Molecular characteristics of organosulfates in the Arctic and Antarctic atmospheric aerosols

Yuqing Ye1, Zhouqing Xie1,2\*, Ming Zhu3, Pengzhen He4,1, Xinming Wang3

1Institute 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, Anhui, 230026, China.

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

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

4School Environment and Tourism, West Anhui University, Lu’an, Anhui, 237012, China.

*Correspondence to*: Zhouqing Xie ([zqxie@ustc.edu.cn](mailto:zqxie@ustc.edu.cn))

**Abstract.** Organosulfates (OSs) are important secondary organic aerosols (SOAs) that have been newly-identified in recent years. Due to their amphipathy and light absorptions, OSs have potential impact on the climate. Moreover, OSs can serve as molecular tracers for precursors and multiple processes leading to SOA. Therefore OSs have been investigated in many areas in the global. However, studies on OSs are rarely reported in the polar region so far, which limits our understanding of their formation pathways and influences in polar environment. Here we present the first overall observation of OSs and other organic compounds in the polar regions covering the Arctic and Antarctic. Organic compounds in aerosol samples from summer polar area during 2014/2015 Chinese National Arctic/Antarctic Research Expedition (CHINARE) were analysed by ultrahigh resolution mass spectrometry coupled with negative ion mode electrospray ionization (ESI(-)-UHRMS). OSs, nitrooxy-organosulfates (NOSs), organonitrates (ONs) and oxygenated hydrocarbons (OxyCs) were detected and tentatively determined by their formulas. Our results show that total OSs (OSs + NOSs), ONs and OxyCs accounted for 28–32%, 28–40% and 32–44% of the total detected formulas in polar areas, respectively. Large differences of the molecular characteristics were observed when aerosol samples between polar area and Guangzhou sites were compared. Total OSs featured by larger percentage of high molecular weight (HMW) formulas and higher oxidation states with wider range were found in the Arctic and Antarctic aerosol samples, which indicated the polar atmosphere is a mixture of fresh and aged organic aerosols. To better understanding the sources of total OSs in the polar regions, the relationships between total OSs and marine phytoplankton, long-range transport and local human activities were investigated. It was found that the total OSs at the Antarctic sampling sites are possibly influenced by nearby scientific stations and relevant research activities while the Arctic sampling sites were possibly influenced by long-range transport from the nearby continents. For different precursor-derived OSs, the anthropogenic precursor-derived (AP-D) OSs were detected in all the four polar sampling sites, suggesting human activities can significantly influence remote polar environment. For biogenic precursor-derived (BP-D) OSs in the polar regions, the coincidence that more BP-D OSs were tentatively identified in more acidic aerosols supports that acid-catalysed epoxy chemistry may be important for the formation of BP-D OSs in acidic atmospheric conditions. However, the precursors of a large number of OSs cannot be identified so far, which comprised more than 70% of total assigned OSs at each site. These un-identified OSs emphasized additional laboratory studies should be carried out in order to further investigate the formation mechanism of OSs and their potential contributions to OSs in the polar atmosphere.

# 1 Introduction

Atmospheric aerosols play a key role in climate system due to their importance in radiative forcing and cloud condensation nuclei (CCN) (Brimblecombe, 1996; Seinfeld et al., 1998; Jacobson et al., 2000). Exposure to high concentrations of aerosol particles can cause respiratory and cardiovascular disease, which contributes to morbidity and mortality rates (Elder and Oberdörster, 2006; Pope Iii et al., 2002; Hallquist et al., 2009). Organic aerosols (OAs) accounts for 20–90% of the submicron atmospheric particulate matter (Kroll and Seinfeld, 2008; Hallquist et al., 2009; Jimenez et al., 2009). However, 70–90% of OAs have not been identified due to the complexity of organic compounds (Hoffmann et al., 2011). The secondary organic aerosols (SOAs), which are formed from gas to particle conversion, are ubiquitous in the atmosphere. Prior studies have shown that biogenic volatile organic compounds (BVOCs) such as isoprene, α-pinene, monoterpene and sesquiterpene are important precursors of SOAs, they can lead to the formation of SOAs through photo-oxidation, heterogeneous and multiphase processes (Ravishankara, 1997; Goldstein and Galbally, 2007; Kroll and Seinfeld, 2008; Jimenez et al., 2009). Therefore the BVOCs-derived SOAs can be used as tracers(Kawamura et al., 1996; Fu et al., 2009; Fu et al., 2013; Hu et al., 2013b).

Organosulfates (OSs) are important SOAs that have been newly identified in recent years. They contribute ~4–30% to submicron OAs in the ambient environment, such as the Arctic, marine, forest, rural and 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; Glasius et al., 2018). As OS molecules contain both hydrophilic and hydrophobic functional groups and have light absorptions, they have potential impact on climate by affecting the hygroscopicity and optical properties of aerosols (Pang et al., 2006) and light absorptions (Song et al., 2013; Jacobson, 1999; Lu et al., 2011; Laskin et al., 2015). Since OSs are formed from the oxidation and reaction of precursors with sulfur-containing nucleophiles such as SO2/SO3 gas, dimethyl sulfide, sulfate acids and SO3/SO4 radicals, OSs can be used as tracers of SOAs formation (Zhang and Worton, 2012; Nozière et al., 2010; Nozière et al., 2015; Hettiyadura et al., 2018).

Previous studies have shown that BVOCs play an important role in the formation of 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 show that anthropogenic VOCs (AVOCs) such as alkanes, polycyclic aromatic hydrocarbons (PAHs), unsaturated fatty acids and diesel fuel may also be OS precursors as a large number of unidentified OSs with aliphatic or aromatic carbon skeletons cannot be explained by BVOCs. This suggests the influence of human 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).

The polar environment is known to be sensitive to the perturbation of radiative budget. The Arctic area is warming at a rate twice of the global average, with the atmospheric temperature increasing by 2–3℃ in the past decades (ACIA, 2004; IPCC, 2013; Bromwich et al., 2012; Cohen et al., 2012). Atmospheric aerosols are pivotal factors in changing the polar radiative balance. Since the Arctic haze was observed for the first time in 1956 (Mitchell, 1957), concerns about polar aerosols and the influence of human activities have increased. The polar aerosols primarily consist of sulfate and organic aerosols (Minikin et al., 1998; Mazzera et al., 2001; Mishra et al., 2004; Quinn et al., 2007; Tunved et al., 2013; Nguyen et al., 2016). By using Fourier transform infrared spectroscopy (FTIR), Frossard et al. (2011) analysed the composition of Arctic aerosols during a haze period and detected organic sulfate functional groups in their samples. Hansen et al. (2014) examined the species of SOAs using high performance liquid chromatography (HPLC) with a quadrupole Time-of-Flight mass spectrometer and found 12 kinds of OSs and one kind of nitrooxy-organosulfate (NOS) in the Arctic aerosols. Moreover, they contributed 7‒20% to the total organic aerosols. However, the investigation of OS aerosols in the Arctic is still rare. And so far, there is no observation of OSs in the Antarctic aerosols has been reported.

This study presents the molecular characteristics of organosulfates (OSs), nitrooxy organosulfates (NOSs), organonitrates (ONs) and certain oxygenated hydrocarbons (OxyCs) found in the Arctic and Antarctic aerosol samples during the 6th Chinese National Arctic Research Expedition (CHINARE) in 2014 and the 31st Chinese National Antarctic Research Expedition (CHINARE) in 2014‒2015. The difference of molecular levels, oxidation state and aromaticity of OSs among aerosol samples in the Arctic, Antarctic and Guangzhou sites were present. The potential precursors and influencing factors of OSs formation in the polar region were discussed.

# 2 Experimental methods

### 2.1 Sample collection

For the Arctic samples, total suspended particles (TSP) were collected along the cruise of 6th CHINARE from the East China Sea (35°N, 130°E) to the Arctic Ocean (81°N, 157°W) from July to September 2014. Along the cruise, two identical high-volume air samplers were installed on the top front deck of the icebreaker *Xuelong* to collect TPS for 24h for each sample, with a sampling flow rate of 1.05 m3 min-1. The filters used to collect TSP were quartz fibre filters (QFFs, Whatman QM-A, 20.3×25.4 cm, UK). Since the air samplers were installed at the top front deck while the exhaust pipe was located in the rear of *Xuelong*, at a distance of more than 100 m from the sampler, aerosol sample is usually unaffected by the ship emission when the icebreaker navigate at normal speed (> 5 m s-1)*.* However, when the icebreaker stops or navigates slowly, the collected aerosol sample may be contaminated by ship emissions.

TSP samples collected at the Arctic pack ice zone (68.45–75.50 °N, 165.10–169.09 °W) on September 7‒8 and the central Arctic Ocean area (81.00–81.09 °N, 157.02–157.67 °W) on August 19‒21 were used for further analysis. The Arctic pack ice zone is located in the Chukchi Sea, where nutrient is relatively rich, especially in summertime when the sea ice retreats (Connell et al., 2018; Arrigo et al., 2012). This area is also massively influenced by the air mass from nearby continents. The central Arctic Ocean site was a temporary ice station surrounded by dense sea ice. This site is the most northerly latitude reached by the 6th CHINARE in 2014, where the icebreaker *Xuelong* was anchored for 7 days. It should be noted that a constraint, that’s CO≤150 ppb, was applied in choosing aerosol samples from the Arctic sites to eliminate the possible contamination from the icebreaker itself (Stehr et al., 2002; Lohmann et al., 2004; Großmann et al., 2013; Sommariva and von Glasow, 2012; Hu et al., 2016). The average concentrations of CO in the central Arctic Ocean site and Arctic pack ice site were 93.74 ppb and 107.66 ppb, with the maximum concentrations being 118.49 ppb and 124.28 ppb, respectively (Fig. S1). In addition, no visible black carbon was found on our selected TSP filters. Therefore, the potential contamination from *Xuelong* emissions is expected to be minor for the selected samples. However, to be not speculative, we cannot completely rule out the possible contribution from ship emissions to OSs for the Arctic samples (Lohmann et al., 2004).

For the Antarctic samples, TSP were collected at Zhongshan Station (70.13°S, 76.58°E) and Kunlun Station (80.42°S, 77.12°E) from January to February 2015. Medium-volume air samplers were installed at these two stations to collect TSP samples through 82 mm QFFs. Each sampling lasted for 12–24 h. The Zhongshan and Kunlun Stations are both Chinese Antarctic scientific research stations. Zhongshan Station is located on the coastal southeast of Prydz Bay, affected by the air mass from both marine and inland ice sheet. The area around Zhongshan Station is strongly influenced by human activities. This station is equipped with dozens of buildings and vehicles, consuming 200 tons of diesel fuel each year for power generation, heating, water production, and equipment operation. An Adélie penguin colony is located ~1 km to the station and the emission of their droppings is a potential source of atmospheric sulfur (Xie et al., 2002). Kunlun Station is about 7.3 km southwest of Dome A (4087 m above sea level), which is the highest research station in Antarctica. The atmospheric condition is relatively stable in Dome A. For such a remote site, a key factor that influences the summer atmosphere is anthropogenic emissions due to research activities. Samples collected during January 12 and 15‒17, 2015 at Kunlun Station and during February 5‒6, 2015 at Zhongshan Staion were used for further analysis.

For samples in Guangzhou, PM2.5 QFF sample were collected for 24 h by a high-volume air sampler in an urban site (Environment Monitoring Station, 23.13°N, 113.27°E) and a rural site (Wangqinsha, 22.42°N, 113.32°E), with a constant ﬂow rate of 1.1 m3 min-1. The PM2.5 filter samples sampled on December 3, 2013 for both the urban and rural Guangzhou site were used for further analysis.

Before sampling, all the QFFs wrapped with aluminium foil were prebaked at 450 ℃ for 4 h to remove potential organic residuals from the filters and aluminium foils. After sampling, QFFs were wrapped back in aluminium foil, zipped in plastic bags and stored in freezers at –20 ℃ before further analysis.

## 2.2 Sample analysis

### 2.2.1 ESI-UHRMS analysis

Considering the concentrations of atmospheric aerosols are generally low in the Arctic and Antarctic, four filter samples for each sampling area in the polar regions were combined for pre-processing and analysis. ~25 cm2 of each filter 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 equipped with a 0.25 μm PTFE membrane to remove insoluble materials. The extraction and filtration steps were performed twice and the extract was acidified to pH=2 using hydrochloric acid and then loaded on a solid-phase extraction (SPE) cartridge (Sigma-Aldrich, USA) followed by eluting using 3 mL mixture of methanol containing 2% aqueous ammonia (*w:w*) (Lin et al., 2012a; Lin et al., 2012b). The elute was then evaporated to dryness under a gentle N2 steam and immediately re-dissolved in 400 μL of 1:1 (*v:v)* mixture of MQ water and acetonitrile. To obtain an overall picture of the molecular characteristics of OSs and NOSs in the polar atmosphere, where the relevant data is still rare so far, liquid chromatography (LC) separation was not used in this study.

Sample aliquots (70 μL) of the extracts were then injected by an auto-sampler and travelled through a steel capillary column for a few seconds. The extracts of the polar samples were analysed by 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 <2 ppm was achieved. The signals of 50–800 m/z range were recorded for data processing. The extracts from the Guangzhou samples 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 a Paracell analyzer cell in 3 kV negative ESI mode. A mass-resolving power > 450,000 at m/z 319 with absolute mass error <0.2 ppm was achieved. The signals of 150–1000 m/z range were recorded. The same procedures were applied for field blank samples.

### 2.3.2 Inorganic ion analysis

Soluble inorganic ions were analysed by an ion chromatography (Dionex DX-120, Dionex Corporation, USA). A 1-inch diameter filter was cut and rinsed with 10 mL of MQ water in an ultrasonic bath for ~40 min. After centrifuging for 10 min, the supernatant was extracted and the rest was rinsed again following the same procedure. The extracts were combined and filtered through a 0.25 μm PTFE membrane before being injected into the IC system. Cations such as Na+, K+, Mg2+, Ca2+ and NH4+ were analysed using a CS12A analytical column with a CDRS600 guard column. Anions such as SO42‒, NO3‒ and Cl‒were analysed using an AS19 analytical column with a CDRS500 guard column.

## 2.4 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. The formulas are expressed as C*c*H*h*O*o*N*n*S*s* with the constraints of 1–80 for *c*, 2–200 for *h*, 0–50 for *o*, 0–5 for *n* and 0–2 for *s*. And 0‒1 of 34S atom was allowed in the calculation of formulas. Further constraints were applied to ensure the retrieved compounds did exist in nature, that’s, H/C, O/C/, N/C, S/C and double bond equivalent to carbon number ratios (DBE) 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 even nitrogen rule were excluded. Compounds with carbon, nitrogen and sulfur numbers satisfying 4*s*+3*n* ≥ *o* were tentatively regarded as organosulfates (OSs), organonitrates (ONs) and nitrooy organosulfates (NOSs). The raw data of blank filters were processed at the same way and the formulas detected from blank filters were subtracted from sample-derived formulas, regardless of the intensity (Lin et al., 2012a; Lin et al., 2012b). For intense ions, the presence of 34S isotope peaks supports the assignment of sulfur-containing formulas (Table S1). The isotope formulas were not included in the following discussion because they shared the same elemental compositions with their corresponding 32S isotope ion peaks.

The DBE value, calculated by Eq. (1), describes the degree of molecular unsaturation.

(1)

Where *c*, *n*, *h* refers to the number of carbon, nitrogen and hydrogen, respectively. Since the two double bonds from sulfate groups were not considered in Eq.(1), the DBE values of OSs calculated here reflects the unsaturation of side carbon chain (Wang et al., 2016).

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

(2)

Where *o*, and *s* refers to the number of oxygen and sulfur atoms, respectively, and *m*, and *n* corresponds to the fraction of oxygen and sulfur involved in the π-bond structure of the compound, respectively. If DBE ≤ (*m*×*o* + *n*×*s*), then Xc = 0 is assumned. In this study, *m*=*n*=0.5 was supposed for the assigned formulas since the negative ESI mode used here is sensitive to carboxylic groups and carboxylic acids characterized by *m*=*n*=0.5. If either *o* or *n* is an odd number, (*m*×*o* + *n*×*s*) is rounded down to the next lower integer. A value of Xc ≥ 2.5000 was supposed as the unambiguous minimum criteria for the presence of an aromatic structure. Xc ≥ 2.7143, 2.8000, 2.8333, 2.9231 were considered as the thresholds for molecules containing cores of naphthalene, anthracene, pyrene and ovalene, respectively.

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

(3)

Where OSi is the oxidation state of element i, and / is the molar ratio of element i to carbon. For organic formulas expressed as C*c*H*h*O*o*N*n*S*s* in this study, where the oxidation state of H, O, N and S is set as +1, ‒2, +5 and +6, respectively, Eq. (3) can be simplified to Eq. (4)

(4)

In which and are the elemental ratios of oxygen-to-carbon and hydrogen-to-carbon, and and are the elemental ratios of nitrogen-to-carbon and sulfur-to-carbon. Eq. (4) was applied in calculating oxidation states of tentatively assigned formulas (C*c*H*h*O*o*N*n*S*s*) on the premise that all assigned nitrogen-containing and sulfur-containing functional groups are regarded as nitrate and sulfate.

## 2.5 Back-trajectory calculations

Air mass back-trajectories for the polar samples were computed using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model from the NOAA Air Resources Laboratory (Draxler and Rolph, 2003). 5 day back-trajectories were run with an interval of 6 h at altitude of 100, 500 and 1000 m above ground level.

## 2.6 Chlorophyll-a measurement

Along the cruise of 6th CHINARE in 2014 and 31st CHINARE in 2014/2015, continuous chlorophyll-a (chl-a) concentrations in sea surface was measured automatically onboard *Xuelong* by a fluorometer from WETStar and Turner Trilogy, respectively. For aerosols sampled at the Arctic pack ice zone, the central Arctic Ocean site and at the Antarctic Zhongshan Station, the measured chl-a in sea surface during the sampling period were used. The measured chl-a was not used for aerosols sampled at the Antarctic Kunlun Station due to that this station is an inland station far from the ocean.

## 2.7 Aerosol pH calculation

The ISORROPIA II model, which is a thermodynamic equilibrium model for the K+–Ca2+–Mg2+–NH4+–Na+–SO42––NO3––Cl––H2O system, was used to predict the pH of the polar aerosol samples (Fountoukis and Nenes, 2007). The model was set up in the forward mode with a metastable state. The concentrations of inorganic ions, relative humidity (RH) and temperature were used as input for the model (Table S2). It should be noted that organic compounds such as OSs is not included in the ISORROPIA II model. The organic aerosols are complex and our understanding of their acidity and hygroscopicity is limited so far. Even though organic compounds may contribute to aerosol pH, their effect is out of our topic. Hence, we do not discuss the influence of organic compounds on the calculated aerosol pH in the present study.

# 3 Results and discussion

## 3.1 General characteristics

In total, there are 25, 487, 124 and 247 kinds of organic formulas tentatively assigned in aerosols from the central Arctic Ocean area (Arc-CO), Arctic pack ice zone (Arc-PI), Antarctic Kunlun Station (Ant-KLS) and Antarctic Zhongshan Station (Ant-ZSS). While the number of total formulas is 2270 and 1918 for urban and rural Guangzhou (GZ-urban and GZ-rural), respectively, which is dozens even hundreds times of that in the polar areas. The Arc-CO, which is the most northerly latitude (81.07°N) reached by the 6th CHINARE in 2014, have the fewest number of formulas, only ~1% of the number of formulas found in Guangzhou aerosols. The detected formulas were classified into four groups by their elemental compositions, that’s, oxygenated hydrocarbons (C*c*H*h*O*o*), organosulfates (C*c*H*h*O*o*S*s*), organonitrates (C*c*H*h*O*o*N*n*) and nitrooxy-organosulfates (C*c*H*h*O*o*N*n*S*s*), abbreviated as OxyCs, OSs, ONs, and NOSs, respectively.

Table 1 and Fig. 1 summarizes molecular characteristics of assigned formulas obtained from aerosols in each sampling site. Among samples from the polar regions, total OSs (OSs + NOSs), ONs and OxyCs accounts for 28–32%, 28‒40% and 32‒44% of the organic formulas. While the fractions of total OSs, ONs and OxyCs were 21–25%, 45–47% and 29–34% in Guangzhou sites, respectively. It’s shown that although much more formulas of OSs and NOSs were detected in samples from Guangzhou, the fraction of OSs and NOSs in Guangzhou was smaller than that in polar regions (~20% *vs* ~30%). However, the fraction of ONs in Guangzhou is larger than that in the polar regions. This may be due to relatively high NOX concentrations and night-time oxidation of NO3 in winter Guangzhou. NOX concentrations in near-surface atmosphere of Guangzhou is up to ~120 μg m-3 due to vehicle exhaust emissions and fossil fuel combustions (Shao et al., 2009), far more than NOx concentrations of ~2 μg m-3 in near-surface in the polar regions (Honrath and Jaffe, 1990; Stroud et al., 2003). In addition, since the Arctic and Antarctic samples were collected during the summertime with polar days, nocturnal oxidation of NO3 was not likely to be important. In the polar regions, samples in higher-latitude sites (i.e. Arc-CO and Ant-KLS) had fewer numbers of assigned formulas than the lower-latitude sites (i.e. Arc-PI and Ant-ZSS). One possible reason for this phenomena is that pollutants from nearby continents have been transported to the Arc-PI and pollutants from local research activities have influenced Ant-ZSS, as shown by the backward trajectories in Fig. S2 and discussed in subsection 3.3.

Fig. 2 shows the differences in molecular weight (MW) distributions of OSs, ONs, NOSs and OxyCs detected in the six sampling sites. Assigned formulas of polar aerosols displayed more dispersive MW ranges with higher fraction of high molecular weight (HMW) compounds, while MW ranges of Guangzhou samples were centred in 300–400 Da. In terms of OSs, only a small number of OSs were detected in the most remote Arc-CO and Ant-KLS, ranging from 200‒500 Da. MWs of OSs at Arc-PI and Ant-ZSS covered a range of 100‒700 Da, with nearly 40% of OSs having MWs larger than 400 Da. Especially at Ant-ZSS, more than 20% of OSs had MWs of 600‒700 Da. In Guangzhou, only less than 5% of OSs had MWs larger than 700 Da, however, OSs with MWs less than 400 Da occupied 60‒80% of OSs. MWs of ONs, NOSs and OxyCs presented similar distributions in the polar regions: about 80% of ONs, NOSs and OxyCs in the polar samples ranged from 200 Da to 500 Da and about 20% ranged from 400 Da to 800 Da. While the majority of organic compounds of Guangzhou was in 100‒400 Da. The discrepancy in MW distributions between polar sites and Guangzhou sites indicated that the role of transport and formation mechanisms may be different at different regions.

## 3.2 Comparison of aromaticity and oxidation state

Xc ≥ 2.5 was used for confirming aromatic structure in this study (Wang et al., 2017a). Aromatic compounds were found to account for 56%, 48%, 49%, 41%, 46% and 53% of total formulas at Arc-CO, Arc-PI, Ant-KLS, Ant-ZSS, GZ-urban and GZ-rural, respectively (Table 1). Fig. 3 shows the fractions of aliphatic and aromatic formulas for OSs, ONs, NOSs and OxyCs at each sampling site. 7% of total OSs (OSs + NOSs) were aromatic with a DBE average of 2.2 in the Guangzhou sites, suggesting OSs and NOSs were mostly aliphatic ones, which is consistent with previous studies in urban area (Stone et al., 2012; Ma et al., 2014; Kuang et al., 2016; Wang et al., 2016; Wang et al., 2017a). In the sampling sites of polar regions, aromatic OSs and NOSs had higher proportions than those in Guangzhou sites, comprising 29%, 38%, 27% and 30% of total total OSs (OSs + NOSs) at the Arc-CO, Arc-PI, Ant-KLS and Ant-ZSS, respectively. Previous studies has identified some aromatic OSs with benzyl and polycyclic aromatic carbon backbone, i.e., C6H6SO4, C7H8SO4, C8H10SO4, C9H12SO4 and several OSs from photo-oxidation of naphthalene (NAP) and 2-methylnaphthalene (2-MeNAP) in urban fine aerosols (Kundu et al., 2013; Staudt et al., 2014; Riva et al., 2015). Although only C7H8SO4 and C9H12SO4 were detected in Ant-ZSS, the relatively high fractions of aromatic OSs and NOSs in the polar aerosols possibly suggest these SOAs had anthropogenic precursors. For aromatic ONs and OxyCs, they accounted for 23‒38% and 55‒88% of total tentatively assigned ONs and OxyCs, respectively, at all the six sampling sites (Fig. 3a&b).

Van Krevelen (VK) diagrams are usually used to describe the compositional characteristics of complex organic mixtures, providing the overall oxidation and unsaturation conditions (Kim et al., 2003; Wu et al., 2004). The *h/c* ratio is plotted versus its (*o*-2*n*-3*s*)/*c* ratio for total OSs (Fig. 4), (*o*-2*n*)/c for ONs(Fig. S3) and *o*/*c* ratio for OxyCs (Fig. S4). It should be noted that due to nitrate and sulfate groups containing more oxygen atoms than common oxygen-containing functional groups, (*o*-2*n*-3*s*)/*c* and (*o*-2*n*)/c was used to replace *o*/*c* to calculate the number of oxygen-containing functional groups of per carbon atom, which is also adopted by Lin et al. (2012b) and Wang et al. (2016). The oxidation state of carbon (OSc) as a function of carbon number (OSC‒nC) can be used to analyse the oxidation state of organic mixture and reflect possible atmospheric reactions. Fig. 5, Fig. S5 and Fig. S6 present the OSC‒nC diagrams of total OSs, ONs, and OxyCs, respectively. Tentatively assigned OSs and NOSs in polar samples distributed dispersedly in the range of 0‒1.2 for (*o*-2*n*-3*s*)/*c* and (–2)–(+2) for OSC, with about 40% OSs and NOSs having high OSC values (0‒(+2)). While OSs and NOSs in Guangzhou samples mainly centralized in 0‒0.5 for (*o*-2*n*-3*s*)/*c* and (–2)–0 for OSC (Fig. 4 & 5). Hence, OSs and NOSs in polar samples were featured by wider ranges and higher values of oxidation state indexes (i.e. (*o*-2*n*-3*s*)/*c* and OSC) compared to those in Guangzhou samples. For oxidation conditions of ONs and OxyCs, they showed similar features with OSs and NOSs (Fig. S3‒S6). The higher oxidation state indicated that there were a large number of aged organic compounds in the polar atmosphere. High oxidation states of polar OSs could result from further oxidation by enhanced photo-oxidation in polar summer or from other oxidants (Mochida et al., 2002; Hawkins et al., 2010; Russell et al., 2010). Meanwhile, the wider range of oxidation state suggested aerosols in polar atmosphere is mixed by newly formed aerosols and highly oxidized (aged) aerosols.

## 3.3 Potential precursors and atmospheric implications

Biogenic VOCs (BVOCs), such as isoprene, monoterpene, sesquiterpene, and other tree or green leaf volatiles are important precursors of OSs according to previous laboratory and field studies (Surratt et al., 2008; Iinuma et al., 2009; Barbara Nozière, 2010; Surratt et al., 2010; Chan et al., 2011; Zhang and Worton, 2012; Lin et al., 2013; Riva et al., 2016a; Shalamzari et al., 2016; Barbosa et al., 2017), More recently, anthropogenic VOCs (AVOCs) were also suggested as important precursors of OSs (Staudt et al., 2014; Tao et al., 2014; Riva et al., 2015; Riva et al., 2016c; Blair et al., 2017). In addition, some precursors of OSs, such as unsaturated fatty acids, glyoxal and glycolaldehyde, have both biogenic and anthropogenic sources (Galloway et al., 2009; Perri et al., 2010; Passananti et al., 2016; Shang et al., 2016). The published OSs whose precursors have been verified, were used as “standard” OSs to estimate potential precursors of observed OSs and NOSs in the polar atmosphere. Assigned OSs and NOSs possessing identical carbon, hydrogen, oxygen, nitrogen and sulfur atoms with the “standard” OSs were temporarily considered to have the same precursors with the “standard” OSs in the present study. By comparing their formulas, the OSs and NOSs were classified as anthropogenic precursor-derived (AP-D), biogenic precursor-derived (BP-D), anthropogenic/biogenic precursor-derived (A/BP-D) and unknown precursor-derived (UP-D) OSs (Fig. 6 and Table 2).

For the two sampling sites in the Arctic, 2 AP-D OS formulas (C9H12O8S1 and C14H20O7S1) out of 7 OSs and NOSs was observed at the Arc-CO, and 21 AP-D OSs, 3 BP-D OSs and 6 A/BP-D OSs were identified from 155 OSs and NOSs at the Arc-PI. In such remote and uninhabited ocean sites, since the effect of *in-situ* ship emissions is expected to be minor, the AP-D OS formulas were possibly transported from the nearby continents as suggested by the air mass back trajectories (Fig. S2A&B). In addition, the high concentration of non-sea-salt sulfate (nss-SO42-) aerosols associated with relatively high concentration of nitrate aerosols at Arc-PI site (Fig. 6) also support influence of human activities on Arctic aerosols. For the two sampling sites at the Antarctic stations, 4 AP-D OS formulas (C8H17O6S1, C15H19O9S1, C16H25O8S1, C25H25O8S1) out of 37 OSs and NOSs were observed in the Ant-KLS, and 17 AP-D OSs, 1 BP-D OSs and 4 A/BP-D OSs were identified from 69 OSs and NOSs at the Ant-ZSS. The Ant-KLS and Ant-ZSS are permanent scientific stations equipped with buildings and vehicles. Research activities at and around these two stations are quite a lot in summer in recent years. So the AP-D OSs deleted at the Antarctic stations, which may originate from the diesel fuel and biodiesel combustion (Blair et al., 2017), is possibly influenced by the scientific stations and relevant research activities. Moreover, 5 day air mass back trajectories in the Ant-KLS and Ant-ZSS only passed through Antarctica and ocean areas but not nearby continents (Fig. S2C&D), which supports the AP-D OSs at these Antarctic stations was from local processes. There are only 0‒4 BP-D OSs and NOSs being detected in the polar samples (Table 2), less than the number of AP-D OSs and NOSs. However, it cannot be concluded that anthropogenic emissions were more important than biogenic emissions for the polar sites. This is because a large number of OSs and NOSs is from un-identified precursors so far, which comprised more than 70% of total tentatively assigned OSs and NOSs at each polar site. These UP-D OSs and NOSs could result from biogenic sources.

Previous studies show that the presence of a homologous series OSs with hydroxyl fatty acids (C9‒C13) at remote marine atmosphere is likely associated with marine phytoplankton (Claeys et al., 2010). They put forward a plausible formation mechanism through the oxidation of hydroxyl aldehydes released by cell membrane lipids, followed by esterification with biogenic sulfuric acid. Very recently, Cui et al. (2019) observed some ONs, OSs, NOSs and OxyCs in a remote open ocean site. These tentatively identified organic compounds appeared to be associated with phytoplankton blooms and bubble-bursting processes. Recent laboratory studies confirmed a new formation pathway of OSs by heterogeneous reactions of SO2 with unsaturated fatty acids and long-chain alkenes (Passananti et al., 2016; Shang et al., 2016). Zhu et al. (2019) detected some potential unsaturated-fatty-acid-derived (USFA-D) OSs in ambient fine aerosols, which were not found in prior laboratory studies. These findings provide the possibility that marine phytoplankton contributes to OSs in polar aerosols in the blooming season. The formation processes could be either reactions of sulfuric acid aerosols with bubble-bursting precursors, or heterogeneous reactions of SO2 with precursors in sea-surface microlayer. Some aliphatic OSs were found to be likely to originate from phytoplankton and could possibly explain several un-identified OSs (Table S3). According to the proposed formation mechanisms in the above-mentioned studies, supposing low-molecular-weight (LMW) saturated OSs (DBE=0) and aliphatic OSs with four oxygen atoms (*o*=4) have a marine phytoplankton origin, they could only be explained by fragmentation of diradical intermediates, which are from a π-interaction between SO2 and the C=C bond. This is because there are no extra double bond or oxygen atom for carboxyl group or other oxygen-containing groups. There were no qualified OSs being detected at the Arc-CO. 24 and 15 OSs of total tentatively assigned OSs at the Arc-PI and the Ant-ZSS appeared to have potential phytoplankton source, respectively, which took up 22% and 27% of total OSs at the Arc-PI and the Ant-ZSS, respectively. Observed sea-surface concentrations of chl-a at Arc-CO, Arc-PI and around Ant-ZSS were used to indicate phytoplankton activities in this study (Table 2). For the Arc-CO, Arc-PI and around Ant-ZSS, sea-surface chl-a concentration was the lowest at Arc-CO, followed by Arc-PI and highest at Ant-ZSS (Table 2). The variation of percentages of potential phytoplankton-derived OSs were in coincidence of with sea-surface chl-a concentrations at these sites (Table 2), which suggested that phytoplankton activities may make an important contribution to UP-D OSs formation at the Ant-ZSS and Arc-PI.

In addition to OSs and NOSs discussed above, two subgroups of UP-D OSs and NOSs had distinctive characteristics in aromaticity and oxidation state at polar sites, as emphasized by black square 1 and red square 2 in Fig. 4 and 5, respectively. A number of OSs and NOSs plotted in black square 1 were featured by high (*o*-2*n*-3*s*)/c of 0.4‒1.1 and high OSC of 0‒(+2) with aliphatic carbon backbone and carbon number no more than 20 (c≤20), which were detected at Arc-PI, Ant-KLS and Ant-ZSS samples, but only a few in Guangzhou samples. Chamber studies reported the aliphatic OSs and NOSs with c≤20 can be formed from BVOCs or AVOCs (e.g., Surratt et al., 2008; Chan et al., 2011; Riva et al., 2016a; Riva et al., 2016b), photo-oxidation of diesel and biodiesel (Blair et al., 2017), heterogeneous reaction of unsaturated fatty acids or long-chain alkenes (Passananti et al., 2016; Shang et al., 2016). However, the aged aliphatic OSs and NOSs were unique in the polar region in this study. These un-identified OSs and NOSs with high oxidation states were likely related with elevated photochemical activity in the polar atmosphere as mentioned above. Several polycyclic aromatic OSs and NOSs in red square 2 characterized by carbon number larger than 20 (c>20) and relatively low oxidation states (OSC of (‒1)‒1 and (*o*-2*n*-3*s*)/*c* of 0‒0.4) were present at polar sites and Guangzhou urban site, but not at Guangzhou rural site. Ding et al. (2007) observed the PAHs in the Arctic atmosphere during 2nd CHINARE between July to September 2003 and suggested that biomass or coal burning might be their major sources over the Arctic Ocean in summer. Previous studies revealed the influence of biomass burning from nearby continents or local stations on the polar regions during summertime, which is the peak burning period (van der Werf et al., 2006; Chaubey et al., 2010; Hu et al., 2013a). Significant concentrations of OSs were observed in spring Arctic haze at Greenland and Barents Sea, which were originated from transport emissions of coal burning and VOCs in north-eastern Europe (Frossard et al., 2011). In this study, back trajectories indicates that the air mass were originated from Siberia and Alaska at the Arc-PI, local stations at the Ant-KLS, and local stations or marine at the Ant-ZSS (Fig. S1B, C & D). Hence, it remains possible that the polycyclic aromatic OSs and NOSs at these sampling areas were associated with coal burning or biomass burning from nearby continents or local research activities.

## 3.4 Influencing factors of OS and NOS formation

Prior studies have investigated the effect of aerosol acidity on the formation of OSs (Iinuma et al., 2007; Surratt et al., 2007; Chan et al., 2011; Riva et al., 2016c). It’s shown that acidic 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 BP-D OSs and NOSs. 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 Arc-CO and Ant-KLS, atmospheric aerosols were neutral/slightly alkaline (pH = 7.7 and 7.8), while aerosols from Arc-PI and Ant-ZSS were slightly acidic (pH = 3.8 and 4.8). Correspondingly, no BP-D OSs or NOSs were tentatively identified at neutral Arc-CO and Ant-KLS, while 3 and 1 BP-D total OSs were identified at acidic Arc-PI and Ant-ZSS (Table 2). The coincidence that more BP-D OSs were tentatively identified in more acidic aerosols supports that acid-catalysed epoxy chemistry may be important for the formation of BP-D OSs in acidic atmospheric conditions.

Relative Humidity RH is another factor influencing OS formations (Li and Jang, 2013; Riva et al., 2015; Riva et al., 2016b; Barbosa et al., 2017; Kwong et al., 2018). High RH conditions inhibit OS formation in an acid-catalysed epoxy system. This is likely due to that high water content in high RH conditions will lead to the decrease of aerosol acidity (Riva et al., 2015; Riva et al., 2016a; Riva et al., 2016b). Meanwhile, some studies found that high RH values increase OS yields at neutral pH (Barbosa, 2017, J. Li, 2013). In our study, the Arctic sites are more moist than the Antarctic sites (RH=90% *vs* RH=50–65%). Between the Arc-CO and Ant-KLS with similar pH conditions (pH=7.7 vs pH=7.8), more OS constituents were detected at the Ant-KLS where RH was lower. This is inconsistent with previous observations that high RH values increase OS yields at neutral pH (Barbosa, 2017, J. Li, 2013). Considering the emissions of local anthropogenic precursors from research work and domestic pollution may be higher at Ant-KLS than Arc-CO site, the higher RH at Arc-CO may not match with the possible higher precursors at Ant-KLS. Moreover, both the atmosphere are under humid conditions at these two sites, so deliquescence may not happen for most aerosols. Therefore, OSs formation during our sampling period at the polar sites may be hardly influenced by RH variations.

# 4 Conclusions

Atmospheric particulate matter collected during 6th Chinese National Arctic Research Expedition in 2014 and the 31st Chinese National Antarctic Research Expedition in 2014‒2015 were analysed by ultra-high-resolution mass spectrometry with negative ESI mode. 25–487 different kinds of organic compounds were identified in the polar sites and about 2000 organic compounds were identified in Guangzhou sites for comparison. Four groups of tentatively assigned compounds (OSs, ONs, NOSs and OxyCs) were observed in the sampling areas and they exhibited different molecular characteristics among each site. Total OSs (OSs + NOSs), ONs and OxyCs accounted for 28–32%, 28–40% and 32–44% of the total detected molecules in polar areas, respectively. Comparing to Guangzhou sites, total OSs were featured by larger percentage of high molecular weight (HMW) formulas and higher oxidation states with wider range at polar regions, which indicated the polar atmosphere is a mixture of fresh and aged organic aerosols.

To investigate the formations of OSs and NOSs at polar areas, OSs and NOSs were classified according to their potential precursors, that’s, anthropogenic precursor-derived (AP-D), biogenic precursor-derived (BP-D), anthropogenic/biogenic precursor-derived (A/BP-D) and unknown precursor-derived (UP-D). The AP-D OSs were detected in all the four polar sampling sites, suggesting human activities can significantly influence remote polar environment. Coincidentally, more BP-D OSs were tentatively identified in more acidic aerosols, supports that acid-catalysed epoxy chemistry may be important for the formation of BP-D OSs in acidic atmospheric conditions. However, more than 70% of total assigned OSs at each site cannot be identified by their precursors so far. In these UP-D OSs, 24 and 15 OSs at the Arc-PI and the Ant-ZSS appeared to have potential phytoplankton source, respectively, which accounts for 22% and 27% of total OSs at the Arc-PI and the Ant-ZSS, respectively. In addition, two specific subgroups of UP-D OSs and NOSs were observed, one were aliphatic OSs and NOSs featured with *c*≤20 and high oxidation states in polar sties, and the other one were polycyclic OSs and NOSs featured with *c*>20 and relatively low oxidation states in polar sites and Guangzhou urban site. These aliphatic UP-D OSs and NOSs with high oxidation states were likely related with elevated photochemical activity in the polar atmosphere while the polycyclic aromatic OSs and NOSs with relatively low oxidation states were possibly associated with coal burning, biomass burning from nearby continents or local human activities.

*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).

*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.W interpreted the data. P.Z.H. sampled TSP during 6th CHINARE in 2014. Y.Q.Y. wrote the manuscript with input from Z.Q.X. and P.Z.H.

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

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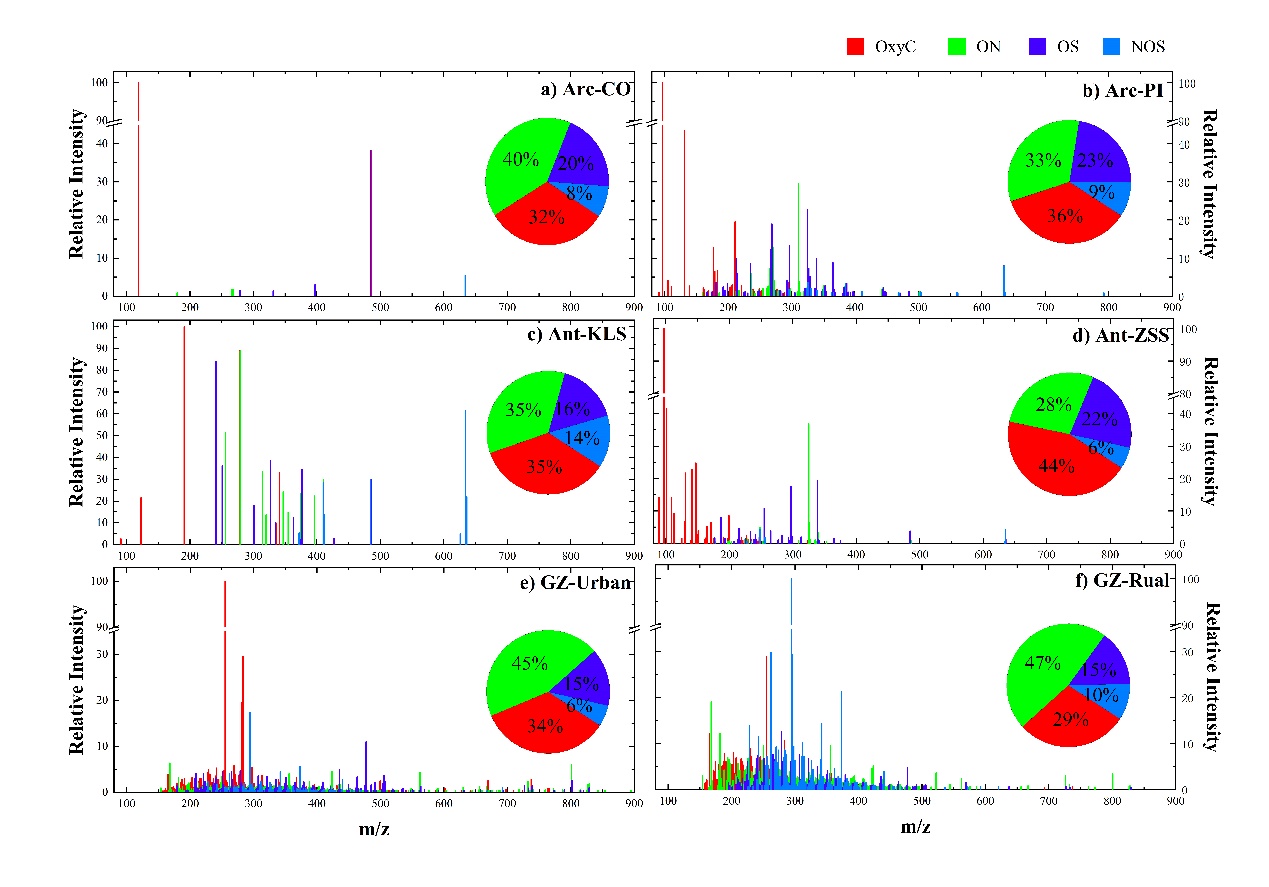
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**Table 1 Summary of molecular characteristics of assigned formulas obtained from the aerosol sampling sites.**

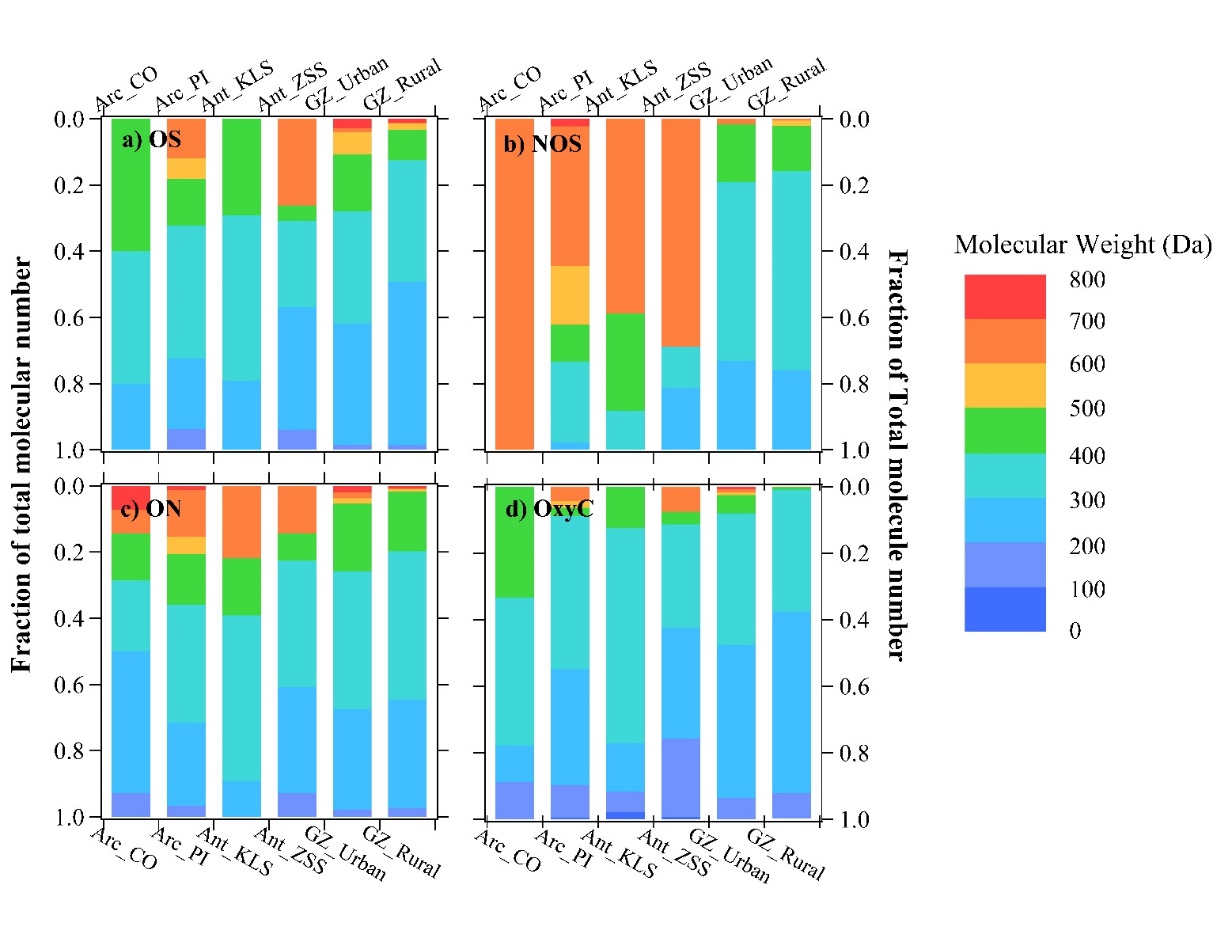
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| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Location** | | **No. of Formulas** | | | | | **C#**  **Range** | **DBE**  **Mean** | **O/C** | **OSc** | **Mass Mean** | **No. of**  **Aliphatic** | **No. of**  **Aromatic** |
| **Total** | **Oxyc** | **ON** | **OS** | **NOS** |
| **Arctic** | **central sea**  (81.00–81.09°N, 157.02–157.67 °W) | 25 | 8  (32%) | 10  (40%) | 5  (20%) | 2  (8%) | 5–35 | 10.9 | 0.45 | –0.33 | 393.05 ± 137.36 | 11 (44%) | 14 (56%) |
| **pack ice**  (68.45–75.50°N, 165.10–169.09 °W) | 487 | 173  (33%) | 159  (36%) | 111  (23%) | 44  (9%) | 3–48 | 7.4 | 0.39 | –0.53 | 340.69 ± 139.01 | 253 (52%) | 234 (48%) |
| **Antarctic** | **Kunlun station**  (80.42°S, 77.12°E) | 124 | 44  (35%) | 43  (35%) | 20  (16%) | 17  (14%) | 6–45 | 8.6 | 0.45 | –0.34 | 368.63 ± 121.96 | 63 (51%) | 61 (49%) |
| **Zhongshan station**  (70.13°S, 76.58°E) | 247 | 109  (44%) | 69  (28%) | 55  (22%) | 14  (6%) | 3–45 | 6.2 | 0.42 | –0.55 | 312.54 ± 160.32 | 145 (59%) | 102 (41%) |
| **Guangzhou** | **urban**  (23.13°N, 113.27°E) | 2270 | 738  (34%) | 1017  (45%) | 344  (15%) | 126  (6%) | 5–64 | 4.2 | 0.33 | –0.94 | 313.03 ± 107.73 | 1216 (54%) | 1054 (46%) |
| **rural**  (22.42°N, 113.32°E) | 1918 | 559  (29%) | 896  (47%) | 280  (15%) | 183  (10%) | 5–49 | 4.7 | 0.41 | –0.70 | 295.46 ± 80.31 | 910 (47%) | 1008 (53%) |

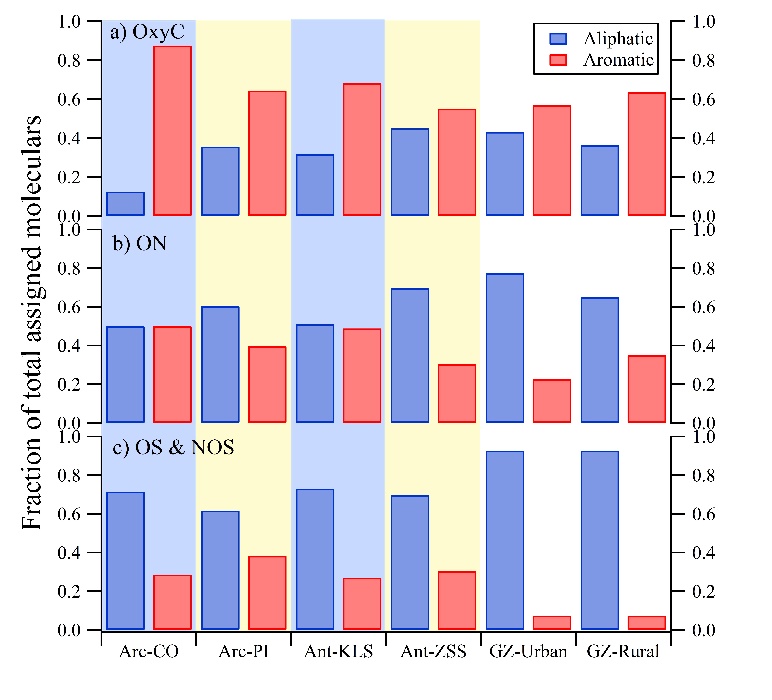
**Table 2 The potential precursors and influencing factors of OS and NOS formation.**

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Sampling Sites** | | **Total**  **OSs** | **AP-D**  **OSs** | **BP-D**  **OSs** | **A/BP-D**  **OSs** | **UP-D**  **OSs** | **nss-SO42-**  **(μg m-3)** | **NO3-**  **(μg m-3)** | **RH (%)** | **pH** | **Chl-a**  **(mg m-3)** |
| Arctic | central ocean | 7 | 2 | 0 | 0 | 5 | 0.03 | 0.02 | 90 | 7.7 | 0.071 |
| pack ice | 155 | 21 | 3 | 6 | 125 | 1.03 | 0.14 | 90 | 3.8 | 0.136 |
| Antarctic | Kunlun Station | 37 | 4 | 0 | 0 | 33 | 0.07 | 0.06 | 65 | 7.8 | No data |
| Zhongshan Station | 69 | 16 | 1 | 2 | 50 | 0.12 | 0.06 | 50 | 4.8 | 0.624 |

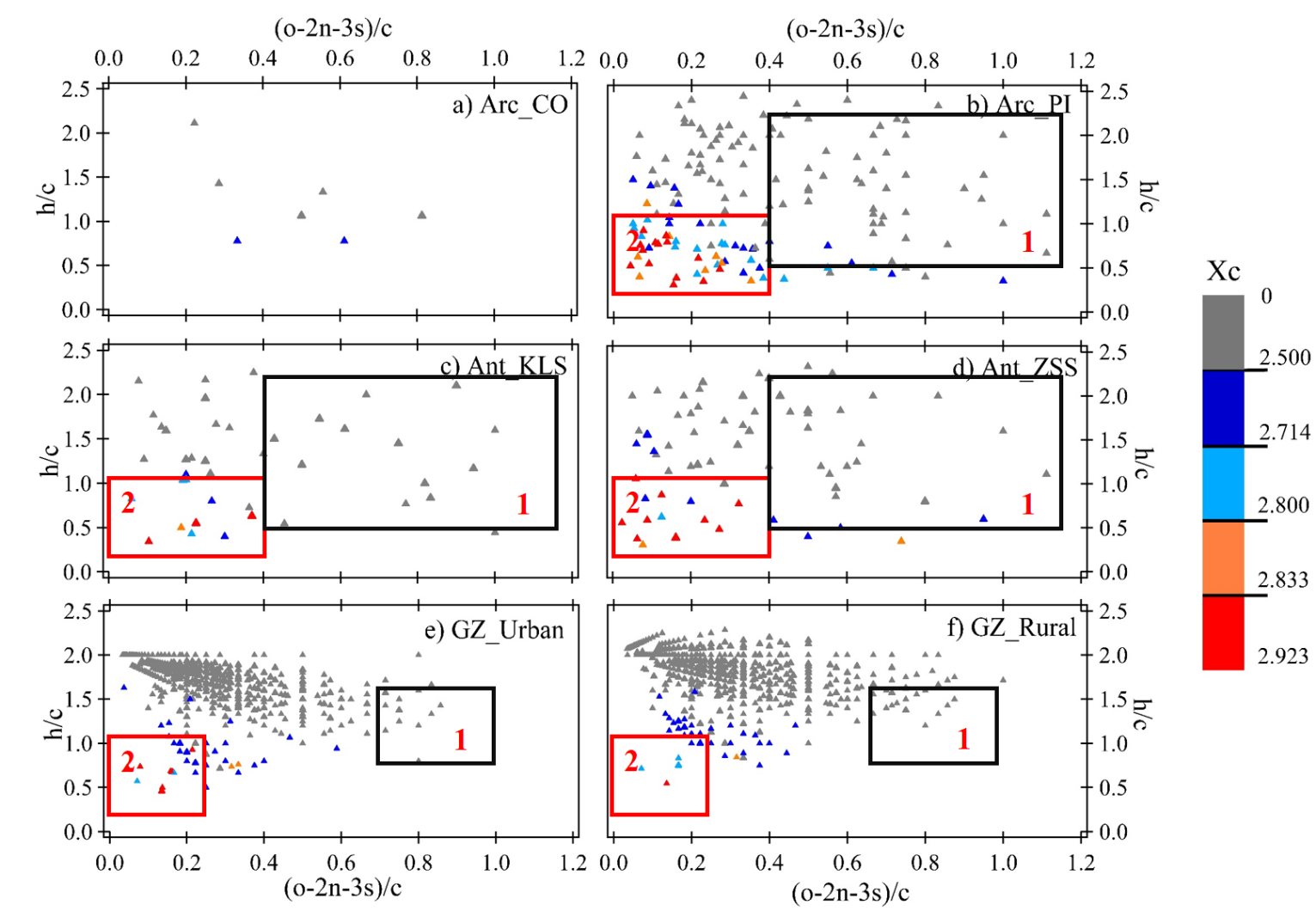


**Figure 1 Mass spectra of organic compounds (OxyC, ON, OS and NOS) reconstructed from Orbitrap MS analysis in the negative ionization mode.** X axis corresponds to the m/z of the assigned species and Y axis corresponds to the relative intensity of each molecular. It should be noted that the most intense peak (OxyC, ON, OS and NOS) was set as 100%. The pie charts showed the percentage of each subgroup in the total number of detected compounds. Arc-CO in a) is for central Arctic Ocean area, Arc-PI in b) is for Arctic pack ice zone, Ant-KLS in c) is for Antarctic Kunlun station, Ant-ZSS in d) is for Antarctic Zhongshan station, GZ-urban in e) is for urban Guangzhou site, GZ-rural in f) is for rural Guangzhou site.

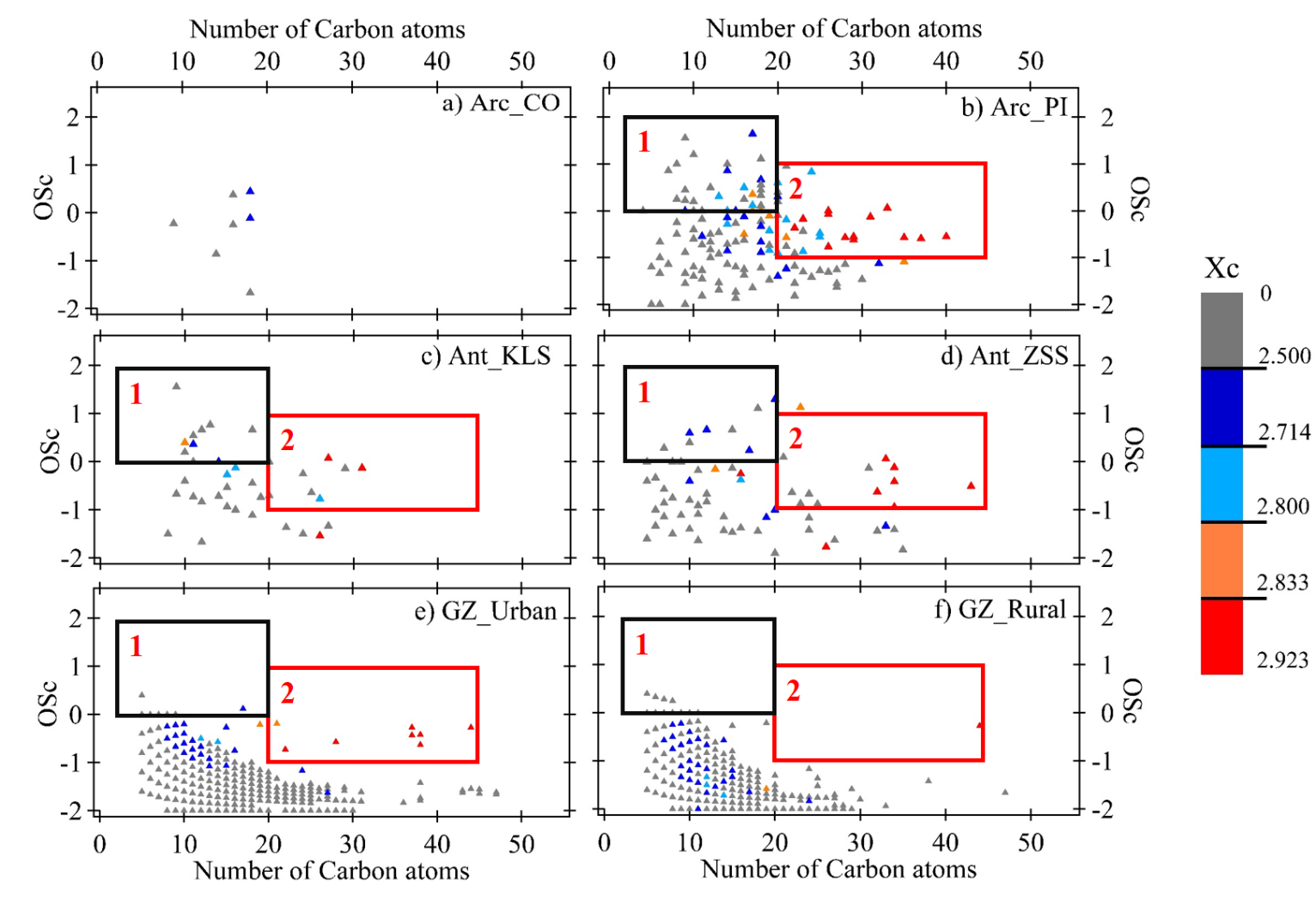
**Figure 2 The distributions of detected OS (a), NOS (b), ON (c) and OxyC (d) molecules in the six sampling sites.** The color-coding represents the molecular weights range from 0 Da to 800 Da.



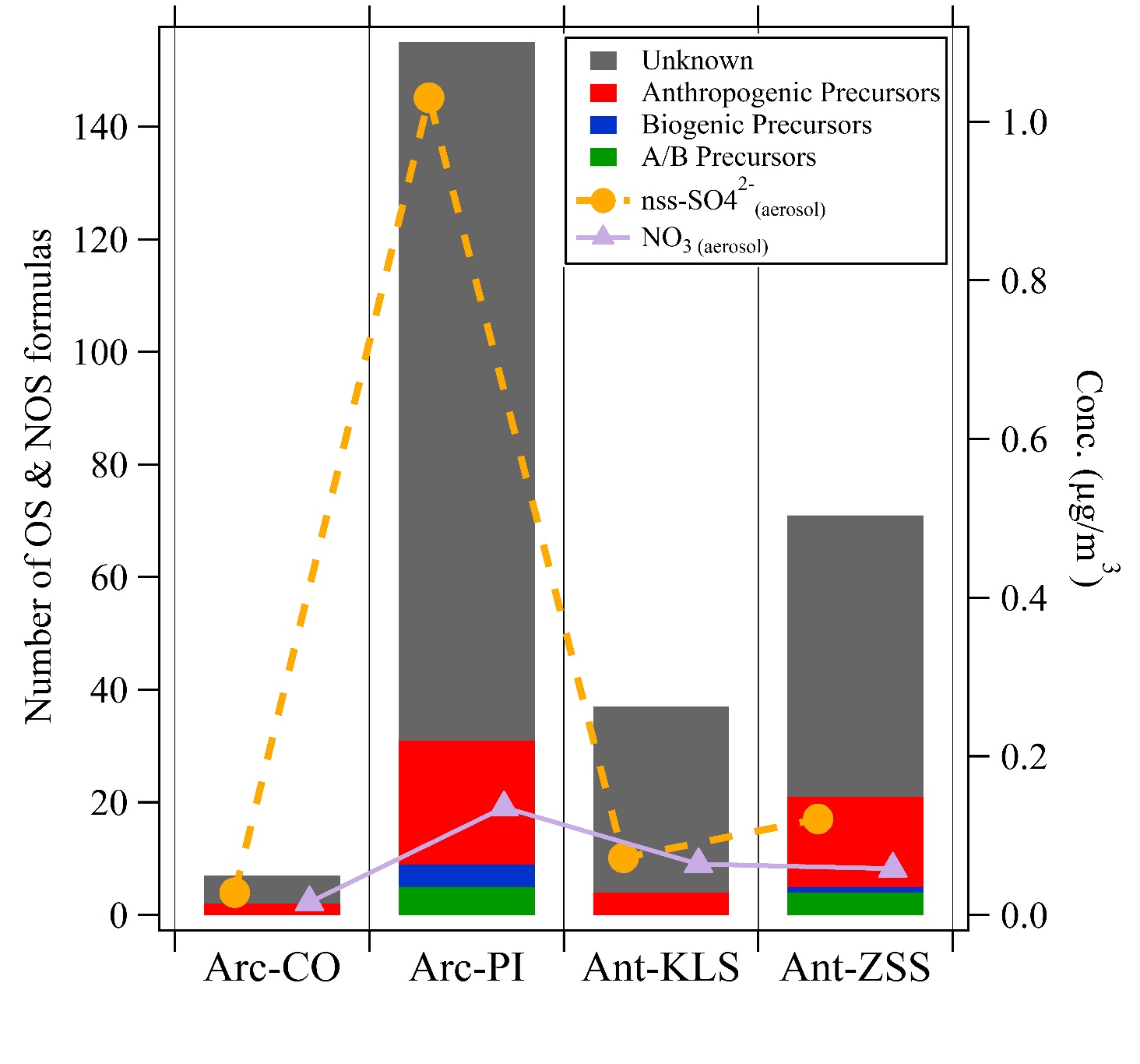
**Figure 3 The aliphatic and aromatic fraction of total molecules in OxyCs (a), ONs (b) and total OSs (OSs + NOSs, d) at the six sampling sites.**

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**Figure 4 Van Krevelen Diagrams for OSs and NOSs molecules in the six sampling sites.** The color-coding represents the Xc values calculated from Eq. (2). The gray marks represent aliphatic compounds (Xc < 2.500), the dark blue marks represent aromatics with a benzene core structure (2.500 ≤ Xc < 2.714), the light blue marks represent aromatics with a naphthalene core structure (2.714 ≤ Xc < 2.800), the orange marks represent aromatics with a anthracene core structure (2.800 ≤ Xc < 2.833), the red marks represent aromatics with a pyrene core structure (2.833 ≤ Xc < 2.923). The black square 1 were featured by high (*o*-2*n*-3*s*)/c of 0.4‒1.1 and high OSC of 0‒(+2) with aliphatic carbon backbone and carbon number no more than 20 (c≤20), The red square 2 were characterized by carbon number larger than 20 (c>20) and relatively low oxidation states (OSC of (‒1)‒1 and (*o*-2*n*-3*s*)/*c* of 0‒0.4)

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**Figure 5 Oxidation State of Carbon (OSc) for OSs and NOSs in the six sampling sites.** The color-coding represents the Xc values calculated from Eq. (2). The gray marks represent aliphatic compounds (Xc < 2.500), the dark blue marks represent aromatics with a benzene core structure (2.500 ≤ Xc < 2.714), the light blue marks represent aromatics with a naphthalene core structure (2.714 ≤ Xc < 2.800), the orange marks represent aromatics with a anthracene core structure (2.800 ≤ Xc < 2.833), the red marks represent aromatics with a pyrene core structure (2.833 ≤ Xc < 2.923).The black square 1 were featured by high (*o*-2*n*-3*s*)/c of 0.4‒1.1 and high OSC of 0‒(+2) with aliphatic carbon backbone and carbon number no more than 20 (c≤20), The red square 2 were characterized by carbon number larger than 20 (c>20) and relatively low oxidation states (OSC of (‒1)‒1 and (*o*-2*n*-3*s*)/*c* of 0‒0.4)

**Figure 6 The potential precursor distributions of detected OSs and NOSs at the polar sampling sites.** The red, blue, green and grey color respectively represent anthropogenic precursor-derived (AP-D), biogenic precursor-derived (BP-D), anthropogenic/biogenic precursor-derived (A/BP-D) and unknown precursor-derived (UP-D) OSs and NOSs. The orange circles indicate the concentrations of non-sea-salt sulfate (nss-SO42-) aerosols and the purple triangles indicate the concentrations of nitrate aerosol at the four polar sampling sites.