

# Temporal trends of the concentration and sources of secondary organic aerosols in PM<sub>2.5</sub> in Shanghai during 2012 and 2018

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## HIGHLIGHTS

- Temporal trend of SOC in PM<sub>2.5</sub> in Shanghai during 2012 and 2018 investigated.
- The concentration of SOC decreasing while the contribution to OC increasing in the last decade.
- Relative contribution of SOA from toluene was found increased but not decreased.
- Biomass burning was the important source of sesquiterpene in Shanghai.
- 2-MG/2-MTLs ratio in urban environment strongly affected by ambient temperature.

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## ABSTRACT

Based on the concentrations of the carbonaceous components and the typical organic tracers in 682 p.m.-2.5 samples collected in Shanghai from 2012 to 2018, the temporal trends of the concentrations and potential sources of the secondary organic aerosols in PM<sub>2.5</sub> in Shanghai were investigated. The annual average concentrations of organic carbon (OC), elemental carbon (EC) and water-soluble organic carbon (WSOC) all showed a decreasing trend along with the PM<sub>2.5</sub> concentration. The annual concentration of total carbon (TC) in 2018 (4.3  $\mu\text{g m}^{-3}$ ) was about 34% of that in 2012. Compared with that in 2013, the concentrations of isoprene and sesquiterpene SOA tracers in 2018 decreased by 48% and 43%. Meanwhile, the concentration of monoterpene SOA tracers kept stable in 2 ng m<sup>-3</sup> to 3 ng m<sup>-3</sup>, and the concentration of toluene SOA tracer decreased slightly from 1.3 ng m<sup>-3</sup> in 2013 to 1.0 ng m<sup>-3</sup> in 2018. Correlation analysis with levoglucosan suggested that biomass burning should be an important source of sesquiterpene in Shanghai. It was found that the 2-MGA/2-MTLs ratio of the isoprene tracers was more strongly affected by the ambient temperature but not NO<sub>x</sub> in Shanghai. The concentration of secondary organic carbon (SOC) estimated with OC/EC-based, WSOC-based and tracer-based methods showed a decreasing trend during the study period, but the contribution of SOC to OC was increasing. Anthropogenic aromatic volatile organic compounds was the increasingly important contributor to the SOC in PM<sub>2.5</sub>, and should be the key pollutants to be controlled to further improve the air quality in Shanghai.

## 1. Introduction

Due to the severe environmental and health impacts, atmospheric fine particles (PM<sub>2.5</sub>) is widely concerned. Organic aerosol (OA) is an important part of PM<sub>2.5</sub>, which is a very complex mixture of different types of organic compounds, and has important potential effects on the earth's radiation balance, water cycle and human health (Yeo et al.,

2019; Li et al., 2020; Khan et al., 2021). Organic aerosols could be either directly emitted (e.g. primary organic aerosol, POA) or indirectly formed in the atmosphere (e.g. secondary organic aerosol, SOA) (Kanakidou et al., 2005). SOA can be formed from the oxidation of volatile organic compounds (VOCs) by O<sub>3</sub>, OH·, NO<sub>3</sub>· or other airborne oxidants through homogeneous (Claeys et al., 2004) or heterogeneous reactions (Jang et al., 2002). OA accounted for 13.0%–40.2% of PM<sub>2.5</sub> in

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different regions of China, and SOA accounted for 24.6%–63.4% of OA (Yao et al., 2016). Therefore, SOA is an important contributor to PM<sub>2.5</sub> (Kramer et al., 2016; Pye et al., 2019).

SOA is generated from both biogenic and anthropogenic VOC precursors. Globally, about 90% of VOCs come from plant emissions, while only 10% come from anthropogenic sources (Atkinson and Arey, 2003; Kleindienst et al., 2009; Ait-Helal et al., 2014). However, anthropogenic SOA may be more important in urban areas (Jiang et al., 2012; Pye et al., 2019). In addition, the chamber experimental data and field observations showed that anthropogenic pollutants such as O<sub>3</sub>, NO<sub>x</sub> and SO<sub>2</sub> had significant impacts on the formation of biological SOA and can accelerate the oxidation of biological VOCs (Paulot et al., 2009; Froyd et al., 2010; Xu et al., 2015; El-Sayed et al., 2018; Hinks et al., 2018; Zhao et al., 2018).

In the past several decades, a great deal of studies on both biogenic and anthropogenic SOA have been conducted, but there are still many uncertainties in the formation mechanism of SOA (Zhang et al., 2011; Zhu et al., 2016; Shen et al., 2018; Liu et al., 2020; Wan et al., 2019; Al-Naiema et al., 2020; Lanzafame et al., 2021). The long-term systematic analysis of the SOA in fine particles is very important to understand its sources and transformation process, and also could help to formulate more effective air quality management strategies.

Shanghai, with a population of nearly 30 million, is one of the most important mega-cities in China and even in the world. The rapid economic growth in the last several decades brought great pressure to the atmospheric environment in Shanghai. In the last decade, a series of laws and regulations, including more stringent emission standards and adjusting the overall industrial and energy structure of Shanghai, have been issued by the Shanghai Municipal Government to protect the atmospheric environment. Continuous investment in environmental protection has improved continuously the air quality of Shanghai (Fig. S1). The annual average concentration of PM<sub>2.5</sub> in Shanghai in 2018 (36 µg m<sup>-3</sup>) was about 26 µg m<sup>-3</sup> lower than that in 2013, and the concentration of SO<sub>2</sub> decreased to 7 µg m<sup>-3</sup>, which was about one third of that in 2013. Meanwhile, the annual concentration of NO<sub>2</sub> decreased slowly and kept at high level, and O<sub>3</sub> showed an increasing trend, suggesting that the atmospheric oxidation capacity in Shanghai is increasing gradually.

In this study, PM<sub>2.5</sub> samples were collected in Shanghai from 2012 to 2018, the temporal trend of concentration, potential sources of the SOA in PM<sub>2.5</sub> in Shanghai were analyzed based on the concentrations of organic carbon (OC), elemental carbon (EC), water-soluble organic carbon (WSOC), and the typical SOA tracers from the oxidation of isoprene, α-pinene, β-caryophyllene and toluene. The purpose of the study is to investigate the possible changes in chemical composition of PM<sub>2.5</sub> during the implementation of various air pollution control measures and with the decreasing PM<sub>2.5</sub> concentration, especially the relative contribution of organic aerosols to PM<sub>2.5</sub> and the contribution of biogenic SOA to organic aerosols in Shanghai.

## 2. Methods and procedures

### 2.1. Sampling

Four sampling sites involved in this study, which were located in Shanghai Baoshan District (BS, E121.394°, N31.314°), Xujiahui District (XH, E121.436°, N31.176°), Qingpu District (QP, E120.988°, N31.096°) and Pudong District (PD, E120.982°, N31.089°) (Fig. 1). The PM<sub>2.5</sub> samples in 2012 were collected at XH, which is located on the rooftop of a building of about 15 m high. Site XH was surrounded by commercial and residential buildings, representing the urban environment of Shanghai. From 2013 to 2014, samples were collected at site BS, which is on the rooftop of a teaching building on the Baoshan Campus (BS) of Shanghai University with a height of about 20 m above the ground. Site BS is located in teaching and residential areas but would be affected by factories 5 or more kilometers away, which is a typical suburban

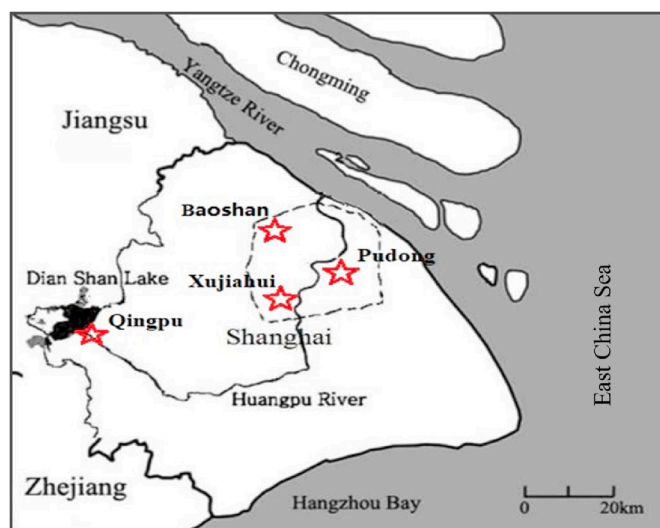


Fig. 1. Map of sampling sites (red stars). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

environment of Shanghai. From 2015 to 2018, PM<sub>2.5</sub> samples were collected simultaneously at PD and QP. The PD site is about 20 m high above the ground, and representative of the densely populated urban areas in Shanghai. The QP site is near the Dianshan Lake, surrounded by farmlands, and representative of Shanghai's suburban environment. But QP is an area with poor air quality in Shanghai due to affections of industrial activities from the surrounding areas and from Zhejiang and Jiangsu Provinces.

Daily PM<sub>2.5</sub> samples were collected in January, March to April, July to August, October to November at XH, and one 24-h PM<sub>2.5</sub> sample was collected every 5 days at BS, QP and XH. A total of 682 samples were collected (2012: 120, 2013–2014: 102, 2015: 112; 2016: 114; 2017: 115; 2018: 119). Samples collected from March to May were regarded as spring samples, June to August for summer, September to November for autumn, and January to February and December for winter. High-volume PM<sub>2.5</sub> samplers (Thermo-Andersen, USA) with a flow rate of 1.13 m<sup>3</sup> min<sup>-1</sup> and quartz fiber filters (20.0 × 25.4 cm, Whatman, UK) were used to collect the samples. Before sampling, the filters were baked at 450 °C for at least 4 h to remove the organic contaminants. PM<sub>2.5</sub> concentration was determined by weighing the filter before and after sampling under constant temperature (20 °C) and humidity (45%).

Based on the meteorological parameters of Shanghai in the past ten years (Fig. S2), the annual average temperature was basically stable and increased slowly. The annual average temperature in 2018 was about 1 °C higher than that in 2012. The relative humidity and wind speed have no obvious changes during the last decade. As a coastal city, Shanghai is affected by the Asian monsoon, the prevailing wind direction in summer is southeasterly (from the sea), while northwesterly in winter, which could be seen from the back trajectories of air parcels arriving in Shanghai in different seasons (Fig. S3).

### 2.2. Chemical analysis

#### 2.2.1. Carbonaceous components

The concentration of OC and EC in PM<sub>2.5</sub> were analyzed with a thermal/optical carbon analyzer (DRI, 2001A, Atmoslytic Inc., USA) with the IMPROVE temperature program and TOT (Thermal/Optical Transmission) method.

To measure the concentration of WSOC, a punch of the sampled filter (3 cm<sup>2</sup>) was ultrasonically extracted with 10 mL Milli-Q water at room temperature for 30 min. The extract was then filtered using 0.45 µm pore syringe filter and analyzed by a carbon analyzer (TOC-LCSH, Shimadzu

Corporation, Japan).

### 2.2.2. Water-soluble inorganic ions

The water-soluble ions were measured by a dual-channel ion chromatography (Metrohm IC, Switzerland). A Metrosep A SUPP5-25 column (length 250 mm, inner diameter 4 mm and particle size 5  $\mu\text{m}$ ) was used to separate the anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ), and a Metrosep C2-250 column (length 250 mm, inner diameter 4 mm and particle size 7  $\mu\text{m}$ ) for the cations ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ). A mixed solution of 3.2 mmol  $\text{L}^{-1}$   $\text{Na}_2\text{CO}_3$  and 1.0 mmol  $\text{L}^{-1}$   $\text{NaHCO}_3$  was used as the anionic eluent, and a mixed solution of 4 mmol  $\text{L}^{-1}$  tartaric acid and 0.75 mmol  $\text{L}^{-1}$  pyridine dicarboxylic acid for cations.

### 2.2.3. Polar organic tracers

The analyzing procedure for polar tracers was adopted from that of Feng et al. (2013) and Kleindienst et al. (2007). 30  $\text{cm}^2$  of each filter was cut and placed in clean glass bottles. Before extraction, methyl- $\beta$ -D-xylanopyranoside (MXP) was spiked into the filters as an internal standard. Ultrasonical extraction with 20 mL of dichloromethane/methanol (1:1 v/v) was conducted at room temperature for three times and the extracts combined. After filtration with quartz wool, the extracts were blown to dryness with ultrapure nitrogen and derivatized with 100  $\mu\text{L}$  N,O-bis-(trimethylsilyl)-trifluoroacetamide (BSTFA, with 1% trimethylchlorosilane as catalyst) and 20  $\mu\text{L}$  pyridine at 75  $^\circ\text{C}$  for 45 min. Hexamethylbenzene was added before injection as injection standard to check the recovery of MXP.

GC-MS analysis was conducted with an Agilent 6890 GC/5975 MSD. The GC was equipped with a DB-5MS capillary column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$  film thickness, J&W Scientific). High-purity helium was used as carrier gas at a flow rate of 1.0  $\text{mL min}^{-1}$ . The MS was operated in EI mode at 70 eV with a scan range of 50–550 amu, and the ion source temperature was 230  $^\circ\text{C}$ . The oven temperature program of the GC and the quantitative method of the target tracers was the same as that of Feng et al. (2013).

### 2.3. Quality assurance and quality control

Field blanks were collected each season and procedure blanks were added every twenty samples, the blank samples were extracted and analyzed in the same way as the ambient samples. Target SOA tracers were not detected in the field and laboratory blanks. Recoveries of MXP were 70%–110% in most samples. The reported results were recovery corrected assuming that the target compounds had the same recovery as MXP. Duplicate analysis showed that the deviation was less than 15%.

## 3. Results and discussions

### 3.1. Temporal trends of carbonaceous aerosols

#### 3.1.1. Concentrations and contributions to $\text{PM}_{2.5}$

Table 1 summarized the annual average concentrations, which was calculated as the average of the seasonal concentrations, of  $\text{PM}_{2.5}$ , OC,

EC, WSOC and ions in Shanghai from 2012 to 2018. We can see that the annual average concentration of the carbonaceous components showed an obvious decreasing trend, similar to that of the  $\text{PM}_{2.5}$  mass. Meanwhile, the WSOC/OC ratio increased from 46% in 2014 to 55% in 2018, suggesting the increasing contribution of WSOC to OC during the last decade.

From 2015 to 2018,  $\text{PM}_{2.5}$  samples were simultaneously collected at PD and QP. QP had higher concentrations of OC, EC, WSOC and ions than that at PD, but the differences were relatively small. Correlation analysis with the daily concentrations showed that the OC, EC and WSOC concentrations between the two sites had strong positive correlations ( $r = 0.87$  for OC, 0.77 for EC and 0.81 for WSOC,  $p < 0.01$ ), suggesting that carbonaceous aerosols in Shanghai had small spatial variation. Previous studies also found that carbonaceous matter in  $\text{PM}_{2.5}$  at different sites in Shanghai had similar concentrations (Ye et al., 2003; Feng et al., 2013). OC concentration in spring of 2012 at XH (7.9  $\mu\text{g m}^{-3}$ ) was very similar with the reported value for the same period at another site in Shanghai (Yangpu, 8.1  $\mu\text{g m}^{-3}$ , Huang et al., 2014). The summer concentration of OC in 2015 in this study (7.1  $\mu\text{g m}^{-3}$  at QP and 6.6  $\mu\text{g m}^{-3}$  at PD) was close to the reported concentration at Xujiahui of Shanghai for the same period (7.2  $\mu\text{g m}^{-3}$ , Zhu et al., 2018). We also analyzed the online monitoring results of  $\text{PM}_{2.5}$  from 2015 to 2019 at nine stations located in different districts of Shanghai, the  $\text{PM}_{2.5}$  concentrations at different sites were strongly correlated and the coefficient of variation for the annual average concentrations at different sites was around 7% (Table S1). Therefore, the current and following comparison and discussions on the results from different sites in Shanghai should be reasonable.

Table 1 showed that the OM/ $\text{PM}_{2.5}$  ratio dropped from 28% in 2012 to 15% in 2018, suggesting that the contribution of organic matter to  $\text{PM}_{2.5}$  mass in Shanghai was decreasing, but not increasing. As shown in Fig. S1, the most impressive achievement of air pollution control in Shanghai was the significant decrease of  $\text{SO}_2$  concentration, we once thought that the relative contribution of organic matter to  $\text{PM}_{2.5}$  would increase. But the inter-annual variation of the OM/Ions ratio (Table 1) indicated that the relative contribution of organic aerosols to inorganic ions kept at stable level during 2013–2018. The results suggested that the air pollution control measures that have been taken in Shanghai/China, such as flue gas desulphurization, more stringent vehicle emission standards, the prohibition of open biomass burning, the reduction of coal usage, were also effective in controlling the organic aerosols.

#### 3.1.2. Seasonal variation

Fig. 2 showed the seasonal concentrations of OC and EC in  $\text{PM}_{2.5}$  in Shanghai from 2012 to 2018, and the daily concentrations could be found in Fig. S4. Distinct seasonal trend of higher in winter and lower in summer was found for both OC and EC, and the seasonal changes in the meteorological conditions in Shanghai should be the main reason (Feng et al., 2013). It can also be seen that the decreasing rate of OC concentration in autumn and winter was significantly higher than that in summer and spring. The winter/summer ratio of OC decrease from about 2.0 in 2012 to about 1.5 in 2018, and the autumn concentration of

**Table 1**  
Annual concentrations of  $\text{PM}_{2.5}$ , carbonaceous species, ions in Shanghai from 2012 to 2018 (unit:  $\mu\text{g m}^{-3}$ ).

Year	2012	2013	2014	2015	2016	2017	2018
Site	XH	BS	BS	QP	PD	QP	PD
$\text{PM}_{2.5}$	58.0	62.7	54.3	61.1	54.0	51.3	43.6
OC	10.2	10.5	9.3	8.5	7.7	4.7	4.5
EC	2.6	2.9	2.8	1.3	1.1	1.0	0.8
WSOC	–	–	4.3	–	–	–	2.2
Levogluconan	–	0.25	0.15	–	–	0.052	0.037
Ions <sup>a</sup>	–	37.6	31.7	–	–	19.0	17.9
OM/ $\text{PM}_{2.5}$ (%) <sup>a</sup>	28	26	27	23	23	15	16
OM/Ions	–	0.45	0.47	–	–	0.40	0.40

<sup>a</sup> Ions was the sum of the measured anions and cations; OM was estimated as  $\text{OC} \times 1.6$  (Turpin and Huntzicker, 1995).

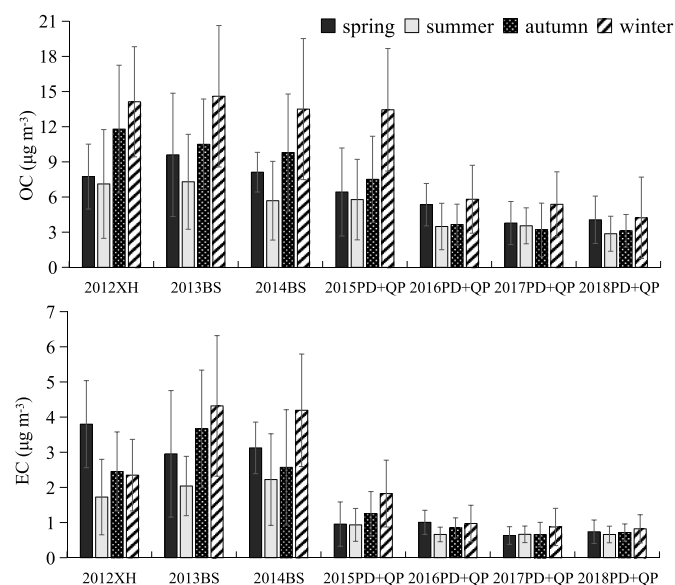


Fig. 2. Seasonal concentrations of OC and EC in Shanghai from 2012 to 2018.

OC was obviously higher than that in summer during 2012–2014, while nearly the same in 2016–2018. As a result, the OC concentration in autumn was higher than that in spring for the year 2012–2015, but lower than that in spring for year 2016–2018, suggesting a changing emission structure in Shanghai during the period. Similar phenomena was also found for the seasonal trend of WSOC. One of the most plausible reason for the changing seasonal trend should be the great reduction of biomass burning in recent years. Strong correlation between OC and levoglucosan, a typical tracer of biomass burning (Simoneit et al., 1999), was found during the whole period ( $r = 0.9$ ,  $p < 0.01$ ), showing that biomass burning was an important contributor to the OC in PM<sub>2.5</sub> in Shanghai. As the impact of biomass burning was stronger in autumn and winter, the fast decrease of the levoglucosan concentration during the period (Table 1) was in agreement with the temporal change in the seasonal trend of the carbonaceous aerosols. Our results also indicated that the national policy of banning open straw burning, which started in 2013, played an important role in improving the air quality in Shanghai and also in China.

### 3.1.3. Estimated contribution of SOC

EC is directly emitted from combustion sources and stable during the atmospheric transport, so it is widely used as a tracer of primary organics (Turpin and Huntzicker, 1995). The concentration of SOC could thus be estimated by the OC/EC-based method presuming that the seasonal minimum OC/EC ratio was the same as that for primary aerosols, and the estimation equation as follow:

$$\text{SOC}_{\text{OC/EC-based}} = \text{OC} - \text{EC} \times (\text{OC/EC})_{\text{min}}$$

The temporal trend of the estimated concentration of SOC<sub>OC/EC-based</sub> and the SOC<sub>OC/EC-based</sub>/OC ratio from 2012 to 2018 were shown in Fig. 3. It can be seen that the SOC<sub>OC/EC-based</sub> concentration showed a decreasing trend, the annual concentration in 2018 was about 43% of that in 2012. While the SOC<sub>OC/EC-based</sub>/OC ratio during 2016–2018 was higher than that in 2012–2013, and also higher than the ratio in 2010 (31%, Feng et al., 2013). As the minimum OC/EC ratio might be higher than the real ratio for the primary particles, the SOC<sub>OC/EC-based</sub> contribution to OC might be underestimated. The lower SOC<sub>OC/EC-based</sub>/OC ratio in 2014 may be due to the disparity between the minimum OC/EC ratio and the primary OC/EC ratio.

It was found that SOA and biomass burning was the main sources of WSOC in PM<sub>2.5</sub> (Weber et al., 2007), and most of the organic matter from biomass burning and SOA were water-soluble (Mayol-Bracero

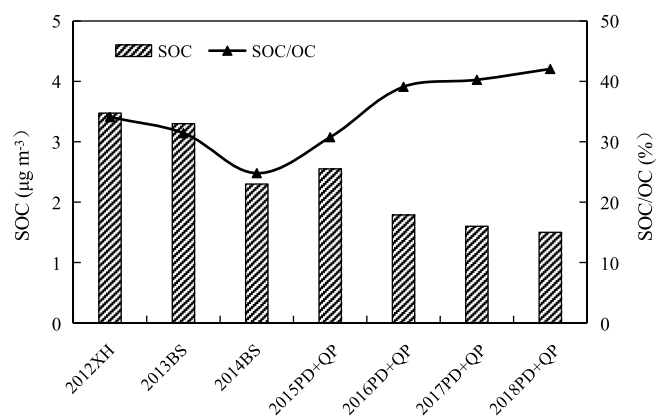


Fig. 3. Temporal trend of SOC<sub>OC/EC-based</sub> in PM<sub>2.5</sub> in Shanghai.

et al., 2002). Therefore, the concentration of SOC in PM<sub>2.5</sub> could be estimated by subtracting the contribution of biomass burning (WSOC<sub>BB</sub>) from the total WSOC with the formula as follows:

$$\text{SOC}_{\text{WSOC-based}} = \text{WSOC}_{\text{total}} - \text{WSOC}_{\text{BB}}$$

Simulated combustion experiments showed that the OC to levoglucosan ratio in the biomass burning emitted fine particles in China was about 8–16 (Zhang et al., 2007). The lowest WSOC/levoglucosan ratio in this study was about 10, so a WSOC/levoglucosan ratio of 10 was used to evaluate the concentration to WSOC<sub>BB</sub> (Feng et al., 2013). The estimated seasonal SOC<sub>WSOC-based</sub> concentrations were shown in Table 2. It can be seen that the SOC<sub>WSOC-based</sub> concentrations in 2017 and 2018 were comparable but lower than that in 2014 in each season, especially in autumn. While the contribution of SOC<sub>WSOC-based</sub> to OC (SOC/OC ratio in Table 2) in 2017–2018 was higher than that in 2014. The highest SOC<sub>WSOC-based</sub>/OC ratio in summer was in accordance with the stronger solar radiation, higher temperature and higher ozone concentration in summer. The annual SOC<sub>WSOC-based</sub>/OC ratio in 2014, 2017 and 2018 were 0.32, 0.45 and 0.51, showing an increasing trend. Estimated WSOC<sub>BB</sub> in 2017–2018 (average at 0.3 µg m<sup>-3</sup>) was less than one fourth of that in 2014, suggesting the greater reduction of primary organic carbon than that of the SOC.

In general, the results from the OC/EC-based and WSOC-based method was comparable, showing that the concentration of SOC in PM<sub>2.5</sub> in Shanghai was decreasing during the study period, while its contribution to OC was increasing.

### 3.2. Concentrations, seasonal variations and temporal trends of SOA tracers

The average seasonal concentrations of the typical SOA tracers during 2016–2018 in Shanghai were listed in Table 3. The annual average concentrations of the SOA tracers from different precursors in 2013–2014, and 2016–2018 were listed in Table 4, and the daily concentrations of the tracers could be found in Fig. S5.

#### 3.2.1. SOA tracers from isoprene

Six tracers of isoprene SOA were quantified, including 2-methylglyceric acid (2-MGA), three C<sub>5</sub>-alkene triols and two 2-methyltetrols (2-

Table 2

Seasonal concentrations and contributions of SOC<sub>WSOC-based</sub> in Shanghai.

SOC (SOC/OC)	Spring	Summer	Autumn	Winter
2014BS	2.6 (33%)	2.3 (40%)	3.1 (31%)	3.1 (24%)
2017QP + PD	1.7 (45%)	1.9 (55%)	1.5 (46%)	2.1 (38%)
2018QP + PD	2.0 (49%)	1.5 (54%)	1.6 (50%)	2.2 (51%)



**Table 3**Concentrations of SOA tracers in PM<sub>2.5</sub> in Shanghai during 2016–2018 (unit: ng m<sup>-3</sup>).

SOA tracer	Spring	Summer	Autumn	Winter
2-MGA <sup>a</sup>	2.2 (0.1–9.3)	2.6 (0.5–9.1)	1.4 (0.2–6.0)	1.6 (0.1–8.9)
cis-2-Methyl-1,3,4-trihydroxy-1-butene	0.2 (0.0–2.4)	1.2 (0.0–11.3)	0.3 (0.0–1.9)	0.1 (0.0–0.5)
3-Methyl-2,3,4-trihydroxy-1-butene	0.3 (0.0–3.0)	1.7 (0.0–18.4)	0.3 (0.0–2.1)	0.1 (0.0–0.5)
trans-2-Methyl-1,3,4-trihydroxy-1-butene	0.5 (0.0–5.4)	2.3 (0.0–24.4)	0.6 (0.0–4.1)	0.2 (0.0–1.0)
2-Methylthreitol	0.6 (0.0–5.8)	3.5 (0.3–30.9)	0.6 (0.0–3.8)	0.2 (0.0–1.2)
2-Methylerythritol	1.3 (0.0–11.5)	9.8 (0.6–82.7)	1.4 (0.0–10.7)	0.4 (0.1–2.2)
2-MTLs <sup>a</sup>	1.9 (0.0–17.3)	13.3 (0.8–113.5)	2.0 (0.1–14.6)	0.6 (0.0–3.4)
Σtracers from isoprene	5.1 (0.2–36.4)	20.6 (1.1–174.5)	4.4 (0.6–24.5)	2.4 (0.2–13.2)
2-MGA/2-MTLs	1.2 (1.0–1.5)	0.2 (0.1–0.3)	0.7 (0.5–0.9)	2.7 (2.4–3.4)
3-Hydroxyglutaric acid	0.2 (0.0–1.5)	0.3 (0.0–1.6)	0.2 (0.0–0.8)	0.2 (0.0–1.2)
3-Hydroxy-4,4-dimethyl-glutaric acid	1.4 (0.0–11.2)	4.0 (0.0–19.1)	1.2 (0.0–6.3)	0.6 (0.0–2.8)
3-Methyl-1,2,3-butane-tricarboxylic acid	0.4 (0.0–3.2)	1.8 (0.0–11.5)	0.5 (0.0–2.9)	0.2 (0.0–1.5)
Σtracers from α-pinene	2.1 (0.0–14.9)	6.1 (0.0–31.3)	1.8 (0.1–9.3)	1.0 (0.1–5.4)
β-Caryophyllinic acid	0.4 (0.0–1.4)	0.3 (0.0–1.6)	0.4 (0.0–1.6)	0.8 (0.1–3.5)
2,3-Dihydroxy-4-oxo-pentanoic acid	1.0 (0.0–5.6)	1.7 (0.0–8.3)	1.0 (0.1–2.9)	0.6 (0.0–3.0)

<sup>a</sup> 2-MGA: 2-Methylglyceric acid; 2-MTLs: 2-Methylthreitol+2-Methylerythritol.

MTLs) which had been confirmed in previous chamber experiments (Claeys et al., 2004; Edney et al., 2005; Kourtev et al., 2005). The concentrations of the isoprene tracers showed a seasonal trend of summer > spring ≈ autumn > winter (Table 3). Similar seasonal trend for the isoprene SOA tracers was also found in other studies (Ding et al., 2011; Feng et al., 2013), and could be attributed to two main reasons. Firstly, the emission of isoprene from plants depends strongly on ambient temperature, the concentration of isoprene in summer would be much higher than that in other seasons. Secondly, higher temperature and stronger solar radiation in summer can promote the oxidation of isoprene and the formation of SOA. The significant correlation between the concentration of isoprene tracers and ambient temperature ( $r = 0.54$ ,  $p < 0.01$ ) verified the impact of temperature on the concentration of isoprene tracers.

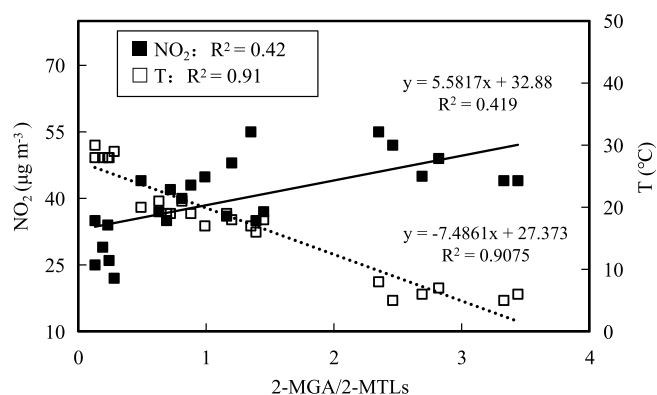
Among the measured isoprene tracers, 2-methyltetrols were the dominant species, accounted for more than 60% of the total amount of the isoprene tracer in summer. A trend of 2-MTLs > C<sub>5</sub>-alkene triols > 2-MGA was found in the summer and autumn samples, while in spring and winter, 2-MGA > 2-MTLs > C<sub>5</sub>-alkene triols. Generally speaking, the

composition of the isoprene tracers in this study was consistent with the results of previous studies in China (Ding et al., 2011; Feng et al., 2013).

Strong correlation between the concentrations of C<sub>5</sub>-alkene triols and 2-methyltetrols ( $r = 0.95$ ,  $p < 0.01$ ) was found, suggesting that they had similar formation ways. However, the formation mechanism of 2-MGA and 2-MTLs was believed to be different (Zhu et al., 2016). 2-MTLs is produced through the HO<sub>2</sub>-pathway, while 2-MGA was formed through the NO<sub>x</sub>-pathway under high NO<sub>x</sub> concentration (Surratt et al., 2010). Lower relative humidity (RH) favored the formation of 2-MGA (Jaoui et al., 2010). The ratio of 2-MGA to 2-MTLs (2-MGA/2-MTLs) was thus be used to reveal the influence of anthropogenic emissions (such as NO<sub>x</sub>) on the formation of isoprene SOA (Claeys et al., 2004).

The seasonal 2-MGA/2-MTLs ratio in PM<sub>2.5</sub> in Shanghai had a distinct trend of summer < autumn < spring < winter (Table 3). Similar results were also obtained in other studies (Ding et al., 2016; Wan et al., 2019), and was attributed to the lower NO<sub>x</sub> concentration, higher RH in summer and the higher NO<sub>x</sub>, lower RH in winter. The correlations of the 2-MGA/2-MTLs ratio with NO<sub>2</sub> and temperature were analyzed with the seasonal average values and shown in Fig. 4. It can be seen that the correlation between the 2-MGA/2-MTLs ratio and temperature was much stronger than that of NO<sub>2</sub>. Significant correlation between the 2-MGA/2-MTLs ratio and temperature ( $r = 0.68$ ,  $p < 0.01$ ) was also found when all the individual samples were used, while no significant correlation was found between 2-MGA/2-MTLs ratio and NO<sub>2</sub>. Therefore, it seemed that the seasonal variation of 2-MGA/2-MTLs ratio was affected more strongly by the ambient temperature. One possible explanation might be the impact of temperature on the formation rate of 2-MTLs and the competition between the HO<sub>2</sub>- and NO<sub>x</sub>-pathways. Ambient temperature and solar radiation have a great influence on the formation of OH free radicals, it has thus a great impact on the formation rate of 2-MTLs. The linear correlation between the logarithm of the 2-MGA/2-MTL ratio and 1/T ( $r = 0.94$ ) might suggest the difference in activation energy for the two reaction pathways. More research on the temperature effect on the formation of the isoprene tracers is needed.

From 2013 to 2018, the annual average concentration of isoprene SOA tracers decreased year by year (Table 4 and Fig. 5a). If isoprene was



**Fig. 4.** The correlations of seasonal average 2-MGA/2-MTLs with NO<sub>2</sub> and temperature in 2016–2018.

**Table 4**The annual average concentrations of SOA tracers in Shanghai during 2013 and 2018 (ng m<sup>-3</sup>).

	2013BS	2014BS	2016		2017		2018	
			QP	PD	QP	PD	QP	PD
Isoprene tracers	15.3	12.3	8.9	8.0	8.1	8.5	7.6	8.2
α-Pinene tracers	2.7	2.1	2.8	2.4	3.0	2.8	3.2	2.5
β-Caryophyllene tracer	0.7	0.7	0.5	0.5	0.5	0.4	0.4	0.4
Toluene tracers	1.3	1.2	1.2	1.1	1.2	1.0	1.1	1.0
Total tracers	20.0	16.3	13.4	12.0	12.8	12.8	12.4	12.2

mainly from biogenic emission, the concentration of isoprene tracers should be stable or increasing, considering the increasing intensity of solar radiation caused by the decreasing PM<sub>2.5</sub> concentration in the last decade in Shanghai. So the decreasing concentration of the isoprene SOA tracers suggested that part of the isoprene was from anthropogenic sources such as traffic emission and solvent usage (Cai et al., 2010; Wagner and Kuttler, 2014), and measures to control the air pollution in Shanghai in the last decade decreased the isoprene emission. Positive correlation between isoprene SOA tracers and SO<sub>4</sub><sup>2-</sup> was found in each season, especially in winter ( $r = 0.83$ ,  $p < 0.01$ ), and the annual concentration of SO<sub>4</sub><sup>2-</sup> in Shanghai had a very similar trend with the isoprene tracers (Fig. 5a). So, sulfate or other particulate pollutants might play a role in the oxidation of isoprene and the formation of SOA by providing a wet aerosol surface that facilitated the uptake of isoprene epoxydiols (Lin et al., 2013; Zhang et al., 2019). Decreasing sulfate concentration would be a potential reason for the decreasing concentration of the isoprene SOA tracers. Although the annual concentration of isoprene SOA tracers was decreasing, the contribution of isoprene SOA to OM in PM<sub>2.5</sub> showed an increasing trend (Fig. 5a), indicating the increasing contribution of SOA to the carbonaceous matter in PM<sub>2.5</sub> in Shanghai.

### 3.2.2. SOA tracers from $\alpha$ -pinene

Three tracers for  $\alpha$ -pinene SOA were quantified, including 3-hydroxyglutaric acid, 3-hydroxy-4,4-dimethylglutaric acid (HDMGA) and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA), and HDMGA and MBTCA dominated the  $\alpha$ -pinene SOA tracers (Table 3). The concentrations of the  $\alpha$ -pinene tracers had a seasonal trend of summer > spring  $\approx$  autumn > winter, with the average summer/winter ratio of about 6, which is similar with that of the isoprene tracers. The significant positive correlation between the concentrations of  $\alpha$ -pinene tracers and 2-MTLs ( $r = 0.83$ ,  $p < 0.01$ ) suggested that the  $\alpha$ -pinene SOA tracers had similar formation pathway with 2-MTLs.

Since 2013, the annual concentration of  $\alpha$ -pinene tracers remained stable at 2–3 ng m<sup>-3</sup> (Fig. 5b), suggesting that the emission of  $\alpha$ -pinene in recent years was stable, and  $\alpha$ -pinene in the atmosphere of Shanghai should be mainly from biogenic emissions (natural).

### 3.2.3. SOA tracer from $\beta$ -caryophyllene

$\beta$ -Caryophyllene is one of the most abundant sesquiterpenes in the atmosphere. It can react with O<sub>3</sub>, OH $\cdot$  and NO<sub>3</sub> $\cdot$  free radicals to form SOA (Calogirou et al., 1997; Hakola et al., 2006; Hallquist et al., 2009). However, no significant correlation between  $\beta$ -caryophyllenic acid, the typical tracer of SOA from  $\beta$ -caryophyllene, and O<sub>3</sub> was found in this

study.

Due to the low volatility of sesquiterpenes, they can accumulate in leaves and tree trunks and could be released through biomass burning (Ciccioli et al., 2014). Correlation analysis showed that  $\beta$ -caryophyllenic acid in PM<sub>2.5</sub> in Shanghai was significantly correlated with levoglucosan ( $r = 0.77$ ,  $p < 0.01$ ), and the correlation coefficient in summer was weaker than that in other seasons. It can also be seen from Table 3 that  $\beta$ -caryophyllenic acid had the highest concentration in winter, and the lowest in summer, obviously different with other SOA tracers. The similarity in the seasonal trends of  $\beta$ -caryophyllenic acid and levoglucosan, and the correlation between the two compounds suggested that biomass burning might be the main source of  $\beta$ -caryophyllene, and biogenic emission was more important in summer. The decreasing trend of the annual average concentration of  $\beta$ -caryophyllenic acid (Fig. 5c) could thus be attributed to the decreasing emissions from biomass burning.

### 3.2.4. SOA tracer from toluene

2,3-dihydroxy-4-oxopentanoic acid (DHOPA) was widely recognized as the tracer of SOA from toluene oxidation (Kleindienst et al., 2004). Toluene and other aromatic volatile organic compounds would come from many emission sources such as solvent usage, vehicle exhaust, coal combustion and biomass burning (Cai et al., 2010; Zhang et al., 2013).

The seasonal concentration of DHOPA in Shanghai was the highest in summer and the lowest in winter. Comparing with the tracers for isoprene and  $\alpha$ -pinene, the seasonal variation of DHOPA was relatively small (Table 3). Although biomass combustion was a potential source of aromatic VOCs (Lewis et al., 2013), the weak declining trend of DHOPA from 2013 to 2018 (Fig. 5d) and the seasonal trend indicated that biomass burning was not the important source of the aromatic VOCs in Shanghai. Wang et al. (2015) reported that only 23.3% of the aromatic VOCs in 2010 in Shanghai was from vehicular emissions. More and more strict vehicle emission standards is adopted in Shanghai in recent years, the contribution of vehicle emission to aromatic VOCs was expected to decrease though the number of vehicles increasing (Liu et al., 2019). Solvent usage (paint and industrial) and chemical industry should be the main sources of aromatic VOCs besides vehicle emission in Shanghai (Wang et al., 2015; Zhang et al., 2018; Liu et al., 2019). Thus, DHOPA in PM<sub>2.5</sub> in Shanghai was mainly from anthropogenic precursors, and the emission of aromatic VOCs in Shanghai was decreasing year by year but kept high in the last decade.

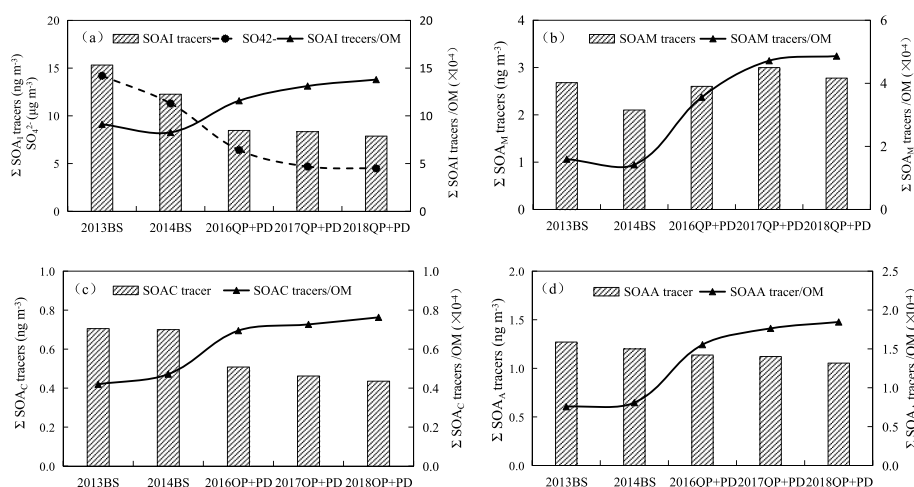


Fig. 5. Temporal trend of annual concentrations of the SOA tracers from 2013 to 2018 (a: isoprene; b:  $\alpha$ -pinene; c:  $\beta$ -caryophyllene; d: toluene).

### 3.3. Temporal trend and sources of the tracer-based SOC

Based on the measured concentrations of the 11 SOA tracers, the concentrations of SOC from different precursors in PM<sub>2.5</sub> in Shanghai were estimated with the tracer yield from the chamber experiments published by Kleindienst et al. (2007). The estimated concentration of SOC<sub>tracer-based</sub> showed a decreasing trend from 2013 to 2018, the SOC<sub>tracer-based</sub> in 2018 (0.21  $\mu\text{g m}^{-3}$ ) was about 70% of that in 2013 (0.31  $\mu\text{g m}^{-3}$ ). While the contribution of SOC<sub>tracer-based</sub> to OC showed an increasing trend, the SOC<sub>tracer-based</sub>/OC ratio in 2018 was about 2 times of that in 2013, in accordance with the temporal trend found by the OC/EC- and WSOC-based methods. The SOC<sub>tracer-based</sub> concentration was obviously lower than the SOC<sub>WSOC-based</sub>, but they were positively correlated ( $r = 0.41$  when all samples used,  $p < 0.01$ , and stronger correlations were found in summer and winter), similar with what found before (Feng et al., 2013).

Fig. 6 showed the normalized contribution of SOC from different precursors to SOC<sub>tracer-based</sub>. It can be seen that the contribution of SOC from isoprene (SOC<sub>isoprene</sub>) showed a decreasing trend from 32% in 2013 to 24% in 2016–2018. While the contribution of SOC from toluene (SOC<sub>toluene</sub>) had an increasing trend, from about 54% in 2013 to a stable value of about 62% in 2016–2018. Therefore, aromatic VOCs from anthropogenic sources should be the main contributor of the SOA in PM<sub>2.5</sub> in Shanghai despite the various measures taken to improve the air quality in the last decade. Reducing the emission of anthropogenic VOCs would be crucial to further reduce the PM<sub>2.5</sub> level in Shanghai.

### 4. Conclusions

From the measurement of the concentration and composition of the carbonaceous matter in PM<sub>2.5</sub> in Shanghai during 2012 and 2018, an obvious decreasing trend of the carbon concentration was found. The concentration of total carbon in 2018 (4.3  $\mu\text{g m}^{-3}$ ) was only 34% of that in 2012, and the WSOC concentration in 2018 (2.1  $\mu\text{g m}^{-3}$ ) was about 50% of that in 2014. The contribution of organic matter to PM<sub>2.5</sub> in Shanghai also declined, indicating that the air pollution control measures adopted in Shanghai in the last decade was effective in reducing the emissions of organic aerosols. The seasonal variation of OC, EC, WSOC and the polar organic tracers in different years suggested that the substantial reduction in biomass burning was one of the important reason for the decreasing contribution of organic matter.

SOC concentration estimated with OC/EC-based, WSOC-based and tracer-based methods all showed a decreasing trend from 2012 to 2018, while the contribution of SOC to OC had an increasing trend. More than half of the OC in PM<sub>2.5</sub> in 2018 Shanghai should be secondary. Temporal trend of the concentrations of the typical SOA tracers showed that SOA from isoprene and sesquiterpene had a distinct decreasing trend, and biomass burning should be the important source of sesquiterpene besides biogenic emission. While the concentrations of the tracers for monoterpene and toluene kept stable or decreased slightly. Aromatic VOCs from anthropogenic sources such as solvent usage and chemical processing was the more and more important contributors to SOA in Shanghai and should be the key pollutants for further improvement of the air quality in Shanghai.

### CRedit authorship contribution statement

**Yan Zhong:** Data curation, Formal analysis, Investigation, Writing – original draft. **Junwei Chen:** Investigation. **Qianbiao Zhao:** Data curation, Project administration, Resources. **Ning Zhang:** Formal analysis, Investigation. **Jialiang Feng:** Conceptualization, Methodology, Resources, Validation, Writing – original draft, Writing – review & editing. **Qingyan Fu:** Conceptualization, Resources, Writing – review & editing.

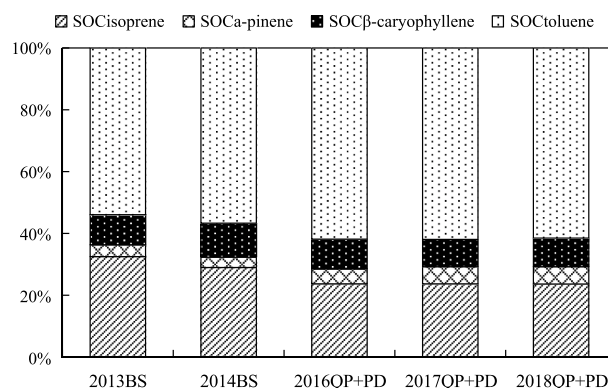


Fig. 6. Sources of SOC in PM<sub>2.5</sub> in Shanghai from 2013 to 2018.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.atmosenv.2021.118596>.

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