precursors and Atmospheric Implications

Biogenic VOCs (BVOCs), such as isoprene, α -pinene, β -pinene and limonene, as well as anthropogenic VOCs (AVOCs)
10 are important precursors of organosulfate aerosols according to previous laboratory and field studies (Surratt et al., 2007; Surratt et al., 2008; Chan et al., 2011; Staudt et al., 2014; Riva et al., 2015; Riva et al., 2016c; Meade et al., 2016; Riva et al., 2016b; Barbara Nozière, 2010; Shang et al., 2016; Olson et al., 2011; Zhang and Worton, 2012; Szmigielski, 2016; Lin et al., 2013). These published organosulfates whose precursors have been verified, were used as “standard” organosulfates to estimate potential precursors of detected OSs and NOSs in the polar atmosphere. Assigned OSs with identical carbon,
15 hydrogen, nitrogen and sulfur atoms but more oxygen atoms than “standard” OSs were temporarily considered to have the same precursors because organic aerosols in polar regions have high oxidation states. By comparing their formulas, the OSs and NOSs were classified as AVOC-derived, BVOC-derived, AVOC/BVOC-derived and unknown-precursor organosulfates (Fig. 5). In the Arctic Centre Sea, none of seven OSs matched the “standard” OSs. However, they were more likely generated from anthropogenic aromatic hydrocarbons (ArHCs), such as benzene, toluene, xylenes, naphthalene and biphenyl
20 because HOM products from these ArHCs had compositions similar to OSs from the Arctic Centre Sea (Molteni et al., 2018). In Arctic pack ice zone, 18% of total OSs were derived from BVOC and 12% from AVOC (AVOC/BVOC-derived OSs account for both sides). BVOC-derived OSs comprised 14% and 19% in the Antarctic Kunlun Station and Zhongshan Station, respectively, and AVOC-derived OSs accounted for 14% and 23%. The percentages of BVOC-derived OSs from
25 sites and the formation of BVOC-derived OSs mainly depended on the reaction steps involving sulfur-containing ingredients. On the other hand, AVOC-derived OSs at the Zhongshan Station sites contained higher percentages than those from the other two sites. Considering human activities, one of the aerosol emission sources over Zhongshan Station was anthropogenic pollution and was attributed to the direct impact of developing research activities on the station and long-distance transporting air pollutants from Southern Hemisphere continents (Jianjun et al., 2010; Thamban and Thakur, 2013;
30 Xu et al., 2019). Kunlun Station is located about 7.3 km southwest to Dome A on the Antarctic plateau at an elevation of 4087 m; the first Chinese Antarctic inland research station suffers from extremely low temperature, an extremely dry atmosphere and low wind speeds. Dome A is a barren field bereft of plants but the human activities from Kunlun research



station. In addition, the back-trajectory result obtained with HYSPLIT analysis (Fig. S1) also provides insight into the impact of sea spray transport, coastal plants and anthropogenic emissions from other research stations.

The noticeable point, however, was a large number of OSs from heretofore unrecognized precursors which comprised more than 60% of total detected OSs at each site. These unexplained OSs emphasized additional laboratory studies should be carried out in order to thoroughly investigate the formation mechanism of OSs and the latent contributions of OSs to atmosphere in the polar area.

The number of detected OSs was directly proportional to the concentration of non-sea-salt-sulfate (nss-SO₄) aerosols, underscoring the nonnegligible contribution of anthropogenic contamination. The exceptionally high concentration of nss-SO₄ aerosols at the Arctic Pack Ice site may be a consequence of ship emissions, since ship exhausts can increase nss-SO₄ by a factor of two (Zhan et al., 2014). In addition, the O/C values from the Arctic Pack Ice site were the smallest among the four polar sites and close to the Guangzhou sites, demonstrating more in-situ production of SOAs derived from ship emissions occurred at this sampling site. Those particles, as well as NO_x, SO_x, O₃ and hydrocarbons (HCs) emitted from the ship cruise accelerated the reaction rate of OS formation due to reactant increases and acidification. Zhongshan Station is located along the Antarctic east coast near Prydz Bay 1 km west of an Adelie penguin colony (Xie et al., 2002). According to previous studies, potential sources of atmospheric sulfur from these sites include marine biogenic emissions, dust from distant continents, aerosols from stratospheric reservoir, VOCs from penguin droppings and exhausts from this station which are equipped with power houses (Xie et al., 2002; Minikin et al., 1998; Bates et al., 1992; Legrand et al., 2017). This may help explain the higher concentration of nss-SO₄ aerosols and more OSs molecules detected in the atmosphere of Zhongshan Station.

The effect of aerosol acidity on the formation of OSs has been investigated (Riva et al., 2016b; Iinuma et al., 2007; Surratt et al., 2007; Chan et al., 2011). Acid conditions significantly enhance OS yields via acid-catalysed ring-opening of epoxy organic intermediates, which facilitates addition of sulfate anion to carbocation. This reactive uptake chemistry of epoxides is a significant pathway to BVOC-derived OSs. Other mechanisms of OS formation are unaffected by acidity, such as the heterogeneous reaction of SO₂ or the sulfate anion radical with unsaturated compounds and nucleophilic substitution of organonitrate by sulfate. We calculated the pH of aerosols at all four polar sites using ISORROPIA II, a thermodynamic equilibrium model (Fountoukis and Nenes, 2007) (Table 2). At the Arctic Centre Sea and Antarctic Kunlun Station, atmospheric aerosols were neutral/slightly alkaline, while aerosols from the Arctic Pack Ice and Antarctic Zhongshan Station were slightly acidic (estimated). The extremely low pH of Arctic Pack Ice samples resulted from the influence of ship emissions, based on the high concentration of nss-SO₄ aerosols. The pH estimation and OS formation mechanisms suggest that acid-catalysed epoxy chemistry was the primary formation pathway in aerosols samples from Arctic Pack Ice and Antarctic Zhongshan Station. This is consistent with the previous discussion on participation of AVOC and BVOC in OS formation. BVOC-derived OSs at the two acid sampling sites (Arctic Pack Ice and Antarctic Zhongshan Station) were higher in both number and percentage than those in the neutral/slightly alkaline (Arctic Centre Sea and Antarctic Kunlun Station). The OSs of the neutral/slightly alkaline atmosphere were due to multiphase oxidation of unsaturated organic interactions



with SO₂ and sulfate anion radicals involving photooxidation with OH/O₂. In addition, small amounts of alkali added to bulk aerosols can accelerate the rate of OS formation by esterification of sulfuric acid with alcohols (Li and Jang, 2013).

RH is considered as a factor influencing OS formation; nevertheless, it can lead to inconclusive OS yields (Li and Jang, 2013; Riva et al., 2015; Riva et al., 2016c; Barbosa et al., 2017; Kwong et al., 2018). Higher RH conditions inhibit OS formation in an acid-catalysed epoxy system; this is likely due to dilution from additional water particles resulting in a decrease in aerosol acidity (Riva et al., 2015; Riva et al., 2016a; Riva et al., 2016c). Meanwhile, some groups have found that higher RH values increased OS yields at neutral pHs (Barbosa, 2017, J. Li, 2013). In our study, Arctic sites are relatively moist (RH=90%) while Antarctic sites are relatively dry (RH=50–65%). The impact of RH on OS formation showed behaviour opposite to what we previously reported and expected. Between the two acidic sites, Arctic Pack Ice had higher RH as well as more OS constituents. Between the two neutral/slightly alkaline sites, more OS constituents were detected at the Antarctic Kunlun Station with lower RH. As a consequence, the effect of RH was not large enough to generate a substantial difference in OS formation and it should be put into comprehensive consideration in the potential impact of VOCs and S/IVOCs concentrations, sulfate aerosols, atmospheric oxidants and their interactions with each other.

4 Conclusions

Atmospheric particulate matter collected during CHINARE 14/15 in Arctic and Antarctic regions (Arctic Centre Sea, Arctic Pack Ice, Antarctic Kunlun Station and Antarctic Zhongshan Station) and Guangzhou urban/rural sites were analysed using ultra-high-resolution mass spectrometry with negative ESI mode. Four groups of tentatively determined compounds in the study areas (OSs, ONs, NOSs and OxyCs) were present and posted different molecular characteristics. In the polar sites, 20–500 organic compounds were identified with masses from 90–800 Da and more than 2000 compounds were identified in Guangzhou sites. The compositions of detected compounds were different between polar areas and the Guangzhou area. OSs/NOSs and ONs represented ~30% and 30–40% of the total compounds detected at polar sites, respectively, while compounds at the Guangzhou site were approximately 20% OSs/NOSs and ~50% ONs. These differences could be explained by elevated NO_x concentrations from vehicle exhausts and night-time oxidation of NO₃ in Guangzhou. Comparing sites in the same polar area (Arctic or Antarctic), more molecules were detected at lower-latitude sites than higher-latitude sites; this suggested influences from other continents as well as human activities on polar area aerosols. In terms of molecular weight distributions, more high-molecular-weight compounds were observed in the polar areas than in Guangzhou. Combining that with the observation that compounds detected in the polar area exhibited a higher oxidation state ($OS_{\text{polar}} = (-0.25) - (+0.04)$, $OS_{\text{GZ}} = (-0.47) - (-0.17)$), we inferred that HMW compounds emitted from other continents were inclined to be initially preserved, transported to remote polar areas, where they participated in further oxidation and photochemical reactions. Additionally, polar sites and the urban Guangzhou site showed similar patterns of polycyclic aromatic OS/NOS molecules in similar oxidative states and differed from the rural Guangzhou site, suggesting polar areas were intensely affected by anthropogenic pollutants.



To investigate OS/NOS formation in polar areas, we examined potential precursors of OSs/NOSs detected at polar sites by comparing our results with those already published, AVOC/BVOC-derived OSs/NOSs and the effects of the atmospheric environment including concentrations of nss-SO₄ aerosols, pH and RH. Of the total OSs observed in the Arctic Pack Ice zone, the Antarctic Kunlun Station and the Antarctic Zhongshan Station, 18%, 14% and 19% were derived from BVOC while 12%, 5 14% and 23% came from AVOC. The relatively high contribution of AVOC to OSs/NOSs in Antarctica was partly due to developing Antarctic research activities and air pollutants transported from Southern Hemisphere continents. Since the precursors and formation mechanisms of OSs have not been unambiguously determined, over 60% of total OSs/NOSs at each site were unrecognized by their precursors. Impacts from human activities were also inferred from the positive correlation of the nss-SO₄ concentration and the number of detected OSs/NOSs compounds. From the perspective of aerosol 10 acidity, pH values at the Arctic Centre Sea and Antarctic Kunlun Station were neutral/slightly alkaline, while Arctic Pack Ice and Antarctic Zhongshan Station were slightly acidic. The reactive uptake of epoxides involving acid-catalysed ring opening is a significant formation pathway for BVOC-derived OS/NOS molecules; this led to conclusion that the formation mechanism of OS aerosols at Arctic Pack Ice and Antarctic Zhongshan Station was dominant by epoxy chemistry. This supposition was in agreement with higher involvement of BVOC in the OSs/NOSs formation at these two sites. Different 15 relative humidity values at these sampling sites had no apparent impact on the OSs/NOSs yields in our study.

Data availability. All data needed to draw the conclusions are present in the main text and/or the Supplement. For additional data, please contact the corresponding author (zqxie@ustc.edu.cn).

20 *Author contributions.* Z.Q.X. conceived and supervised this study. Y.Q.Y. and M.Z. performed the measurement. Y.Q.Y., Z.Q.X. and X.M.Wang interpreted the data. Y.Q.Y. wrote the manuscript with input from Z.Q.X.

Competing interests. The authors declare that they have no conflict of interest.

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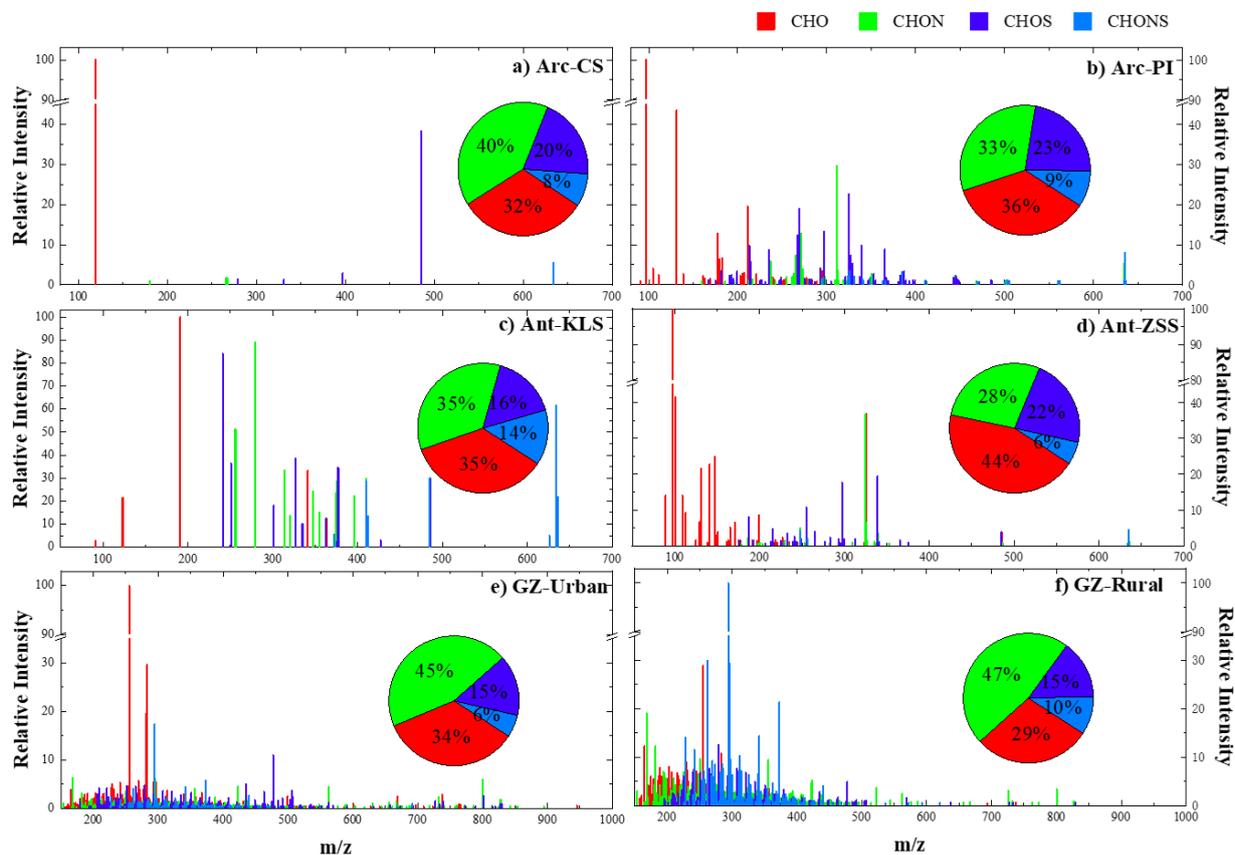
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**Table 1. Summary of tentatively assigned formulas of atmospheric particles observed in the six aerosol sampling sites.**

Location	No. of Formulas					C# Range	DBE Mean	O/C	O/Sc	Mass Mean	No. of Aliphatic	No. of Aromatic
	Total	CHO	CHON	CHOS	CHONS							
Centre Sea 81.05 °N, 157.4 °W	25	8 (32%)	10 (40%)	5 (20%)	2 (8%)	5 ~ 35	10.9	0.45	0.00	393.05 ± 137.36	9 (46%)	14 (56%)
Arctic												
Pack Ice 71.5 °N, 168.05 °W	487	174 (33%)	159 (36%)	110 (23%)	44 (9%)	3 ~ 48	7.4	0.39	-0.17	340.69 ± 139.01	253 (52%)	234 (48%)
Kunlun Station												
80.42 °S, 77.12 °E	124	44 (35%)	43 (35%)	20 (16%)	17 (14%)	6 ~ 45	8.6	0.45	0.04	368.63 ± 121.96	63 (51%)	61 (49%)
Antarctic												
Zhongshan Station 70.13 °S, 76.58 °E	247	109 (44%)	69 (28%)	55 (22%)	14 (6%)	3 ~ 45	6.2	0.42	-0.25	312.54 ± 160.32	145 (59%)	102 (41%)
Urban												
23.13 °N, 113.27 °E	2270	738 (34%)	1017 (45%)	344 (15%)	126 (6%)	5 ~ 64	4.2	0.33	-0.47	313.03 ± 107.73	1216 (54%)	1054 (46%)
Guangzhou												
Rural 22.42 °N, 113.32 °E	1918	559 (29%)	896 (47%)	280 (15%)	183 (10%)	5 ~ 49	4.7	0.41	-0.17	295.46 ± 80.31	910 (47%)	1008 (53%)


Table 2. The concentrations of inorganic aerosols, RH, temperature and calculated pH in polar sampling sites.

Sampling Sites	Na ⁺ (µg/m ³)	K ⁺ (µg/m ³)	Mg ²⁺ (µg/m ³)	Ca ²⁺ (µg/m ³)	NH ₄ ⁺ (µg/m ³)	SO ₄ ²⁻ (µg/m ³)	NO ₃ ⁻ (µg/m ³)	Cl ⁻ (µg/m ³)	RH (%)	Temp (K)	pH	
Arctic	Centre Sea	0.3426	-	0.0485	0.0275	0.1487	0.2360	0.0160	0.0287	90	275.15	7.7
	Pack Ice	0.6834	0.1212	0.0690	0.0200	0.1697	2.0452	0.1356	0.2643	90	260.05	3.8
Antarctic	Kunlun Station	0.4776	0.1140	0.0195	0.0473	-	0.4041	0.0641	0.1849	65	246.98	7.8
	Zhongshan Station	0.1058	0.1244	0.0537	0.0729	-	0.3066	0.0583	0.1576	50	266.10	4.8



5 **Figure 1.** Mass spectra of detected compounds (CHO, CHON, CHOS, CHONS) reconstructed from Orbitrap MS analysis in the negative ionization mode. X axis corresponds to the m/z of the assigned species and Y axis corresponds to the relative intensity of each molecular. Note that the most abundant peak (CHO, CHON, CHOS and CHONS) was set as 100%. The pie charts showed the percentage of each subgroup were taken up in the total number of detected compounds. a) Arc-CS, Arctic Centre Sea Zone; b) Arc-PI, Arctic Pack Ice Zone; c) Ant-KLS, Antarctic Kunlun Station; d) Ant-ZSS, Antarctic Zhongshan Station; e) GZ-Urban, Guangzhou Urban Sampling Site (Environment Monitoring Station); f) GZ-Rural, Guangzhou Rural Sampling Site (Wangqinsha).

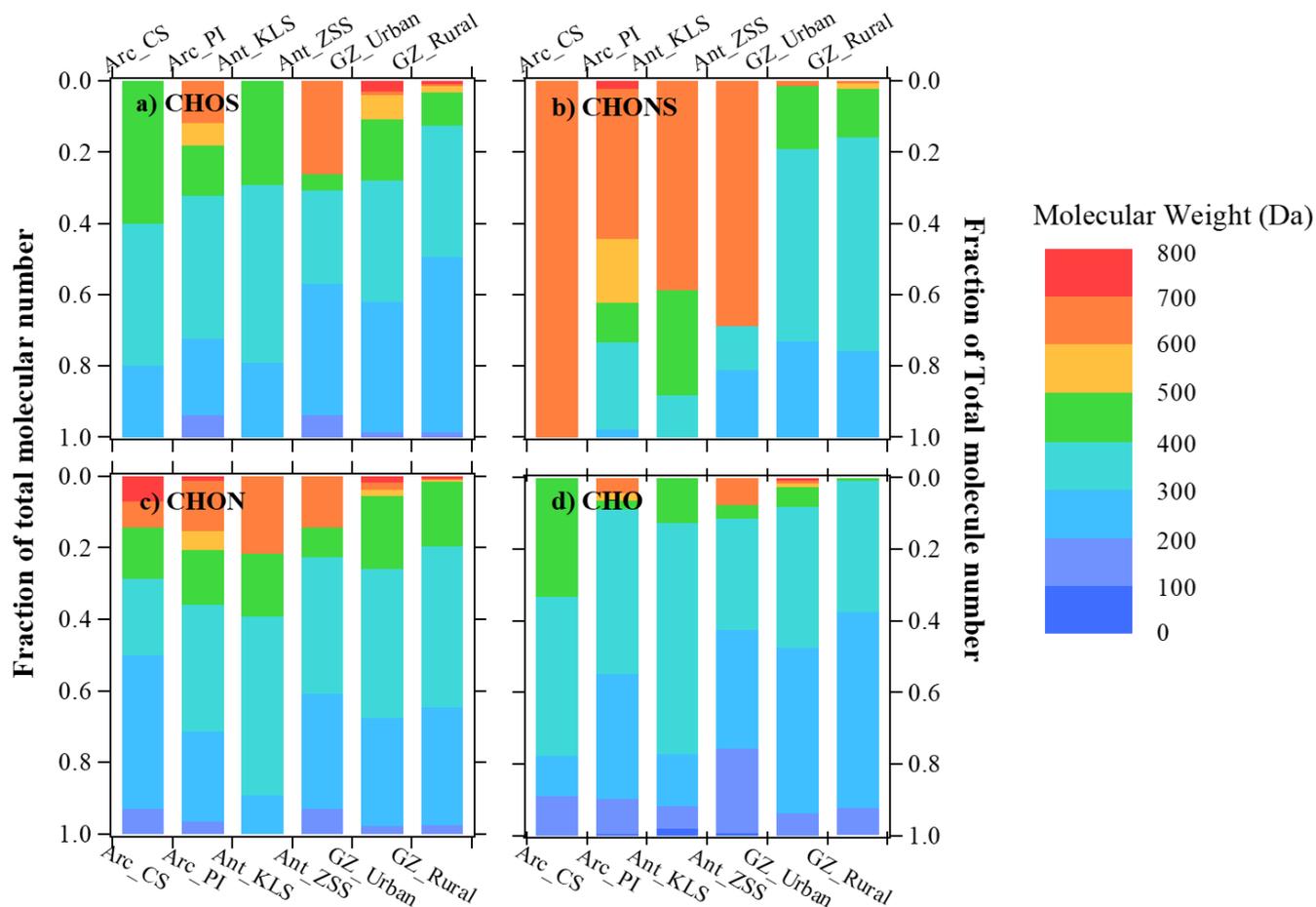
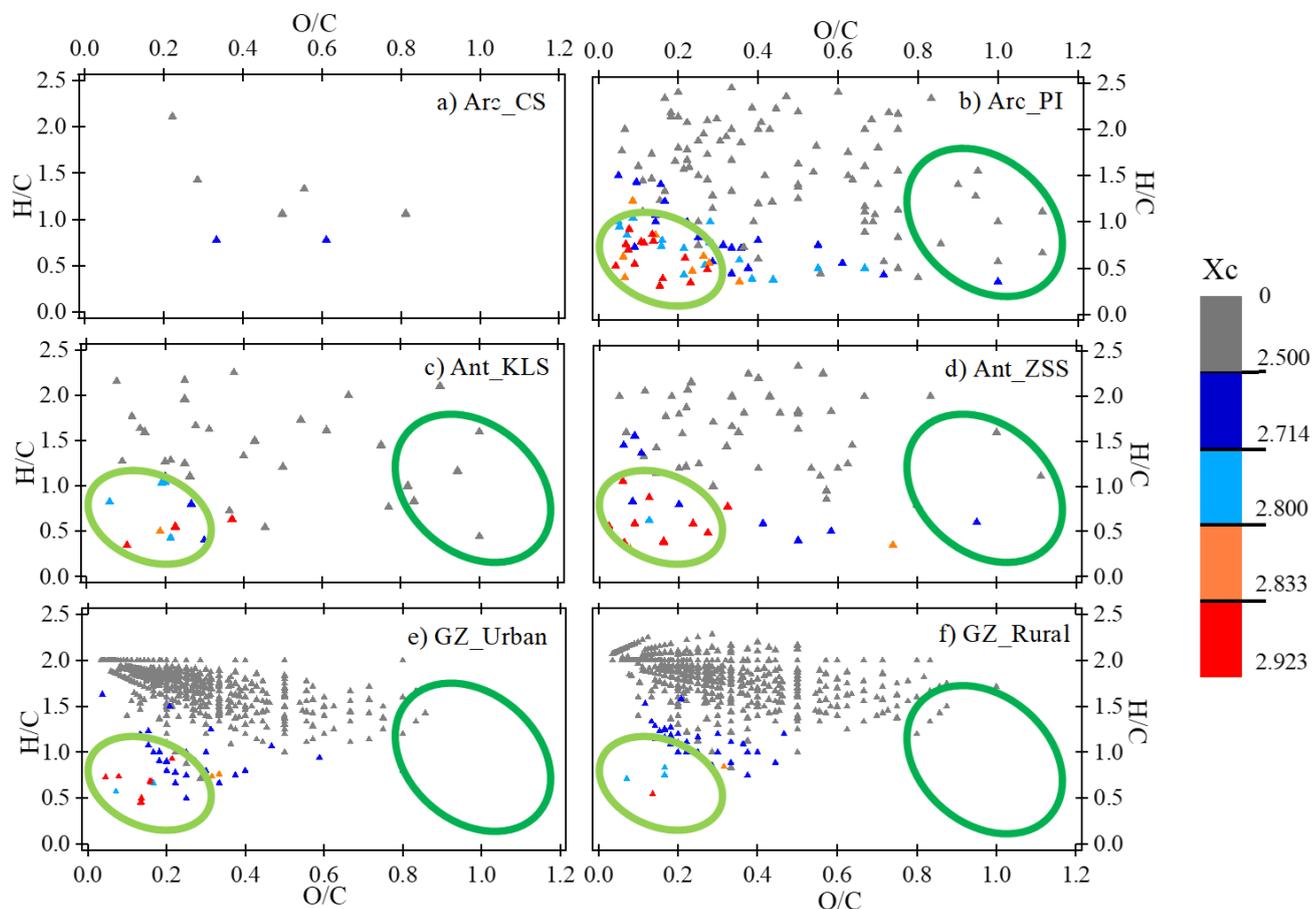


Figure 2. The distributions of detected CHOS (a), CHONS (b), CHON (c) and CHO (d) molecules in the molecular weight range in the six sampling sites. The color-coding indicates the molecular weights range from 0 Da to 800 Da.



5 **Figure 3.** Van Krevelen Diagrams for OSs and NOSs molecules in the six sampling sites. The color-coding indicates the X_c values calculated from Eq. (2). The gray marks represent aliphatic compounds ($X_c < 2.500$); the dark blue marks represent aromatics with a benzene core structure ($2.500 \leq X_c < 2.714$); the light blue marks represent aromatics with a naphthalene core structure ($2.714 \leq X_c < 2.800$); the orange marks represent aromatics with a anthracene core structure ($2.800 \leq X_c < 2.833$); the red marks represent aromatics with a pyrene core structure ($2.833 \leq X_c < 2.923$).

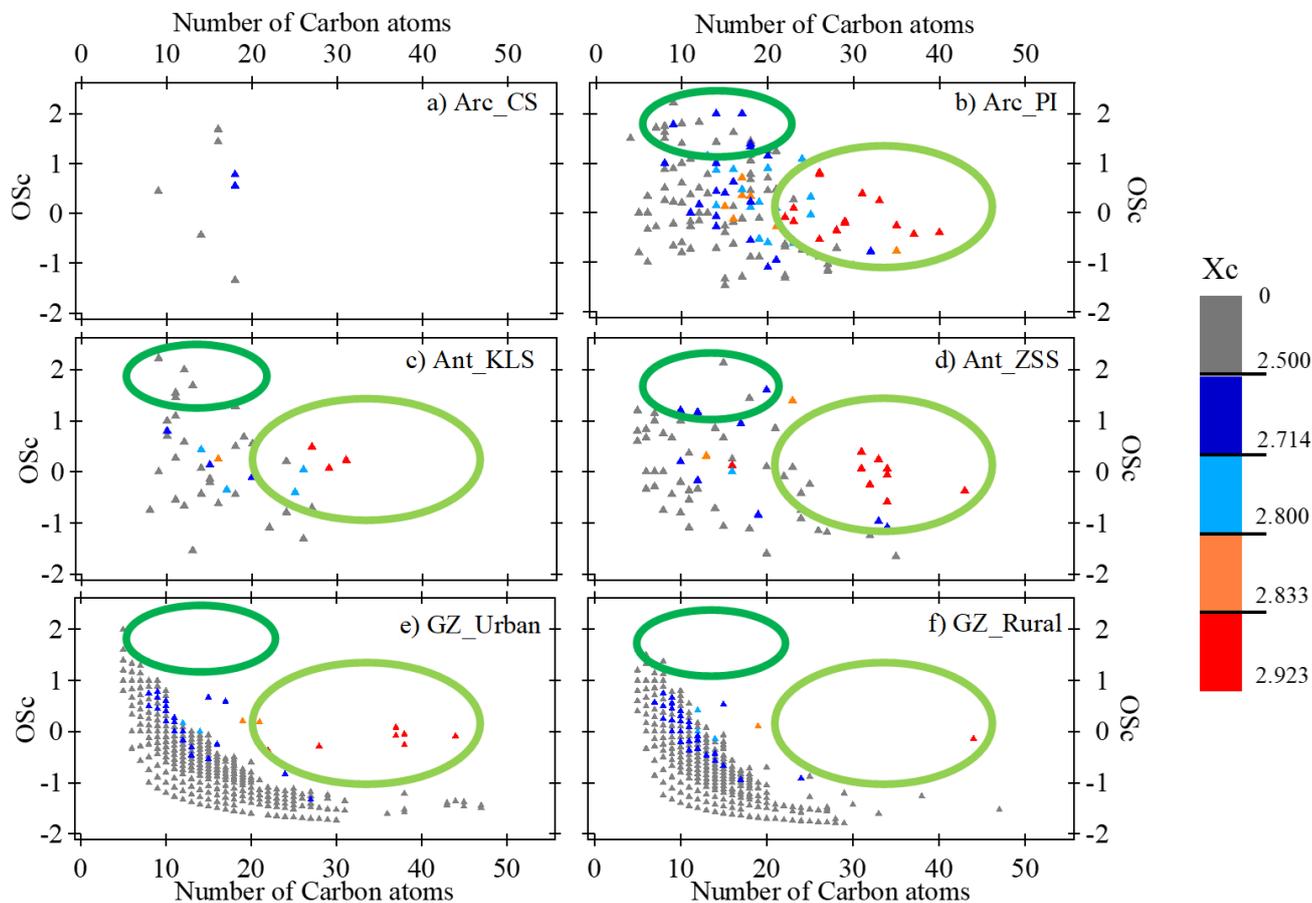
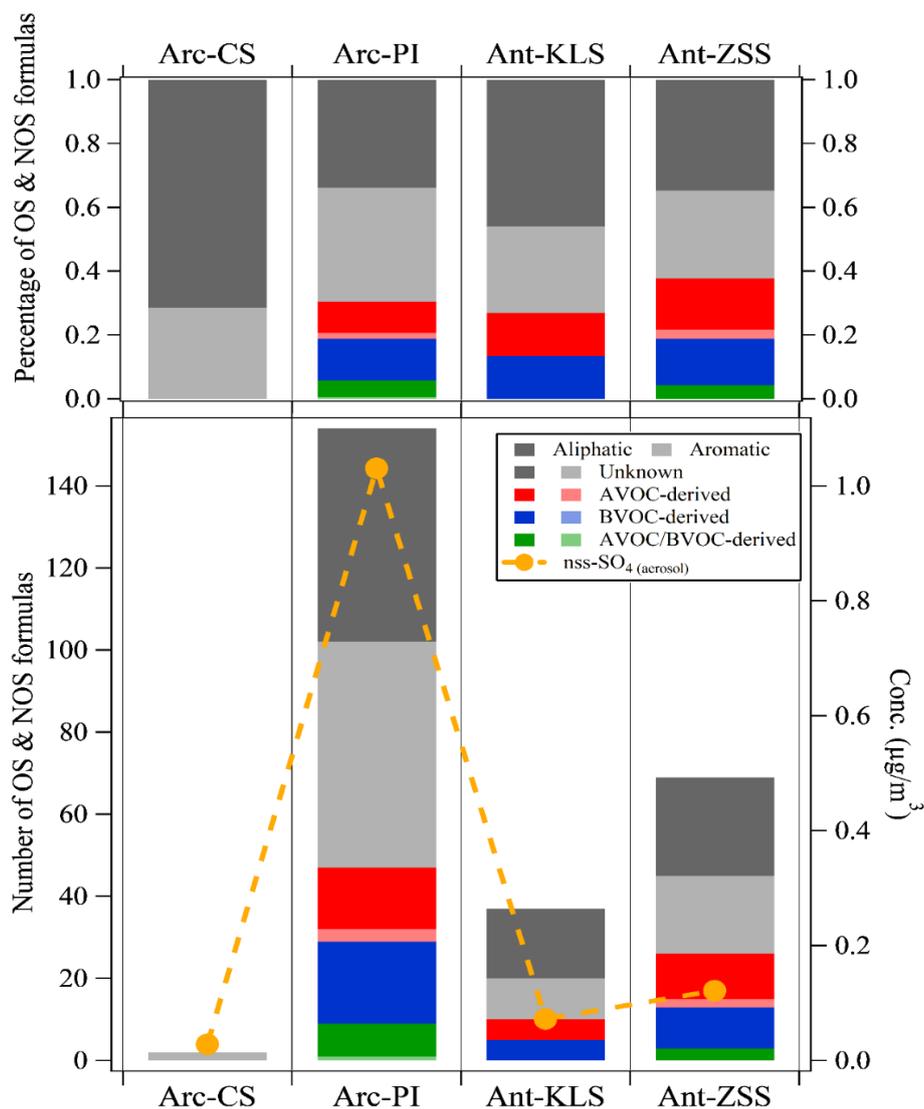


Figure 4. Carbon Oxidation State (OSc) plots for OSs and NOSs molecules in the six sampling sites. The color-coding indicates the X_c values calculated from Eq. (2). The gray marks represent aliphatic compounds ($X_c < 2.500$); the dark blue marks represent aromatics with a benzene core structure ($2.500 \leq X_c < 2.714$); the light blue marks represent aromatics with a naphthalene core structure ($2.714 \leq X_c < 2.800$); the orange marks represent aromatics with a anthracene core structure ($2.800 \leq X_c < 2.833$); the red marks represent aromatics with a pyrene core structure ($2.833 \leq X_c < 2.923$).

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5 **Figure 5.** The potential precursor distributions of detected OSs and NOSs in Arctic Center Sea, Arctic Pack Ice, Antarctic Kunlun Station and Antarctic Zhongshan Station sampling sites. The dark color and light color indicate aliphatics and aromatics, relatively. The red, blue, green and grey color represent OSs derived from anthropogenic VOCs, biogenic VOCs, both of the two kinds of VOCs and unidentified precursors. The orange circle indicates the concentrations of nss-SO₄ aerosols in the four polar sampling sites.