Impact of anthropogenic emissions on biogenic secondary organic aerosol: observation in the Pearl River Delta, southern China

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Abstract. Secondary organic aerosol (SOA) formation from biogenic precursors is affected by anthropogenic emissions, which are not well understood in polluted areas. In this study, we accomplished a year-round campaign at nine sites in polluted areas located in the Pearl River Delta (PRD) region during 2015. We measured typical biogenic SOA (BSOA) tracers from isoprene, monoterpenes, and \( \beta \)-caryophyllene, as well as major gaseous and particulate pollutants and investigated the impact of anthropogenic pollutants on BSOA formation. The concentrations of BSOA tracers were in the range of 45.4 to 109 ng m\(^{-3} \) with the majority composed of products from monoterpenes (SOA\(_{M} \), 47.2 \( \pm \) 9.29 ng m\(^{-3} \)), isoprene (SOA\(_{I} \), 23.1 \( \pm \) 10.8 ng m\(^{-3} \)), and \( \beta \)-caryophyllene (SOA\(_{C} \), 3.85 \( \pm \) 1.75 ng m\(^{-3} \)). We found that atmospheric oxidants, \( O_3 \) (O\(_3\) plus NO\(_2\)), and sulfate correlated well with later-generation SOA\(_{M} \) tracers, but this was not the case for first-generation SOA\(_{M} \) products. This suggested that high \( O_3 \) and sulfate levels could promote the formation of later-generation SOA\(_{M} \) products, which probably led to the relatively aged SOA\(_{M} \) that we observed in the PRD. For the SOA\(_I \) tracers, both 2-methylglyceric acid (NO/NO\(_2\)-channel product) and the ratio of 2-methylglyceric acid to 2-methyltetrols (HO\(_2\)-channel products) exhibit NO\(_x\) dependence, indicating the significant impact of NO\(_x\) on SOA\(_I \) formation pathways. The SOA\(_C \) tracer was elevated in winter at all sites and was positively correlated with levoglucosan, \( O_3 \), and sulfate. Thus, the unexpected increase in SOA\(_C \) in wintertime might be highly associated with the enhancement of biomass burning, \( O_3 \) chemistry, and the sulfate component in the PRD. The BSOAs that were estimated using the SOA tracer approach showed the highest concentration in fall and the lowest concentration in spring with an annual average concentration of 1.68 \( \pm \) 0.40 \( \mu \)g m\(^{-3} \). SOA\(_M \) dominated the BSOA mass all year round. We also found that BSOA correlated well with sulfate and \( O_3 \). This implied a significant effect from anthropogenic pollutants on BSOA formation and highlighted that we could reduce BSOA by controlling the anthropogenic emissions of sulfate and \( O_3 \) precursors in polluted regions.

1 Introduction

Secondary organic aerosols (SOAs) that are produced through homogenous and heterogeneous processes of volatile organic compounds (VOCs) have significant effects on global climate change and regional air quality (Von Schneidemesser et al., 2015). Globally, the emissions of biogenic VOCs (BVOCs) are dominant over anthropogenic VOCs (AVOCs). Thus, biogenic SOA (BSOA) is predomi-
nant with respect to anthropogenic SOA. In the past decade, laboratorial, field, and modeling studies have demonstrated that BSOA formation is highly affected by anthropogenic emissions (Zhang et al., 2015; Hoyle et al., 2011; Carlton et al., 2010). Increasing NO$_x$ shifts isoprene oxidation from low-NO$_x$ conditions to high-NO$_x$ conditions (Surratt et al., 2010) and enhances nighttime SOA formation via nitrate radical oxidation of monoterpenes (Xu et al., 2015). High SO$_2$ emission leads to abundant sulfate and acidic particles, which accelerate BSOA production due to the “salting-in” effect and acid-catalyzed reactions (Offenberg et al., 2009; Xu et al., 2016). In polluted regions, the increase in O$_3$ levels due to high emissions of NO$_x$ and VOCs likely results in significant SOA formation via the ozonolysis of BVOCs (Sipilä et al., 2014; Riva et al., 2017). In addition, the large emission and formation of anthropogenic organic matter (OM) in urban areas enhance the incorporation of BVOC oxidation products into the condensed phase (Donahue et al., 2006). Recently, Carlton et al. (2018) found that the removal of anthropogenic emissions of NO$_x$, SO$_2$, and primary OA in the Community Multiscale Air Quality Model (CMAQ) simulations could reduce BSOA by 23%, 14%, and 8% in sum-mertime, respectively.

The Pearl River Delta (PRD) region (Fig. 1a) is the most developed area in China. Rapid economic growth in this region during the past 3 decades has resulted in high anthropogenic emissions (Lu et al., 2013). Our observation during the fall–winter season in 2008 at a regional site in the PRD showed that daily PM$_{2.5}$ was as high as 150 µg m$^{-3}$ (Ding et al., 2012). Fortunately, due to increasingly strict and effective pollution controls in the PRD, PM$_{2.5}$ concentrations have significantly decreased over the last decade and have met the national ambient air quality standard (NAAQS) for annual mean PM$_{2.5}$ (35 µg m$^{-3}$) since the year 2015 (Figure 1b). However, O$_3$ and oxidant species (O$_3$, O$_{35}$ = O$_3$ + NO$_2$) are still at high levels and have shown no apparent decrease (Fig. 1b). Hofzumahaus et al. (2009) observed extremely high OH concentrations in the PRD and proposed a recycling mechanism that increases the stability of OH in the air of polluted regions. All of the abovementioned results indicate a high atmospheric oxidative capacity in the PRD, as O$_3$, NO$_x$, and OH are intimately linked in atmospheric chemistry. Moreover, BVOC emissions in the PRD are expected to be high year-round due to the area’s subtropical climate (Zheng et al., 2010). During the process of such dramatic changes in air pollution characteristics (e.g., PM$_{2.5}$ and O$_3$), BSOA origins and formation mechanisms in the PRD should have been profoundly affected over the last decade.

In this study, year-round PM$_{2.5}$ samples were collected at nine sites in the PRD during 2015. We investigated SOA tracers from typical BVOCs (isoprene, monoterpenes, and β-caryophyllene) across the PRD for the first time. We checked seasonal variations in the concentrations and compositions of these BSOA tracers and evaluated the impact of anthropogenic pollutants on BSOA formation in the PRD. We also accessed the SOA origins and discussed the possibility of further reducing BSOA by controlling anthropogenic emissions.

2 Experimental section

2.1 Field sampling

Concurrent sampling was performed at 9 of the 23 Guangdong–Hong Kong–Macao regional air quality monitoring network sites (http://gdee.gd.gov.cn/kqjc/, last access: 26 November 2019). The red dashed line indicates the NAAQS for annual mean PM$_{2.5}$ concentrations (35 µg m$^{-3}$).

![Figure 1](image.png)

**Figure 1.** (a) Sampling sites in the PRD, including Zhaoqing (ZQ), Guangzhou (GZ), Dongguan (DG), Nansha (NS), Zhuhai (ZH), Tianhu (TH), Boluo (BL), Heshan (HS), and Taishan (TS), and (b) long-term trends of annual mean PM$_{2.5}$, O$_3$, SO$_2$, and O$_3$ recorded by the Guangdong–Hong Kong–Macao regional air quality monitoring network (http://gdee.gd.gov.cn/kqjc/, last access: 26 November 2019).
1.1 m³ min⁻¹. Additionally, field blanks were collected at all sites at a monthly interval. Blank filters were covered with aluminum foil, baked at 500 °C for 12 h, and stored in a container with silica gel. After sampling, the filter samples were stored at −20 °C.

In this study, the filters collected in January, April, July, and October 2015 were selected to represent winter, spring, summer, and fall, respectively. A total of 170 field samples (4–5 samples for each season at each site) were analyzed in the current study.

2.2 Chemical analysis

For each filter, organic carbon (OC) and elemental carbon (EC) were measured using an OC–EC aerosol analyzer (Sunset Laboratory Inc.). Water-soluble ions were analyzed by ion chromatography (Metrohm). All of these species are major components in PM₂.₅ (see Fig. 2). Meteorological parameters (temperature and relative humidity) and gaseous pollutants (SO₂, CO, NOₓ, NO, and O₃) at each site were recorded hourly. We also calculated the daily averages to probe the potential influence of air pollutants on BSOA formation.

For BSOA tracer analysis, detailed information regarding the processes used is given in the existing literature (Shen et al., 2015; Ding et al., 2012). Isotope-labeled standard mixtures, including dodecanedioic acid-d₂₃, hexadecanoic acid-d₃₁, docosanoic acid-d₄₃, and levoglucosan, were added into each sample as internal standards. Samples were then extracted by sonication with the mixed solvents of dichloromethane (DCM)/hexane (1 : 1, v/v) and DCM/methanol (1 : 1, v/v), sequentially. The extraction solutions of each sample were combined, filtered, and concentrated to ∼2 mL. Each concentrated sample was split into two parts for silylation and methylation, respectively.

We analyzed 14 BSOA tracers in the derivatized samples using GC-MSD (Agilent 7890/5975C). The isoprene-derived SOA (SOAᵢ) tracers were composed of 2-methyltetrols (2-MTLs, 2-methylthreitol, and 2-methylerythritol) (Claeys et al., 2004a), 2-methylglyceric acid (2-MGA) (Claeys et al., 2004b), 3-MeTHF-3,4-diols (cis-3-methyltetrahydrofuran-3,4-diol and trans-3-methyltetrahydrofuran-3,4-diol) (Lin et al., 2012), and C₅-alkene triols (cis-2-methyl-1,3,4-trihydroxy-1-butene, trans-2-methyl-1,3,4-trihydroxy-1-butene, and 3-methyl-2,3,4-trihydroxy-1-butene) (Wang et al., 2005). The monoterpene-derived SOA (SOAM) tracers included 3-hydroxy-4,4-dimethylglutaric acid (HDMGA), 3-hydroxyglutaric acid (HGA) (Claeys et al., 2007), pinic acid (PA), cis-pinic acid (PNA) (Christoffersen et al., 1998), and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) (Szmigielski et al., 2007). The β-caryophyllene-derived SOA (SOAC) tracer was β-caryophyllenic acid (CA) (Joulli et al., 2007). Due to the lack of authentic standards, surrogate standards were used to quantify BSOA tracers except PNA. Specifically, erythritol, PNA, and octadecanoic acid were used for the quantification of SOAᵢ tracers (Ding et al., 2008), other SOAM tracers (Ding et al., 2014), and CA (Ding et al., 2011), respectively. The method detection limits (MDLs) for erythritol, PNA, and octadecanoic acid were 0.01, 0.02, and 0.02 ng m⁻³, respectively. Table S1 in the Supplement summarizes BSOA data from each site in the PRD.

2.3 Quality assurance/quality control

The target BSOA tracers were not detected or were lower than the MDLs in the field blanks. The results of spiked samples (erythritol-, PNA-, and octadecanoic-acid-spiked in prebaked quartz filters) indicated that the recoveries were 65% ± 14% for erythritol, 101% ± 3% for PNA, and 83% ± 7% for octadecanoic acid. The results of paired duplicate samples indicated that all of the relative differences for target BSOA tracers were lower than 15%.

It should be noted that the application of surrogate quantification introduces additional errors to the results. Based on the empirical approach of calculating uncertainties from surrogate quantification (Stone et al., 2012), we estimated the errors in analyte measurement that were propagated from the uncertainties in field blanks, spike recoveries, repeatability, and surrogate quantification. As Table S2 shows, the estimated uncertainties in the tracers’ measurement ranged from 15% (PNA) to 157% (CA).

3 Results and discussion

3.1 PM₂.₅ and gaseous pollutants

Figure 2 presents the spatial and seasonal variations of PM₂.₅ and its major components. Although annual mean PM₂.₅ (34.8 ± 6.1 µg m⁻³) in the PRD met the NAAQS value of 35 µg m⁻³, PM₂.₅ concentrations at the urban sites (ZQ, GZ, and DG) all exceeded the NAAQS value. The rural TH site in the northern part of the PRD witnessed the lowest PM₂.₅ concentration (25.0 µg m⁻³) among the nine sites. PM₂.₅ levels were highest in winter (60.1 ± 21.6 µg m⁻³ on average) and lowest in summer (22.8 ± 3.3 µg m⁻³ on average). Carbonaceous aerosols and water-soluble ions together explained 98% ± 11% of the PM₂.₅ mass. OM (OC × 1.6) was the most abundant component in PM₂.₅, followed by sulfate, ammonium, nitrate, and EC. Similar to PM₂.₅, the five major components all increased in winter and fall (Fig. S1), suggesting severe PM₂.₅ pollution during the fall–winter season in the PRD.

In the gas phase, SO₂, CO, NOₓ, and NO₃ presented similar seasonal trends to PM₂.₅; i.e., higher levels occurred during fall and winter and lower concentrations during spring and summer (Fig. 3a, b, c, d). Annual mean SO₂ and NO₂ in the PRD both met the NAAQS values of 60 and 40 µg m⁻³, respectively (Fig. 3a, c). As a typical secondary pollutant, O₃ was highest in summer (Fig. 3e), probably due to the strong photochemistry. Due to the compromise of opposite seasonal
trends of O$_3$ and NO$_2$. O$_3$ showed less seasonal variation (Fig. 3f) compared with other gaseous pollutants, and the annual mean for O$_3$ reached 96.1 ± 14.9 µg m$^{-3}$. This indicated significant year-round O$_3$ pollution in the PRD.

3.2 Spatial distribution and seasonal variation of SOA tracers

The total concentrations of BSOA tracers ranged from 45.4 to 109 ng m$^{-3}$ among the nine sites. SOA$_M$ tracers (47.2 ± 9.29 ng m$^{-3}$) were predominant, followed by SOA$_I$ tracers (23.1 ± 10.8 ng m$^{-3}$) and SOA$_C$ tracers (3.85 ± 1.75 ng m$^{-3}$).

3.2.1 Monoterpene-derived SOA tracers

Annual averages of total SOA$_M$ tracers at the nine sites were in the range of 26.5 to 57.4 ng m$^{-3}$ (Table S1). Figures 4 and S2a show the spatial distribution of SOA$_M$ tracers and monoterpene emissions in the PRD (Zheng et al., 2010). The highest concentration of SOA$_M$ tracers was observed at the rural TH site, where monoterpene emissions were high. Figure 4 also presents seasonal variations of SOA$_M$ tracers. At most sites, high levels occurred in summer and fall. Monoterpene emission rates are influenced by temperature and solar radiation (Guenther et al., 2012). Thus, high temperature and intensive solar radiation during summer and fall in the PRD (Zheng et al., 2010) could stimulate monoterpene emissions and subsequent SOA$_M$ formation.

Among the five SOA$_M$ tracers, HGA (20.1 ± 4.28 ng m$^{-3}$) showed the highest concentration, followed by HDMGA (14.7 ± 2.93 ng m$^{-3}$), MBTCA (7.63 ± 1.49 ng m$^{-3}$), PNA (3.75 ± 2.72 ng m$^{-3}$), and PA (1.01 ± 0.48 ng m$^{-3}$). SOA$_M$ formation undergoes multigenerational reactions. The first-generation SOA$_M$ (SOA$_M$$_F$) products, PNA and PA, can be further oxidized and form the later-generation (SOA$_M$$_L$) products, e.g., MBTCA (Müller et al., 2012). Thus, the (PNA + PA)/MBTCA ratio has been used to probe SOA$_M$ aging (Haque et al., 2016; Ding et al., 2014). The (PNA + PA)/MBTCA ratios in chamber-generated α-pinene SOA samples were reported to be in the range of 1.51 to 5.91, depending on different oxidation conditions (Offenberg et al., 2007; Eddingsaas et al., 2012). In this study, the median values of (PNA + PA)/MBTCA varied from 0.27 at ZH to 1.67 at TH. The ratios observed in this study were consistent with our previous observations at the regional site, Wanqingsha (WQS) in the PRD (Ding et al., 2012), but lower than those in fresh α-pinene SOA samples from chamber experiments (Fig. S3), indicating relatively aged SOA$_M$ in the air of the PRD.

Moreover, the levels of SOA$_{M,L}$ tracers (HGA + HDMGA + MBTCA) were much higher than those of SOA$_M$$_F$ tracers (PNA + PA), with mean mass fractions of SOA$_{M,L}$ tracers reaching 86% (Fig. 4).
fractions of SOA$_M$$_F$ tracers decreased in the summer samples (Fig. 4), probably resulting from strong photochemistry and more intensive subsequent oxidation during summer. High abundances of SOA$_M$$_L$ tracers in the PRD were different from our year-round observations at 12 sites across China (Ding et al., 2016b). Ding et al. (2016b) found that the (PNA + PA)/MBTCA ratio suggested generally fresh SOA$_M$ and that SOA$_M$$_F$ tracers were predominant. Thus, we see more aged SOA$_M$ in the PRD.

As Figs. 5a–b, S4, and S5 show, the SOA$_M$$_F$ tracers did not show good correlations with O$_x$ at most sites, whereas the SOA$_M$$_L$ tracers exhibited significant O$_x$ dependence. When O$_x$ is high, strong photooxidation of PNA and PA could reduce their concentrations and promote the formation of SOA$_M$$_L$ tracers (Müller et al., 2012). Thus, the levels of SOA$_M$$_L$ tracers would increase with increasing O$_x$, whereas this is not the case for SOA$_M$$_F$ tracers. Moreover, sulfate could influence SOA formation. Sulfate is a key species in particles that determines the aerosol liquid water amount, aerosol acidity, and particle surface area (Xu et al., 2015, 2016). Thus, an increase in sulfate could promote aqueous and heterogeneous reactions. In this study, the SOA$_M$$_F$ tracers poorly correlated with sulfate (Fig. 5c), whereas the SOA$_M$$_L$ tracers positively correlated with sulfate at all nine sites (Fig. 5d). At each site, the SOA$_M$$_L$ tracers exhibited more sulfate dependence than the SOA$_M$$_F$ tracers (Fig. S5). This suggested that sulfate also played a critical role in forming SOA$_M$$_L$ tracers through particle-phase reactions. In addition to gas-phase OH oxidation (Müller et al., 2012), the heterogeneous OH oxidation of PNA could also produce SOA$_M$$_L$ tracers (Lai et al., 2015). Aljawhary et al. (2016) reported the kinetics and mechanism of PNA oxidation in acidic solutions and found that the molar yields of MBTCA via aqueous-phase reactions were similar to those in gas-phase oxidation. Here, we conclude that high concentrations of O$_x$ and sulfate could stimulate SOA$_M$$_L$ tracer production and thereby lead to aged SOA$_M$ in the PRD.

### 3.2.2 Isoprene-derived SOA tracers

Annual averages of total SOA$_I$ tracers at the nine sites were in the range of 10.8 to 49.3 ng m$^{-3}$ (Table S1). Figures 6 and S2b show the spatial distribution of SOA$_I$ tracers and isoprene emissions in the PRD (Zheng et al., 2010), respectively. The highest concentration occurred at ZQ, where emissions were high. Figure 6 also presents seasonal variations of SOA$_I$ tracers at the nine sites. High levels occurred in summer and fall. Similar to monoterpenes, the emission rate of isoprene is influenced by temperature and solar radiation (Guenther et al., 2012), which are both expected to be higher in summer and fall in the PRD (Zheng et al., 2010). Among these SOA$_I$ tracers, 2-MTLs (14.2 ± 5.61 ng m$^{-3}$) were the most abundant products, followed by C$_5$-alkene triols (6.81 ± 5.05 ng m$^{-3}$), 2-MGA (1.99 ± 0.72 ng m$^{-3}$), and 3-MeTHF-3,4-diols (0.19 ± 0.08 ng m$^{-3}$).

SOA$_I$ formation is highly affected by NO$_x$ (Surratt et al., 2010). Under low-NO$_x$ or NO$_x$-free conditions, isoprene is oxidized by the OH and HO$_2$ radicals via the HO$_2$ channel which generates a hydroxy hydroperoxide (ISOPOOH) and then forms epoxydiols (IEPOX) (Paulot et al., 2009). Reactive uptake of IEPOX on acidic particles eventually produces 2-MTLs, C$_5$-alkene triols, 3-MeTHF-3,4-diols, 2-MTLs-organosulfates, and oligomers (Lin et al., 2012). Under high-NO$_x$ conditions, isoprene undergoes oxidation by NO$_x$ via the NO/NO$_2$ channel, generates methacrolein (MACR), and then forms peroxymethylacrylic nitric anhydride (MPAN). Further oxidation of MPAN by the OH radical produces hydroxymethyl-methyl-α-lactone (HMML) and/or methacrylic acid epoxide (MAE). HMML and MAE are the direct precursors of 2-MGA, 2-MGA-organosulfate, and its corresponding oligomers (Nguyen et al., 2015). As Fig. 6 shows, the concentrations of HO$_2$-channel tracers (2-MTLs + C$_5$-alkene triols + 3-MeTHF-3,4-diols) were much higher than those of the NO/NO$_2$-channel product (2-MGA) at all the nine sites. The dominance of HO$_2$-channel products was also observed at another regional site (WQS) in the PRD (He et al., 2018).

Figure 6 also shows seasonal trends of the 2-MGA to 2-MTLs ratio (2-MGA/2-MTLs) which is often applied to probe the influence of NO$_x$ on the formation of SOA$_I$ (Ding et al., 2013, 2016a; Pye et al., 2013). The ratios were highest in wintertime and lowest in summertime; these results are
consistent with the seasonal trend of NO\textsubscript{x} during our campaign (Fig. 3d). As Table 1 shows, 2-MGA was positively correlated with NO\textsubscript{2}, probably due to the enhanced formation of MPAN from the peroxymethacryloyl (PMA) radical which reacted with NO\textsubscript{2} (Worton et al., 2013; Chan et al., 2010). Previous laboratory studies have shown that increasing the NO\textsubscript{2}/NO ratio could promote the formation of 2-MGA and its corresponding oligoesters (Chan et al., 2010; Surratt et al., 2010). However, we did not see a significant correlation between 2-MGA and the NO\textsubscript{2}/NO ratio in the PRD. Instead, the 2-MGA/2-MTLs ratio correlated well with NO, NO\textsubscript{2}, and the NO\textsubscript{2}/NO ratio (Table 1). Increasing NO limits the formation of ISOPOOH but prefers the production of MACR, and increasing NO\textsubscript{2} enhances MPAN formation. Thus, it is expected that the 2-MGA/2-MTLs ratio will show stronger NO\textsubscript{x} dependence than 2-MGA. These findings demonstrate the significant impact of NO\textsubscript{x} on SOA\textsubscript{I} formation pathways in the atmosphere. We also checked the correlations of SOA\textsubscript{I} tracers with O\textsubscript{3} and sulfate (Fig. S6). The NO/NO\textsubscript{2}-channel product exhibited more O\textsubscript{3} and sulfate dependance than the HO\textsubscript{2}-channel products.

Recent studies have indicated that isoprene ozonolysis might play a role in SOA\textsubscript{I} formation in the ambient air. Riva et al. (2016) found that isoprene ozonolysis with acidic particles could produce substantial 2-MTLs, but this was not the case for C\textsubscript{5}-alkene triols and 3-MeTHF-3,4-diols. Li et al. (2018) observed a positive correlation between 2-MTLs and O\textsubscript{3} on the North China Plain. In the PRD, we also saw
weak but significant correlations of 2-MTLs with $O_3$ (Table S3). However, 3-MeTHF-3,4-diols and C$_5$-alkene triols were detected in all samples, and 2-MTLs, C$_5$-alkene triols, and 3-MeTHF-3,4-diols correlated well with each other (Table S4), which was apparently different from the results reported by Riva et al. (2016). Moreover, the ratios of 2-MTLs isomers in the PRD samples (2.00–2.85) were much lower than those (10–22; Fig. S7) reported in the SOA from isoprene ozonolysis (Riva et al., 2016). Furthermore, isoprene oxidation by the OH radical is much faster than oxidation by $O_3$ under polluted PRD conditions (Table S5), and IEPOX yields via ISOPOOH oxidation by the OH radical are more than 75% in the atmosphere (St. Clair et al., 2016). Thus, isoprene ozonolysis might be not the major formation pathway of SOA$_I$, even though the annual mean $O_3$ level reached 67.7 µg m$^{-3}$ in the PRD (Table S1).

Previous studies have found that thermal decomposition of low-volatility organics in IEPOX-derived SOA could produce SOA$_I$ tracers, e.g., 2-MTLs, C$_5$-alkene triols, and 3-MeTHF-3,4-diols (Lopez-Hilfiker et al., 2016; Watanabe et al., 2018). This means that these tracers detected by GC-MSD might be generated from the thermal decomposition of IEPOX-derived SOA. As estimated by Cui et al. (2018), 14.7%–42.8% of C$_5$-alkene triols, 11.1% of 2-MTLs, and approximately all 3-MeTHF-3,4-diols measured by GC-MSD could be attributed to the thermal degradation of 2-MTL-derived organosulfates (MTL-OSs). We also measured MTL-OSs in two samples at the HS and TS sites (Table S6), respectively, utilizing the widely used LC-MS approach (He et al., 2014, 2018). Assuming that all MTL-OSs decomposed to these tracers, the thermal decomposition of MTL-OSs would account for 15.1%–31.6% of C$_5$-alkene triols, 6.0%–10.0% of 2-MTLs, and approximately all 3-MeTHF-3,4-diols measured by GC/MSD. Thus, C$_5$-alkene triols and 2-MTLs are major products of isoprene oxidation rather than products of the thermal decomposition of MTL-OSs, whereas 3-MeTHF-3,4-diols are only present in trace amount in the air and might be produced largely from thermal degradation.
Moreover, we see significant variations in SOA tracer compositions in the PRD. For instance, C5-alkene triols have three isomers. If these tracers were mainly generated from a thermal process, their compositions should be similar in different samples. In fact, the relative abundances of the three C5-alkene triol isomers significantly changed from site to site (Fig. 7) and from season to season (Fig. S8), and their compositions in the PRD were different from those measured in the chamber samples (Lin et al., 2012). In addition, the slopes of linear correlations among these IEPOX-derived SOA tracers also varied from site to site (Fig. S9). Coupled with the seasonal trend of 2-MGA/2-MLTs ratios, the apparent variations in SOA tracer compositions demonstrate that these SOA tracers are mainly formed via different pathways in the ambient atmosphere; however, they might partly arise from the thermal decomposition of different dimers/OSs, and the parent dimers/OSs vary with site and seasons.

### 3.2.3 Sesquiterpene-derived SOA tracer

Annual averages of CA at the nine sites ranged from 1.82 to 7.07 ng m\(^{-3}\). The levels of CA at the inland sites (e.g., GZ, ZQ, and TH) were higher than those at the coastal sites (ZH and NS; Fig. 8). As sesquiterpenes are typical BVOCs, it is unexpected that the concentrations of CA were highest during winter in the PRD (Fig. 8). Interestingly, the seasonal trend of CA was consistent with that of the biomass burning (BB) tracer, levoglucosan (Fig. 8), and CA correlated well with levoglucosan at eight sites in the PRD (Fig. 9a). Sesquiterpenes are stored in plant tissues, partly to protect the plants from insects and pathogens (Keeling and Bohlmann, 2006). BB can not only stimulate sesquiterpene emissions (Ciccioli et al., 2014) but can also substantially alter SOA formation and yields (Mentel et al., 2013). Emissions inventories in the PRD showed that BB emissions were enhanced during winter (He et al., 2011). This suggested that the unexpected increase in SOA in wintertime could be highly associated with BB emissions in the PRD.

Besides the impact of BB, we also found positive correlations of CA with O\(_x\) (Fig. 9b) and sulfate (Fig. 9c). The oxidation of \(\beta\)-caryophyllene by the OH radical and O\(_3\) is very rapid. Under typical oxidation conditions in the air of the PRD, the lifetimes of \(\beta\)-caryophyllene are only several minutes (Table S5). Once emitted from vegetation or biomass burning, \(\beta\)-caryophyllene will react rapidly and form CA immediately. This partly explains the positive correlations between CA and levoglucosan in this region. The unexpected high levels of CA in the winter indicated that biomass burning could be an important source of SOA in the PRD, especially in wintertime. In addition, the increase in sulfate could raise aerosol acidity and thereby promote aqueous and heterogeneous reactions to form SOA. In the PRD, both O\(_x\) (Fig. 3f) and sulfate (Fig. S1) increased during winter, which could promote SOA formation. Here, we conclude that the enhancement of BB emissions as well as the increase in O\(_x\) and sulfate in wintertime led to high SOA production during this season in the PRD.
Figure 9. Significant correlations of CA with levoglucosan (a), OIC (b), and sulfate (c).

3.3 Source apportionment and atmospheric implications

We further attributed BSOA using the SOA tracer approach, which was first developed by Kleindienst et al. (2007). This method has been applied to SOA apportionment at multiple sites across the United States (Lewandowski et al., 2013) and China (Ding et al., 2016b), and over global oceans from the Arctic to the Antarctic (Hu et al., 2013). Details of the SOA tracer method and its application in this study as well as the uncertainty of the estimation procedure are described in Sect. S1. Table S1 lists the results of estimated SOAs from different BVOCs.

Figure 10a exhibits the spatial distribution of BSOA components (SOAM + SOAq + SOAC). The annual average at the nine sites ranged from 0.97 µg m\(^{-3}\) (NS) to 2.19 µg m\(^{-3}\) (ZQ), accounting for 9%–15% of OM. SOAM was the largest BSOA contributor with an average contribution of 64% ± 7%, followed by SOAC (21% ± 6%), and SOAq (14% ± 4%). Figure 10b presents the seasonal variation of BSOA components. The levels were highest in fall (2.35 ± 0.95 µg m\(^{-3}\)) and lowest in spring (1.06 ± 0.42 µg m\(^{-3}\)). SOAM contributions ranged from 57% in winter to 68% in spring. The contribution of SOAq was only 5% in winter and reached up to 22% in summer. The contribution of SOAC increased to 40% in wintertime.
It is interesting to note that SOA\textsubscript{M}, SOA\textsubscript{I}, and SOA\textsubscript{C} all positively correlated with sulfate and O\textsubscript{X} in the PRD (Table 2). As anthropogenic emissions can enhance BSOA formation (Hoyle et al., 2011), the reduction of anthropogenic emissions indeed lowers BSOA production (Carlton et al., 2018). As the oxidation product of SO\textsubscript{2}, sulfate is a key species in particles and determines aerosol acidity and surface area (Xu et al., 2015, 2016); thus, sulfate could promote BSOA formation via acid-catalyzed heterogeneous reactions. A recent study found that SO\textsubscript{2} could directly react with organic peroxides from monoterpene ozonolysis and form substantial organosulfates (Ye et al., 2018). Thus, a decrease in SO\textsubscript{2} emissions indeed reduces SO\textsubscript{2} and sulfate in the ambient air, which leads to less acidic particles and a reduction in BSOA production. For O\textsubscript{X}, the increase in O\textsubscript{X} likely results in significant SOA formation via BVOC ozonolysis (Sipili et al., 2014; Riva et al., 2017). Hence, the decrease in O\textsubscript{X} resulting from the control of VOC and NO\textsubscript{X} emissions could reduce BSOA formation through O\textsubscript{X} chemistry. Based on the observed sulfate and O\textsubscript{X} dependence of BSOA in this study, a reduction of 1 µg m\textsuperscript{-3} in sulfate and O\textsubscript{X} in the air of the PRD could lower BSOA levels by 0.17 and 0.02 µg m\textsuperscript{-3}, respectively. If both concentrations decline by 50 %, the reduction of O\textsubscript{X} is more efficient than the reduction of sulfate with respect to reducing BSOA in the PRD (Table 2).

We further compared the results from 2015 with those from the fall–winter season of 2008 at WQS (Ding et al., 2012). We found that all BSOA species positively correlated with sulfate but exhibited no O\textsubscript{X} dependence (Table S7). Thus, BSOA formation was largely influenced by sulfate in 2008, probably due to high sulfate levels during this period (as high as 46.8 µg m\textsuperscript{-3}). Owing to subsequent strict control of SO\textsubscript{2} emissions (Wang et al., 2013), ambient SO\textsubscript{2} has significantly decreased over the PRD (Fig. 1b). Our long-term observation during the fall–winter season at WQS also witnessed a decreasing trend in sulfate from 2007 to 2016 (Fig. S10). However, O\textsubscript{X} levels have not decreased during the past decade (Fig. 1b), and O\textsubscript{X} concentrations were much higher than sulfate in 2015 in the PRD (96.1 ± 14.9 µg m\textsuperscript{-3} vs. 8.44 ± 1.09 µg m\textsuperscript{-3} on average). These results emphasize the current importance of O\textsubscript{X} in BSOA formation in the PRD. At present, short-term despiking and long-term attainment of O\textsubscript{X} concentrations are challenges for air pollution control in the PRD (Ou et al., 2016). Thus, lowering O\textsubscript{X} is critical to improve the air quality in the PRD. Our results highlight the importance of future reductions of anthropogenic pollutant emissions (e.g., SO\textsubscript{2} and O\textsubscript{X} precursors) in order to considerably reduce the BSOA burden in polluted regions.

Table 2. Correlations of BSOA with sulfate and O\textsubscript{X}.

|          | Sulfate |       | Ox   |       |
|----------|---------|-------|------|-------|
|          | Slope   | p value | %a   | Slope | p value | %a |
| SOA\textsubscript{M} | 0.112   | < 0.001 | 45   | 0.013 | < 0.001 | 57  |
| SOA\textsubscript{I} | 0.020   | < 0.001 | 34   | 0.003 | < 0.001 | 50  |
| SOA\textsubscript{C} | 0.041   | < 0.001 | 46   | 0.004 | < 0.001 | 55  |
| BSOA    | 0.172   | < 0.001 | 44   | 0.019 | < 0.001 | 55  |

a Percentage reduction of SOA due to a 50 % decline in sulfate or O\textsubscript{X}.

It is interesting to note that SOA\textsubscript{M}, SOA\textsubscript{I}, and SOA\textsubscript{C} all positively correlated with sulfate and O\textsubscript{X} in the PRD (Table 2). As anthropogenic emissions can enhance BSOA formation (Hoyle et al., 2011), the reduction of anthropogenic emissions indeed lowers BSOA production (Carlton et al., 2018). As the oxidation product of SO\textsubscript{2}, sulfate is a key species in particles and determines aerosol acidity and surface area (Xu et al., 2015, 2016); thus, sulfate could promote BSOA formation via acid-catalyzed heterogeneous reactions. A recent study found that SO\textsubscript{2} could directly react with organic peroxides from monoterpene ozonolysis and form substantial organosulfates (Ye et al., 2018). Thus, a decrease in SO\textsubscript{2} emissions indeed reduces SO\textsubscript{2} and sulfate in the ambient air, which leads to less acidic particles and a reduction in BSOA production. For O\textsubscript{X}, the increase in O\textsubscript{X} likely results in significant SOA formation via BVOC ozonolysis (Sipili et al., 2014; Riva et al., 2017). Hence, the decrease in O\textsubscript{X} resulting from the control of VOC and NO\textsubscript{X} emissions could reduce BSOA formation through O\textsubscript{X} chemistry. Based on the observed sulfate and O\textsubscript{X} dependence of BSOA in this study, a reduction of 1 µg m\textsuperscript{-3} in sulfate and O\textsubscript{X} in the air of the PRD could lower BSOA levels by 0.17 and 0.02 µg m\textsuperscript{-3}, respectively. If both concentrations decline by 50 %, the reduction of O\textsubscript{X} is more efficient than the reduction of sulfate with respect to reducing BSOA in the PRD (Table 2).

We further compared the results from 2015 with those from the fall–winter season of 2008 at WQS (Ding et al., 2012). We found that all BSOA species positively correlated with sulfate but exhibited no O\textsubscript{X} dependence (Table S7). Thus, BSOA formation was largely influenced by sulfate in 2008, probably due to high sulfate levels during this period (as high as 46.8 µg m\textsuperscript{-3}). Owing to subsequent strict control of SO\textsubscript{2} emissions (Wang et al., 2013), ambient SO\textsubscript{2} has significantly decreased over the PRD (Fig. 1b). Our long-term observation during the fall–winter season at WQS also witnessed a decreasing trend in sulfate from 2007 to 2016 (Fig. S10). However, O\textsubscript{X} levels have not decreased during the past decade (Fig. 1b), and O\textsubscript{X} concentrations were much higher than sulfate in 2015 in the PRD (96.1 ± 14.9 µg m\textsuperscript{-3} vs. 8.44 ± 1.09 µg m\textsuperscript{-3} on average). These results emphasize the current importance of O\textsubscript{X} in BSOA formation in the PRD. At present, short-term despiking and long-term attainment of O\textsubscript{X} concentrations are challenges for air pollution control in the PRD (Ou et al., 2016). Thus, lowering O\textsubscript{X} is critical to improve the air quality in the PRD. Our results highlight the importance of future reductions of anthropogenic pollutant emissions (e.g., SO\textsubscript{2} and O\textsubscript{X} precursors) in order to considerably reduce the BSOA burden in polluted regions.

**Code and data availability.** The experimental data in this study are available upon request to the corresponding author by email.

**Supplement.** The supplement related to this article is available online at: https://doi.org/10.5194/acp-19-14403-2019-supplement.

**Author contributions.** XD, D-HC, and JL conceived the project and designed the study. Y-QZ and D-HC performed the data analysis and wrote the paper. D-HC, TZ, and Y-BO arranged the sample collection and assisted with the data analysis. J-QW, QC, and HJ analyzed the samples. XD, P-LY, WS, GZ, and X-MW performed the data interpretation and edited the paper. All authors contributed to the development of the final paper.

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

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