Spatial and Diurnal Variations of Aerosol Organosulfates in Summertime Shanghai, China: Potential Influence of Photochemical Process and Anthropogenic Sulfate Pollution

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ABSTRACT: Organosulfates (OSs) are ubiquitous aerosol components with intense research over years. However, spatial and diurnal variations in OS formation in polluted atmosphere remain poorly understood. In this study, 130 OS species were quantified in ambient fine particulate matter (PM$_{2.5}$) collected in urban and suburban Shanghai (East China) in summer 2021. Isoprene- and monoterpenes-derived OSs were dominant OS groups (averaging 51% and 19% of total quantified OSs, respectively), likely indicating a large biogenic contribution to OS formation in summer. Most OSs peaked during daytime, while monoterpenes-derived nitrooxy-OSs (NOS$_m$) increased during nighttime. Accordingly, OSs were largely produced via daytime formation processes, rather than nighttime chemistry, excepting NOS$_m$. Additionally, although OS formation in the urban and suburban areas exhibited similar diurnal variations, the average concentrations of biogenic and anthropogenic OSs decreased significantly from the urban site to the suburban site. Furthermore, we concretized daytime OS formation based on the interactions among OSs, ultraviolet (UV), ozone (O$_3$), and sulfate (SO$_4^{2-}$). Indeed, the concentrations of most OSs were significantly correlated with the values of UV[O$_3$][SO$_4^{2-}$] during daytime in both urban and suburban Shanghai. In particular, the correlation between major OSs and UV[O$_3$][SO$_4^{2-}$] was stronger than the correlation of major OSs with O$_3$ and SO$_4^{2-}$; moreover, there was no significant correlation between major OSs and UV. Thus, higher urban OS events were attributed to the enhanced photochemical processes and sulfate level in the urban area. Overall, this study provides field evidence for the influence of photochemical process and anthropogenic sulfate on OS formation and has important implications for the mitigation of organic particulate
1. Introduction

Organosulfates (OSs) are ubiquitous constituents in secondary organic aerosol (SOA) and can contribute up to ~30% of organic mass in atmospheric fine particles (PM$_{2.5}$) (Tolocka and Turpin 2012; Stone et al. 2012; Surratt et al. 2008). OSs affect the formation, hygroscopicity, light-absorbing, and acidity of organic aerosols as well as biogeochemical cycles of sulfur (Estillore et al. 2016; Riva et al. 2019; Fleming et al. 2019), which are tightly associated with air quality, human health, and regional climate (Ramanathan et al. 2001; Menon et al. 2008). Thus, understanding the mechanisms and key influencing factors of OS formation in the ambient atmosphere is of great significance for an effective assessment of environment and climate effects of OSs.

Many laboratory studies have suggested that heterogeneous and multiphase reactions involving biogenic and anthropogenic volatile organic compounds (VOCs), their oxidation intermediates, and sulfate or gas-phase sulfur dioxide (SO$_2$) are important pathways for the formation of OSs (Blair et al. 2017; Riva et al. 2016b; Ye et al. 2018). For example, the formation of 2-methyltetrol sulfate ester (2-MT-OS) and 2-methylglyceric acid sulfate ester (2-MGA-OS) can be attributed to the reactive uptake of isoprene epoxide (IEPOX) and isoprene-derived hydroxymethyl-methyl-α-lactone (HMML) by acidic particles, respectively (Surratt et al. 2010; Nguyen et al. 2015). The ozonolysis of α-pinene and limonene in the presence of SO$_2$ can contribute...
to the production of monoterpene-derived OSs (e.g., C₉H₁₅O₇S⁻ and C₁₀H₁₇O₇S⁻) (Ye et al. 2018). Chamber experiments by Riva et al., (2015) showed that the photooxidation of C₁₀–C₁₂ alkanes is associated with the formation of aliphatic OSs. More recently, the aliphatic OSs have been identified based on the uptake experiments of SO₂ by oleic acid and other unsaturated fatty acids (Shang et al. 2016; Passananti et al. 2016). In addition, the gas-phase oxidation of polycyclic aromatic hydrocarbons was found to be an important source of aromatic OSs (Riva et al. 2015).

Furthermore, OSs have been identified in different ambient atmospheres, including suburban, rural, urban, marine, polar, and forest areas (Kristensen and Glasius 2011; Tao et al. 2014; Hettiyadura et al. 2017; Vandergrift et al. 2022; Hawkins et al. 2010; Ye et al. 2021). Owing to different levels of precursors and atmospheric pollution, the abundance and formation pathways of OSs change substantially in temporal and spatial scales (Lin et al. 2022; Wang et al. 2021). Patently, field observations are valuable for verifying the mechanistic understanding of OS formation obtained in the laboratory studies. The importance of atmospheric oxidants and sulfate (or SO₂) in the OS formation was proposed in field observations according to a correlation analysis of OSs with ozone (O₃) (or the sum of O₃ and NO₂ concentrations) and sulfate (or SO₂) (Nguyen et al. 2014; Hettiyadura et al. 2019; Wang et al. 2018). Notably, these observation-based studies also highlighted the role of photochemistry of OS precursors. However, the interactions among ultraviolet (UV), O₃, and sulfate have not been well investigated. In particular, few studies were performed to systematically reveal the difference in the formation processes of OSs in polluted and clean areas, as well as
Shanghai is a megacity in the Yangtze River Delta (YRD) region of China. Locally varied ambient conditions such as $\text{O}_3$, $\text{SO}_2$, and $\text{NO}_x$, relative humidity (RH), and aerosol acidity affect the formation of OSs significantly (Cai et al. 2020; Wang et al. 2021). Here, 130 OS species were quantified in PM$_{2.5}$ samples collected in urban and suburban Shanghai in summer 2021 to investigate the relative influence of photochemistry and nighttime chemistry on OS formation and their linkages with anthropogenic sulfate pollution. In addition, the potential impacts of aerosol acidity and aerosol liquid water (ALW) on OS formation were discussed. This study can help to deepen the understanding of photochemical process and nighttime chemistry of OSs in the atmosphere.

2. Materials and Methods

2.1 Site Description and Sample Collection

Ambient PM$_{2.5}$ samples were continuously collected in the urban center and suburban area in Shanghai from 11 to 23 July 2021 (Figure S1). The sampling site in the urban center is located on the roof of a building (~20 m above the ground) in the Xuhui Campus of Shanghai Jiao Tong University. The site is characterized by a typical urban environment with heavy traffic and dense population. The aerosol sampler in the suburban area was placed on the roof of a ~20 m high building in a monitoring station of Pudong Huinan. This site is closer to the coastline than the urban sampling site (Figure S1). Thus, the suburban site is expected to be more affected by clean air mass...
from the sea. PM$_{2.5}$ was sampled onto the prebaked (550°C for ∼8 h) quartz fiber filters (8 × 10 in., Whatman) using a high-volume air sampler (HiVol 3000, Ecotech) at a flow rate of 67.8 m$^{3}$ min$^{-1}$. The duration of each sample collection in both urban and suburban areas was approximately 11 h during the daytime (8:30−19:30 LT) and 12 h during the nighttime (20:00−8:00 LT). Two blank filter samples were collected at each site during the campaign. A total of 50 filter samples were collected, which were stored at −30°C until analysis.

2.2 Chemical Analysis and Prediction of Aerosol Acidity and ALW

A portion of the filter (~15.9 cm$^2$) was extracted with 3 mL methanol in an ultrasonic bath for 30 min for two times. The camphorsulfonic acid (1 ppm) was spiked on the filter punches as an internal standard before extracting. The extracts obtained each time were combined and filtered through a 0.22 μm Teflon syringe filter (CNW Technologies GmbH) and then concentrated to 300 μL under a gentle stream of ultra-high-purity nitrogen gas. Subsequently, 300 μL ultrapure water was added into the concentrated samples, followed by centrifugation to get the supernatant for analysis. OSs were analyzed using an Acquity UPLC (Waters, USA) coupled to a Xevo G2-XS Qudropole time-of-flight mass spectrometer (ToF-MS, Waters, USA) equipped with an electrospray ionization (ESI) source operated in the negative ion mode. The chromatographic conditions and analytical procedures were detailed in our recent publication (Wang et al. 2021). A total of 212 OSs were identified by UPLC-MS analysis, in which 130 OS species were quantified (Table 1 and Table S1). The
quantified species included isoprene-derived OSs (OS\textsubscript{i}), monoterpane-derived OSs (OS\textsubscript{m}), C\textsubscript{2}-C\textsubscript{3} OSs, aliphatic OSs, and aromatic OSs (Hettiyadura et al. 2019). The recoveries of OS standards ranged from 84\% to 94\%. Detailed data quality control was described in our recent publication (Wang et al. 2021). In addition, more details about the classification and quantification of OSs were described in the Supplementary Information (Sect. S1) and Table S1.

The mass concentrations of organic carbon (OC) and elemental carbon (EC) were determined via an OC/EC analyzer (DRI Model 2015). The mass concentrations of OC were converted to those of organic matter (OM) using a conversion factor of 1.6 (Turpin and Lim 2001; Wang et al. 2021; Wang et al. 2018). The mass concentrations of inorganic ions in PM\textsubscript{2.5} samples, including Na\textsuperscript{+}, NH\textsubscript{4}\textsuperscript{+}, K\textsuperscript{+}, Mg\textsuperscript{2+}, Ca\textsuperscript{2+}, Cl\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}, and SO\textsubscript{4}\textsuperscript{2-}, were measured using an ion chromatograph system (ICS-5000+, Thermo, USA).

A thermodynamic model (ISORROPIA-II) was used to predict the mass concentration of ALW and pH (Guo et al. 2015; Hennigan et al. 2015). The model was operated with particle-phase concentrations of Na\textsuperscript{+}, SO\textsubscript{4}\textsuperscript{2-}, NH\textsubscript{4}\textsuperscript{+}, NO\textsubscript{3}\textsuperscript{-}, Cl\textsuperscript{-}, Ca\textsuperscript{2+}, K\textsuperscript{+}, and Mg\textsuperscript{2+}, as well as ambient temperature (T) and RH as the inputs. Moreover, the forward mode with the thermodynamically metastable state was selected. The detailed descriptions on ALW and pH predictions were shown in our previous studies (Wang et al. 2021; Xu et al. 2020).

2.3. Auxiliary Data and Data Analysis

The transport trajectories of air masses arriving at the sampling sites during the
sampling period were created using the database of NOAA’s Air Resources Laboratory (NOAA’s Air Resources Laboratory, USA) and MeteoInfoMap software coupled with TrajStat program (Chinese Academy of Meteorological Sciences, China). The data of T, RH, wind speed, and UV irradiation as well as the concentrations of NO, NO₂, O₃, SO₂, and PM₂.₅ at the urban and suburban sites were obtained from the environmental monitoring stations of Xuhui (~4 km away from the sampling site) and Pudong Huinan (~10 m away from the sampling site), respectively. The ventilation coefficient (VC) can be used to characterize the state of atmospheric dilution in pollutant concentrations (Gani et al. 2019). The VC value can be expressed as a product of wind speed and planetary boundary layer height (PBLH).

3. Results and Discussion

3.1. Molecular compositions and concentrations of OSs

The mass concentrations and mass fractions of the OS species in PM₂.₅ collected in Shanghai were shown in Figure 1, with a focus on their spatial and diurnal differences. On average, isoprene-derived OSs (i.e., OSᵢ) were the dominant components at both urban and suburban sites (Figures 1a,d), which accounted for 53.9 ± 0.1% and 48.1 ± 0.1% of the total OS masses, respectively. The mass fractions and concentrations of C₅H₁₁O₃S⁻ were the highest among all kinds of OSᵢ. In contrast, OSᵢ containing nitrogen atoms only accounted for a small proportion of OSᵢ in both urban and suburban areas (Figures 1a,d and Table S2). Monoterpene-derived OSs (OSₘ) were the second most abundant OS components, whose concentrations averaged 30.6
Moreover, the abundance of OS$_m$ was also less controlled by nitrogen-containing OS$_m$.

On average, the OS species with two or three carbon atoms (C$_2$-C$_3$ OSs) and anthropogenic OSs (OS$_a$) together contributed to 26.8% and 33.1% of total OS concentrations in the urban and suburban areas, respectively (Figures 1a,d and Table S3). A similar pattern in the relative abundance of different groups of OSs was also observed at the same sites in summer 2020 (Figure S2). The predominance of OS$_i$ was well documented by many previous observations in Beijing, China (Wang et al. 2018), Guangzhou, China (Bryant et al. 2021), and Atlanta, Georgia, USA (Hettiyadura et al. 2019), Hong Kong, China (Wang et al. 2022), Copenhagen, Denmark (Nguyen et al. 2014), Centreville, AL, USA (Hettiyadura et al. 2017), Zion, Illinois, USA (Hughes et al. 2021). A reasonable explanation for these cases is that there is a large biogenic emission of isoprene, particularly during summer days with higher temperature than in other seasons (Bryant et al. 2021). Interestingly, we found that the mass concentrations of all types of OSs (i.e., total OS$_i$, OS$_m$, C$_2$-C$_3$ OSs, and OS$_a$) tended to decrease from the urban area to the suburban area. This spatial difference in OS concentrations can be attributed to varied atmospheric oxidation capacity and aerosol properties (e.g., sulfate, acidity, and ALW) (Wang et al. 2021), which will be discussed in detail below.

Table S4 gives an overview of OSs in PM$_{2.5}$ in different regions around the world. The concentrations of total OSs in our study (more than 102.3 ng m$^{-3}$) were higher than those in Copenhagen, Denmark (75.7 ng m$^{-3}$) (Nguyen et al. 2014), and Beijing, China (27.4 ng m$^{-3}$) (Wang et al. 2018). However, the OSs showed a lower concentration in
Shanghai compared to the observations in Guangzhou (486.4 ng m\(^{-3}\)) (Wang et al. 2022) and Atlanta, USA (Hettiyadura et al. 2019) (1249.4 ng m\(^{-3}\)). The concentrations of OS\(_i\) in this study were lower than those observed in summertime Atlanta, USA (1123.0 ng m\(^{-3}\)) (Hettiyadura et al. 2019), Guangzhou, China (460.2 ng m\(^{-3}\)) (Wang et al. 2022), and Hongkong, China (163.2 ng m\(^{-3}\)) (Wang et al. 2022), but higher than Copenhagen, Denmark (11.3 ng m\(^{-3}\)) (Nguyen et al. 2014). For OS\(_m\) and C\(_2\)-C\(_3\) OSs, their concentrations also showed a variable range in different regions (Table S4). The concentrations of OS\(_a\) in this study were much higher than those in previous observations (Hettiyadura et al. 2017; Kanellopoulos et al. 2022), which is likely explained by more OS\(_a\) species being quantified or higher air pollution levels in this study.

In general, the abundances of OS\(_i\) and OS\(_m\) were higher than those of other quantified OSs in summer (Table S4). Thus, the yield of summertime OSs in different regions largely depends on the emission level of biogenic VOCs and the air pollution status.

We found that the contributions of total OSs to OM were 1.3 ± 0.5% and 1.9 ± 0.5% at urban and suburban sites in summer 2021, respectively. These proportions of total OSs in OM were larger than those observed in Beijing, China (0.3%) (Wang et al. 2018) and Centreville, USA (0.2%) (Hettiyadura et al. 2017). However, significant higher contribution of total OSs to OM was observed in Atlanta, USA (10.3%) (Hettiyadura et al. 2019) where the formation of OSs was dominated by the oxidation of biogenic VOCs.

In particular, total OSs contributed to 1.2 ± 0.8% of OM in summer 2015 and 1.1 ± 0.8% of OM in summer 2019 in urban Shanghai (Wang et al. 2021). Thus, although anthropogenic emission reduction has been vigorously promoted by the local
government in recent years, the contribution of SOA to OM in Shanghai has not decreased significantly as expected.

Figures 1b,e show diurnal differences in the mass concentrations and mass fractions of the OS components in PM$_{2.5}$ collected at the urban site. The OS$_i$ was the dominant sulfur-containing species regardless of in daytime and nighttime. However, the concentrations of OS$_i$ exhibited a significant decrease from the daytime (117.8 ± 148.1 ng m$^{-3}$) to the nighttime (43.9 ± 62.0 ng m$^{-3}$), except for isoprene-derived nitrooxyorganosulfates (NOS$_i$). Moreover, the variations in OS$_i$ mass concentrations (~2 times) were much larger than those in OS$_i$ mass fractions (< 1.2 times). These results indicate that the production of major OS$_i$ (e.g., C$_{5}$H$_{11}$O$_{7}$S$^-$, C$_{5}$H$_{6}$O$_{2}$S$^-$ and C$_{2}$H$_{5}$O$_{2}$S$^-$) was weakened during the nighttime. In contrast, the higher concentration for these OS$_i$ in the daytime can be attributed to the increased levels of precursors (e.g., isoprene) (Bryant et al. 2021) and oxidants (e.g., O$_3$) (Table S5) as well as the strong photochemistry in the daytime. Although the average fraction of NOS$_i$ was higher in the nighttime than in the daytime, their concentration was similar between the daytime and nighttime. This is because that several special NOS$_i$ (e.g., C$_{5}$H$_{10}$NO$_{9}$S$^-$, C$_{5}$H$_{6}$NO$_{10}$S$^-$, C$_{4}$H$_{8}$NO$_{2}$S$^-$, and C$_{3}$H$_{5}$NO$_{3}$S$^-$) peaked in the daytime, although C$_{5}$H$_{9}$N$_{2}$O$_{13}$S$^-$ showed maximum in the nighttime (Table S2). Previous laboratory studies have suggested that the formation of C$_{5}$H$_{10}$NO$_{9}$S$^-$ is mainly related to •OH oxidation processes (Hamilton et al. 2021). Thus, a strong photochemical oxidation during daytime can be responsible for the increases in concentrations of these NOS$_i$ (particularly C$_{5}$H$_{10}$NO$_{9}$S$^-$) from the nighttime to the daytime. Overall, the diurnal
variations of other OSs including OS\textsubscript{m}, C\textsubscript{2}-C\textsubscript{3} OSs, and OS\textsubscript{a} were similar to that of OS\textsubscript{i}, with a higher level in the daytime than in the nighttime excepting for NOSs (Figure 1 and Tables S2 and S3). It is noteworthy that the fractions and concentrations of monoterpane-derived NOSs (NOS\textsubscript{m}) were higher in the nighttime than in the daytime (Table S2). This case can be attributed to NO\textsubscript{3}\textsuperscript{-}-related nighttime chemistry (Wang et al. 2018). Thus, these findings further emphasize the importance of photochemistry for daytime OS formation and nighttime chemistry for NOS (in particular NOS\textsubscript{m}) formation in urban Shanghai.

The concentrations of various types of OSs at the suburban site were lower than those at the urban site in both daytime and nighttime (Figures 1e,f). However, the characteristics of diurnal difference in various OSs at the suburban site were similar to those observed at the urban site, which showed a substantially higher OS level in the daytime. A similar case was also found in Beijing in 2016 (Wang et al. 2018) and Shanghai in 2017 (Cai et al. 2020). Clearly, the aerosol OS abundance in Shanghai was mainly controlled by the OS formation process in the daytime rather than in the nighttime.

3.2. Time series of the major OSs

Figures 2a-2h compare the time series of the major OS species and inorganic ions in PM\textsubscript{2.5} collected at urban and suburban sites. The OS\textsubscript{i} concentrations peaked during daytime on July 11 and 12, with maximum values of 479.8 ng m\textsuperscript{-3} and 309.5 ng m\textsuperscript{-3} at urban and suburban sites, respectively. Owing to the high proportion of OS\textsubscript{i} in total OSs,
total OS concentrations also showed maximum values during July 11 and 12. The mass concentrations of total OSs, OS$_i$, and C$_5$H$_{12}$O$_7$S$^-$ (a major OS$_i$ component) decreased from July 11 to July 14 (period A; i.e., relatively polluted period) in both urban and suburban areas, whereas their concentrations exhibited a quite small fluctuation after July 14 (period B; i.e., clean period). As a result, the mean concentrations of total OSs and OS$_i$ were ~4 times higher in the period A than in the period B. The temporal variations in the concentrations of OS$_m$, C$_8$H$_{13}$O$_7$S$^-$ (a major component of OS$_m$) (Schindelka et al. 2013), OS$_a$, and C$_2$-C$_3$ OSs were similar to those of total OSs and OS$_i$. However, the dissimilarities in the diurnal variations of OSs in period A and period B suggest that the sources or levels of precursors and oxidants associated with OS formation differed between these two periods. This consideration was further supported by decreasing O$_3$ and NO$_2$ levels from period A to period B (Table S5 and Figures 2i,j).

Sulfate showed a temporal variation similar to total OSs, OS$_i$, and OS$_m$ concentrations in most days (Figures 2g,h). We observed several abnormally high sulfate events during period B (from the evening of the 17th to 18th). The transport distance of air mass on July 18 was found to be shorter than that in other days (Figure S3); moreover, VC value was lower on July 18 than on other days (Figure S4). Thus, this high sulfate case can be partly attributed to the special meteorological conditions on July 18. In general, sulfate concentrations showed a strong correlation with total OSs, OS$_i$, and OS$_m$ concentrations at both sites ($P < 0.01$, $r = 0.76$–0.78). These results indicate that the abundances of OSs in these two study areas were tightly associated with sulfate-related particle-phase chemistry (Surratt et al. 2008).
The concentrations of total OSs, OS, and OSm exhibited a distinct diurnal variation during period A at both sites, with a higher concentration in the daytime. The diurnal variation pattern of OSs was similar to those of O₃ and sulfate. These findings imply an important role of atmospheric oxidation capacity and sulfate in daytime OS formation. Exceptionally, although a clear diurnal pattern was also observed for NOSₘ, their concentrations peaked in the nighttime, suggesting that the formation of NOSₘ was highly affected by the NO₂⁻-related nighttime chemistry (Iinuma et al. 2007; Surratt et al. 2008). In the period B, the concentrations of various OSs showed a weak diurnal variation, with a slightly higher level in the daytime.

As mentioned above, the ambient levels of oxidants (e.g., O₃ and NO₂) and sulfates showed a significant difference in period A and period B, which were tightly associated with the formation of OSs (Wang et al. 2021). Cluster analysis of backward trajectories showed that air masses arriving at both urban and suburban sites in the period A mainly originated from the continental region, with significant influences of anthropogenic emissions (e.g., NOₓ and SO₂) from southern YRD. Furthermore, considering the distinct and similar diurnal variation of O₃, NO₂, SO₂, sulfate, and OSs during period A at both sites, aerosol OSs can be assumed to be mainly formed in local areas. In contrast, these two sampling sites were primarily affected by air masses transported from the East China Sea in the period B. Moreover, the average VC value in the period A was two times lower than that in the period B (Table S5), implying relatively weaker diffusion and dilution of air pollutants in the period A. These factors can be partly responsible for the higher oxidant and sulfate concentrations in the period A than in the
period B. Similarly, since the suburban site is closer to the East China Sea with a decreased influence from anthropogenic emissions (Figure 3), the levels of O₃, NOₓ, and sulfate were higher at the urban site than at the suburban site (Figure 2 and Table S5). The differences in the concentration of oxidants and sulfate might provide an explanation for the difference in the concentrations of OSs between periods A and B as well as between urban and suburban sites.

3.3. Formation mechanisms of OSs

3.3.1 Isoprene-derived OSs

Previous laboratory studies have suggested that isoprene can react with •OH to form IEPOX in the gas phase under low NOₓ conditions (Fabien et al. 2009). In the daytime, ambient O₃ can be rapidly photolyzed to generate •OH under the influence of UV (Kourtchev et al. 2015). Thus, O₃ and UV could serve as a proxy of •OH. Considering a significant role of photochemistry and sulfate-related heterogeneous chemistry in the formation of OSs, OS production is expected to be closely associated with isoprene, O₃, UV, and sulfate. Specifically, the simplified pathways leading to the formation of OSᵢ in the atmosphere can be derived as follows.

\[
\begin{align*}
\text{O}_3 + h\nu &\rightarrow \text{O}^1(\text{D}) + \text{O}_2 & J_{\text{O}_3} && (1) \\
\text{O}^1(\text{D}) + \text{H}_2\text{O} &\rightarrow 2 \cdot\text{OH} & k_1 && (2) \\
\text{O}^1(\text{D}) + \text{M} &\rightarrow \text{O}^3(\text{P}) + \text{M} & k_2 && (3) \\
\text{Isoprene} + \cdot\text{OH} &\rightarrow \text{X} & k_3 && (4) \\
\text{X} + \text{SO}_4^{2-} &\rightarrow \text{OS}_i & k_4 && (5)
\end{align*}
\]
Where \( J_{O_3} \) is the photolysis rate constant, \( k_{1-4} \) is the second-order rate coefficient, \( M \) is \( \text{N}_2 \) or \( \text{O}_2 \), and \( X \) represents the potential products (e.g., IEPOX and HMML) of isoprene oxidation by •OH.

Assuming the concentrations of \( \text{O}(^1\text{D}) \) and •OH are in the steady state, we can derive the following equations (Seinfeld and Pandis, 2016).

\[
[\text{O}(^1\text{D})] = \frac{J_{O_3}[O_3]}{k_1[H_2O] + k_2[M]} \quad (6)
\]

\[
[\text{•OH}] = 2\tau_{\text{OH}}k_1[\text{O}(^1\text{D})][H_2O] \quad (7)
\]

Where \( \tau_{\text{OH}} \) is the average lifetime of •OH. In general, \( J_{O_3} \) is linearly dependent on the UV radiation, i.e., \( J_{O_3} = \varphi \text{UV} \), where \( \varphi \) is the slope of the linear fitting between \( J_{O_3} \) and UV radiation (Li et al. 2022). Combining equation (6) and (7), the steady-state •OH concentration can be expressed as:

\[
[\text{•OH}] = \frac{2\tau_{\text{OH}}k_3[H_2O][O_3][I\text{soprene}]}{k_1[H_2O] + k_2[M]} = \alpha \varphi \tau_{\text{OH}} \text{UV}[O_3] \quad (8)
\]

\[
\alpha = \frac{2k_3[H_2O]}{k_1[H_2O] + k_2[M]} \quad (9)
\]

Also, assuming a steady-state to the oxygenated organic intermediates (i.e., \( X \)), we can derive:

\[
[X] = k_3\tau_X[I\text{soprene}][\text{OH}] = \alpha \varphi k_3\tau_X\tau_{\text{OH}}[I\text{soprene}]\text{UV}[O_3] \quad (10)
\]

Where \( \tau_X \) is the average lifetime of \( X \) in the atmosphere.

During the strong formation of OSi via the heterogeneous reactions of \( X \) on acidic sulfate, the change in the abundance of OSi is expected to be proportional to its formation rate:

\[
\frac{d[\text{OSi}]}{dt} \propto k_4[SO_4^{2-}][X] \propto \alpha \varphi k_3k_4\tau_X\tau_{\text{OH}}[I\text{soprene}]\text{UV}[O_3][SO_4^{2-}] \quad (11)
\]

It should be noted that the above equations are derived based on the assumption...
that the reaction between O(\(^1\)D) and H\(_2\)O is a major source of summertime •OH in the studied areas. Given that a linear relationship was observed between atmospheric •OH and \(J(\text{O}(\text{1D}))\) in different atmospheres (Stone et al., 2012), such an assumption seems to be reasonable. When isoprene is in a steady state in the atmosphere, OS\(_i\) production is expected to be proportional to the product of O\(_3\), UV, and sulfate.

\[
\frac{d[\text{OS}\_i]}{dt} \propto \text{UV}[\text{O}_3][\text{SO}_4^{2-}] \tag{12}
\]

It should be noted that equation (12) did not consider the influences of aerosol acidity, ALW, and other factors (e.g., •OH production from the photolysis of nitrous acid and aldehydes during the daytime). However, the deduction can at least suggest that the secondary production of OS\(_i\) is positively correlated with the value of UV[O\(_3\)][SO\(_4^{2-}\)]. Indeed, the concentrations of daytime OS\(_i\) and major OS\(_i\) species showed a linear positive relationship with the value of UV[O\(_3\)][SO\(_4^{2-}\)] at both urban and suburban sites (\(r = 0.84\)–\(0.92, P < 0.01\)) (Figure 4a-c). We found that the correlation between major OS\(_i\) species and UV[O\(_3\)][SO\(_4^{2-}\)] was stronger than the correlation of major OS\(_i\) species with O\(_3\) and SO\(_4^{2-}\) (\(r < 0.82, P < 0.01\)); moreover, there was no significant correlation between major OSs and UV (\(P > 0.05\)). Thus, our results provide field evidence that the formation of daytime OS\(_i\) in these two study areas was mainly controlled by •OH oxidation of isoprene; moreover, the higher concentration of OS\(_i\) in the urban area can be attributed to the stronger atmospheric oxidation capacity (i.e., higher UV[O\(_3\)] value) and more serious anthropogenic sulfate pollution (particularly during period A). We also observed that the OS concentrations did not significantly increase in several high sulfate events in the period B. One possible explanation is that
these abnormal high sulfate events resulted in excessive $\text{SO}_4^{2-}$ in the formation of OSs. 2-MT-OS and 2-MGA-OS have been identified as important tracers of isoprene-derived SOA (Hettiyadura et al. 2019; Cai et al. 2020). During isoprene oxidation by •OH, these two OS species are produced under low (i.e., IEPOX pathway) and high (i.e., HMML or methacrylic acid epoxide (MAE) pathways) NO$_x$ conditions, respectively (Surratt et al. 2010; Nguyen et al. 2015). The ratios of 2-MT-OS concentration to 2-MGA-OS concentration in the daytime were 9.7 ± 3.1 and 12.1 ± 5.5 at urban and suburban sites, respectively (Figure S5b). A 2-MT-OS/2-MGA-OS ratio of larger than 1 was also found in observations in summer 2020 (Figure S5a), suggesting low NO$_x$ channel dominated the formation of daytime OS$_i$ in the two study areas. This finding was similar to previous observations in Beijing (3.2) (Wang et al. 2020) and Guangzhou (7.6) (Bryant et al. 2021). Other abundant OS$_i$ compounds including C$_5$H$_7$O$_7$S$^-$, C$_4$H$_7$O$_6$S$^-$, and C$_5$H$_9$O$_7$S$^-$ can be produced by the photooxidation of isoprene, heterogeneous oxidative aging of 2-MT-OS, or sulfate radical-initiated reaction with methacrolein and methyl vinyl ketone in the aqueous phase (Schindelka et al. 2013; Wach et al. 2019; Hettiyadura et al. 2015). These OSs showed strong correlations ($r = 0.74$–0.90, $P < 0.01$) with UV[O$_3$][SO$_4^{2-}$], which further highlights the significance of the photochemistry in OS$_i$ formation.

In the nighttime, the formation •OH can be primarily attributed to the reactions of olefins and O$_3$ (Paulson and Orlando 1996). As shown in Figures 4d-f, total OS$_i$ and major OS$_i$ compounds were significantly correlated with the product of O$_3$ and SO$_4^{2-}$ concentrations ($P < 0.01$, $r = 0.96$–0.98). Since the nighttime oxidant level (including
O₃ and •OH) was substantially lower than that in the daytime (Table S5), the production of OSᵢ was weakened in the nighttime (Table S2). It is interesting to note the 2-MT-OS/2-MGA-OS mean ratio in the nighttime was 13.1–15.0 (Figure S5(b)), significantly higher than the mean ratio (9.7–12.1) in the daytime, indicating that the IEPOX pathway may be a potential mechanism to generate OSᵢ in the nighttime. Another possible explanation for the smaller OS concentration in the nighttime is that these OSs were mainly formed during the daytime, but had a significantly lower concentration in the nighttime due to the dilution and deposition.

Furthermore, NO₃• chemistry in the nighttime was another possible pathway to form OSᵢ, particularly NOSs. The nighttime NOS concentration was linearly correlated with the product of NO₂ and O₃ ([NO₂][O₃], i.e., a proxy of NO₃•) (Figure S6).

Interestingly, most of NOSᵢ (e.g., C₅H₁₀NO₃S⁻, C₅H₈NO₁₀S⁻, C₆H₇NO₂S⁻, and C₇H₈NO₂S⁻) have higher concentrations in the daytime, excepting for C₅H₆N₂O₁₁S⁻.

Thus, although nighttime NO₃• chemistry was important, the NOSᵢ formed via photochemistry under the influence of NOₓ in the daytime was still dominant contributors to total NOSᵢ in our study areas. Regarding C₅H₆N₂O₁₁S⁻, its formation pathway is mainly the NO₃• oxidation of C₅H₆NO₃ as illustrated in Figure S7 (Hamilton et al. 2021). Accordingly, the abundance of C₅H₆N₂O₁₁S⁻ peaked during the nighttime (Figure S8). It should be pointed out that the •OH oxidation of C₅H₆NO₃ can also contribute to the production of C₇H₁₀NO₅S⁻ (Figure S7). Clearly, this mechanism can be responsible for the higher C₅H₁₀NO₅S⁻ concentrations in the daytime as mentioned above. In general, increased OSᵢ level in the daytime demonstrated that the
formation of OS$_i$ in urban and suburban areas was largely controlled by photooxidation
of isoprene in the presence of sulfate in the daytime, rather than nighttime NO$_3$•
chemistry. Moreover, a decrease in average OS$_i$ level from the urban area to the
suburban area can be explained by the weakened photooxidation of isoprene and the
decreased anthropogenic sulfate pollution (particularly in the relatively polluted period).

3.3.2 Monoterpene-derived OSs

The concentrations of the most abundant OS$_m$ species ($C_{10}H_{15}O_7S^-$ and $C_{8}H_{13}O_7S^-$)
showed a strong correlation with the value of UV[O$_3$][SO$_4^{2-}$] (and UV[O$_3$][SO$_2$]) in the
daytime at both urban and suburban sites ($r = 0.82–0.86, P < 0.01$), indicating that the
photooxidation of monoterpenes was a significant source for OS$_m$. Previous studies also
demonstrated that $C_{10}H_{15}O_7S^-$ can be produced through the photooxidation of
monoterpenes or sulfate radical reaction with α-pinene (Surratt et al. 2008; Nozière et
al. 2010).

In the nighttime, the concentrations of nitrogen-free OS$_m$ species decreased
significantly with a decrease in the O$_3$ levels (Wang et al. 2020). However, NOS$_m$
species increased in concentration in the nighttime and showed a significant correlation
with the value of [O$_3$][NO$_2$] (the proxy of NO$_3$•, as mentioned above) ($r = 0.90–0.95, P$
$< 0.01$). Accordingly, nighttime NO$_3$• chemistry exerted a significant influence on the
abundance of NOS$_m$ in these study areas. A study by Hamilton et al., (2021) has reported
that NO$_3$• chemistry plays an important role in the production of NOS$_m$. However, the
overall lower OS$_m$ level in the nighttime (Table S2) suggests that daytime OS$_m$
production via monoterpenes photooxidation was still the dominant contributor to total OS$_m$ throughout the day. Although several field studies have reported the abundance of various NOS$_m$ (e.g., C$_{16}$H$_{16}$NO$_7$S$^-$ and C$_{8}$H$_{14}$NO$_8$S$^-$) (Wang et al. 2018; Bryant et al. 2021; Cai et al. 2020), their structures, formation mechanisms, and relevant diurnal variations remain large uncertainties, which need to be deeply explored in the future research.

### 3.3.3 C$_2$-C$_3$ and anthropogenic OSs

The OS species with two or three carbon atoms (C$_2$-C$_3$ OSs) are generally considered to originate from both biogenic and anthropogenic emissions (Wang et al. 2020). The abundant C$_2$-C$_3$ OS species, including C$_2$H$_3$O$_6$S$^-$ (glycolic acid sulfate; GAS), C$_3$H$_5$O$_5$S$^-$ (hydroxyacetone sulfate; HAS), and C$_3$H$_5$O$_6$S$^-$ (lactic acid sulfate; LAS), were significantly correlated with the values of UV[O$_3$][SO$_4^{2-}$] in the daytime at both urban and suburban sites ($r = 0.79$–$0.91$, $P < 0.01$), indicating that the photochemical processes largely contributed to the formation of C$_2$-C$_3$ OSs. Recently, the heterogeneous •OH oxidation of particulate 2-MT-OS has been shown to generate a series of C$_2$-C$_3$ OSs (e.g., C$_2$H$_3$O$_6$S$^-$, C$_3$H$_5$O$_6$S$^-$, and C$_3$H$_5$O$_5$S$^-$) (Chen et al. 2020). Moreover, C$_3$H$_5$O$_6$S$^-$ and C$_3$H$_5$O$_5$S$^-$ have previously been reported to be produced by the photooxidation of diesel vehicle exhausts (Blair et al. 2017).

Most of the quantified OS$_a$ compounds, including C$_{13}$H$_{25}$O$_5$S$^-$, C$_6$H$_{15}$O$_3$S$^-$, C$_3$H$_7$O$_4$S$^-$, benzyl sulfate (C$_7$H$_7$O$_4$S$^-$), phenyl sulfate (C$_6$H$_5$O$_4$S$^-$), as well as C$_6$H$_6$O$_3$S$^-$, C$_3$H$_4$O$_4$S$^-$, and C$_4$H$_2$O$_2$S$^-$, exhibited a strong correlation ($P < 0.01$) with the values of UV[O$_3$][SO$_4^{2-}$] in the daytime. C$_{13}$H$_{25}$O$_5$S$^-$ has been detected in diesel exhaust
(Cui et al. 2019), which is the homologous compound of C_{12}H_{23}O_{5}S^- produced from dodecane photooxidation (Riva et al. 2016b). A chamber study has detected C_{9}H_{15}O_{7}S^- in decalin SOA and speculated that it was produced via •OH oxidation of a C_9-carbonyl hydroperoxide (C_{9}H_{10}O_2) and subsequent reaction on acidic sulfate aerosols (Riva et al. 2016b). In addition, photooxidation of diesel fuel vapor in the presence of SO_2 has been suggested to be an important source of C_{8}H_{14}O_{6}S^-, C_{7}H_{16}O_{3}S^-, and C_{6}H_{12}O_{4}S^- species (Blair et al. 2017). The formation of C_{7}H_{14}O_{5}S^- and C_{6}H_{15}O_{4}S^- can also be attributed to the photooxidation of naphthalene and 2-methylnaphthalene (Riva et al. 2015).

We note that the concentrations of most of C_2-C_3 OS and OS_a species decreased significantly from the daytime to the nighttime (Table S2 and Table S3). The dilution and deposition effects from the daytime to the nighttime were important factors controlling nighttime levels of C_2-C_3 OSs and OS_a. In addition, the nighttime gas-phase oxidation process was also likely associated with C_2-C_3 and anthropogenic OS formation at both urban and suburban sites, as suggested by the significant correlations of C_2-C_3 OSs and OS_a with O_3 and [O_3][NO_2] in the nighttime ($r = 0.89-0.91$, $P < 0.01$).

Overall, these results further highlight the importance of photochemistry in controlling the all-day abundance of OSs, as discussed earlier.

### 3.3.4 The effects of ALW and pH on OS formation

We have demonstrated that the atmospheric oxidation capacity (e.g., UV[O_3] and [O_3 + NO_2]), sulfate pollution, and nighttime NO_3• chemistry exerted considerable influences on the formation of OSs in both urban and suburban areas. In addition,
laboratory and field studies have suggested that aerosol properties including acidity and ALW also play important roles in OS formation (Inuma et al. 2007; Surratt et al. 2007b; Wang et al. 2020; Wang et al. 2018; 2022). The aerosol pH in Shanghai in summer averaged 2.7 ± 0.9 and 2.2 ± 0.7 in urban and suburban areas, respectively. The mean pH value was similar to that in northern China (summer) (Ding et al. 2019; Wang et al. 2018), but higher than that in the Pearl River Delta (PRD) region (Fu et al. 2015). In this study, only the 2-MT-OS concentration showed an evident negative correlation with the pH value ($r = 0.58$, $P < 0.05$), suggesting the aerosol acidity is not a limiting factor for the formation of most OS species.

A positive correlation was observed between the concentrations of OSs and ALW only in the urban area during both daytime and nighttime (Figure 5), consistent with our previous observations in urban Shanghai (Wang et al. 2021). It is interesting to note that although higher ALW concentrations and lower pH values were observed at the suburban site, the OS concentrations were significantly higher at the urban site (Table S5). This result further confirms that atmospheric oxidation capacity and sulfate pollution level governed the formation of OSs in urban and suburban Shanghai (particularly in the relatively polluted period), though ALW and aerosol acidity also played a role. Therefore, a synergistic regulation of atmospheric oxidation capacity and anthropogenic SO$_2$ emissions would be important for the mitigation of OS and SOA pollution in the megacity Shanghai.

4. Conclusions
We investigated the spatial and diurnal variations of aerosol OS formation in Shanghai in summer. Isoprene- and monoterpened-derived OSs were found to be the dominant OS groups during the entire sampling campaign, likely suggesting that the formation of OSs was largely controlled by biogenic VOCs. Most OSs decreased from the daytime to the nighttime, while NOS$_m$ peaked during nighttime. These findings suggested that OSs were mainly produced via daytime formation processes in both urban and suburban areas, excepting NOS$_m$. Moreover, the average abundance of various types of OSs showed a decrease trend from the urban area to the suburban area, which can be explained by weakened atmospheric oxidation capacity and sulfate pollution in the suburban area (primarily in the relatively polluted period). Further, daytime OS formation was concretized according to the interactions among OSs, UV, O$_3$, and SO$_4^{2-}$, suggesting that the concentrations of most OSs were significantly correlated with the values of UV[$O_3$][SO$_4^{2-}$] during daytime in both urban and suburban Shanghai. We concluded that an enhancement in the photochemical process and sulfate level can exacerbate OS pollution in the urban area. These findings were summarized in a diagram (Figure 6). Generally, our study not only deepens the understanding about the importance of photochemical process and anthropogenic sulfate pollution in controlling OS formation but also provides potential management strategies to decrease the abundance of particulate OSs.

**Data availability**

The data presented in this work are available upon request from the corresponding
Supplement

Supplementary information includes the classification of OSs, Table S1-S5, and Figure S1–S8.

Competing interests

The authors declare no competing financial interest.

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Table S1. Organosulfate quantification using UPLC-ESI(-)-QToFMS/(MS).

<table>
<thead>
<tr>
<th>Formula</th>
<th>MW (Da)</th>
<th>Standard</th>
<th>Reference</th>
</tr>
</thead>
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<tr>
<td><strong>Isoprene-derived OSs (n = 19)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₆H₈O₂S⁻</td>
<td>167.0014</td>
<td>Lactic acid sulfate (LAS)</td>
<td>(Schindelka et al. 2013)</td>
</tr>
<tr>
<td>C₆H₈O₂S⁻</td>
<td>182.9963</td>
<td>LAS</td>
<td>(Shalamzari 2013)</td>
</tr>
<tr>
<td>C₆H₈O₂S⁻</td>
<td>197.0120</td>
<td>LAS</td>
<td>(Riva et al. 2016a)</td>
</tr>
<tr>
<td>C₆H₈O₂S⁻</td>
<td>198.9912</td>
<td>LAS</td>
<td>(Hettiyadura et al. 2015)</td>
</tr>
<tr>
<td>C₆H₈O₂S⁻</td>
<td>199.0276</td>
<td>LAS</td>
<td>(Riva et al. 2016a)</td>
</tr>
<tr>
<td>C₆H₈O₂S⁻</td>
<td>210.9912</td>
<td>LAS</td>
<td>(Hettiyadura et al. 2015)</td>
</tr>
<tr>
<td>C₆H₈O₂S⁻</td>
<td>213.0069</td>
<td>LAS</td>
<td>(Riva et al. 2016a)</td>
</tr>
<tr>
<td>C₆H₈O₂S⁻</td>
<td>215.0225</td>
<td>LAS</td>
<td>(Surratt et al. 2010)</td>
</tr>
<tr>
<td>C₆H₈O₂S⁻</td>
<td>237.0069</td>
<td>LAS</td>
<td>(Nozière et al. 2010)</td>
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<td>C₆H₈O₂S⁻</td>
<td>260.0076</td>
<td>LAS</td>
<td>(Surratt et al. 2007a)</td>
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<tr>
<td>C₆H₈O₂S⁻</td>
<td>273.9869</td>
<td>GAS</td>
<td>(Nestorowicz et al. 2018)</td>
</tr>
<tr>
<td>Other quantified isoprene-derived OSs were shown in SI</td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

| **Monoterpene-derived OSs (n = 17)** | | | |
| C₅H₉O₂S⁻ | 223.0276 | Glycolic acid sulfate (GAS) | (Yassine et al. 2012) |
| C₅H₉O₂S⁻ | 239.0225 | GAS | (Nozière et al. 2010) |
| C₅H₉O₂S⁻ | 249.0797 | α-Pinene sulfate | (Wang et al. 2017) |
| C₅H₉O₂S⁻ | 253.0382 | GAS | (Schindelka et al. 2013) |
| C₅H₉O₂S⁻ | 279.0538 | GAS | (Surratt et al. 2007a) |
| C₅H₉O₂S⁻ | 281.0695 | α-Pinene sulfate | (Nozière et al. 2010) |
| C₅H₉O₂S⁻ | 294.0647 | α-Pinene sulfate | (Surratt et al. 2008) |
| C₅H₉O₂S⁻ | 296.0440 | Limonaketone sulfate | (Surratt et al. 2008) |
| C₅H₉O₂S⁻ | 342.0495 | Limonaketone sulfate | (Yassine et al. 2012) |
| C₅H₉O₂S⁻ | 251.0589 | Limonaketone sulfate | (Wang et al. 2017) |
| Other quantified monoterpene-derived OSs were shown in SI | | | |

| **C₂-C₃ OSs (n = 6)** | | | |
| C₄H₈O₂S⁻ | 136.9909 | GAS | (Yassine et al. 2012) |
| C₄H₈O₂S⁻ | 138.9701 | GAS | (Yassine et al. 2012) |
| C₄H₈O₂S⁻ | 152.9858 | GAS | (Hettiyadura et al. 2015) |
| C₄H₈O₂S⁻ | 154.9650 | GAS | (Olson et al. 2011) |
| C₄H₈O₂S⁻ | 155.0014 | GAS | (Hettiyadura et al. 2019) |
| C₄H₈O₂S⁻ | 168.9807 | LAS | (Olson et al. 2011) |
| **OSa (aliphatic-OSs) (n = 53)** | | | |
| C₆H₁₁O₃S⁻ | 210.926 | Sodium octyl | (Wang et al. 2021) |
| Other quantified aliphatic-derived OSs were shown in SI | | | |

| **OSa (aromatic-OSs) (n = 32)** | | | |
| C₆H₈O₃S⁻ | 172.9909 | Methyl sulfate | (Wang et al. 2021) |
| C₆H₈O₃S⁻ | 218.9786 | Methyl sulfate | (Wang et al. 2021) |
| Other quantified aromatic-derived OSs were shown in SI | | | |

| **OSₐ-other (n = 3)** | | | |
| C₆H₈O₃S⁻ | 151.0065 | Methyl sulfate | (Wang et al. 2021) |
| C₆H₈O₃S⁻ | 194.9963 | GAS | (Wang et al. 2021) |
| C₆H₈O₃S⁻ | 209.0120 | GAS | (Berndt et al. 2016) |

* These compounds have been confirmed through structural identification with MS/MS.
Figure 1. Average distributions in the mass concentrations and mass fractions of various OSs in PM$_{2.5}$ in different cases: (a–d) urban vs suburban for all the data, (b–e) daytime vs nighttime in the urban area, as well as (c–f) daytime vs nighttime in the suburban area.
Figure 2. Temporal variations of OSs and other chemical components in PM$_{2.5}$ as well as other data measured in urban and suburban Shanghai in summer. (a–b) OSs, OS$_i$, C$_5$H$_{12}$O$_7$S$^-$, NOS$_i$, and OS/OM; (c–d) OS$_{m_i}$, C$_8$H$_{13}$O$_7$S$^-$, and NOS$_{m_i}$; (e–f) OS$_a$ and C$_2$-C$_3$ OSs; (g–h) PM$_{2.5}$, SO$_4^{2-}$, and NO$_2$; and (i–j) NO$_2$, NO, SO$_2$, and O$_3$. The sampling period A and B indicate the relatively polluted period and the clean period, respectively.
Figure 3. Air mass backward trajectories of the major clusters in different periods in the (a‒b) urban and (c‒d) suburban areas.
Figure 4. Mass concentrations of (a and d) OS_i, (b and e) 2-MT-OS, and (c and f) C_5H_7O_7S⁻ as functions of UV[O_3][SO_4^{2-}] and [O_3][SO_4^{2-}] during daytime and nighttime in the urban (red solid circles) and suburban sites (blue solid circles). The open circles represent outliers, which was attributed to several particularly high sulfate events.
Figure 5. Scatterplots of the ALW concentrations with the mass concentrations of total OSs in PM$_{2.5}$ collected in the (a) urban and (b) suburban areas. Yellow and grey lines show regression lines in the daytime and nighttime, respectively.
Figure 6. Conceptual picture showing the characteristic and atmospheric process of OSs in urban and suburban Shanghai.