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Original Research

Characteristics of Secondary Organic Aerosol Tracers in $PM_{2.5}$ during O_3 and Haze Pollution Days in A Relatively Clean City, Tai'an

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Abstract

Secondary organic aerosol (SOA) contributes greatly to atmospheric environmental pollution, and SOA tracers provide direct insights into the chemical composition, source identification, and formation pathways of SOA. Observations of SOA tracers were performed in Tai'an, a relatively clean city located in the North China Plain. Seventeen SOA tracers in $PM_{2.5}$, which originated from isoprene (SOA_I), monoterpene (SOA_M), β-caryophyllene (SOA_C), and aromatic hydrocarbon (SOA_A), were measured and investigated. Characteristics of SOA tracers in different seasons and during different pollution days were revealed. The concentrations of these four kinds of tracers in summer were 28.5±7.49 ng m^{-3}, 41.4±11.2 ng m^{-3}, 1.94±0.72 ng m^{-3}, and 1.26±0.51 ng m^{-3}, respectively, indicating strong oxidation processes under high biogenic emissions. In winter, SOA_I and SOA_M decreased significantly by more than 65%, but the SOA_A concentration increased by a factor of 2.65. These opposing trends collectively resulted in the same secondary organic carbon concentration (0.60 μg m^{-3}) in summer and winter. Compared with non-pollution days, SOA was found to be fresher during O_3 pollution days in summer and haze days in winter, but the underlying mechanisms were different. Through the combined analysis of malic acid, levoglucosan, and SO_4^{2-}, the importance of biomass burning and secondary inorganic formation to SOA was revealed. This study provides insights into SOA characteristics in a mountain city under relatively clean conditions.

Keywords: SOA tracers, concentration characteristics, O_3 and haze pollution, aerosol aging

Introduction

Secondary organic aerosol (SOA) is a major fraction of organic carbon (OC) in fine particulate matter ($PM_{2.5}$), contributing to 30%-70% of OC mass across different regions in China. Precursor volatile organic compounds (VOCs) originating from biogenic sources, including isoprene, monoterpenes, and sesquiterpenes emitted by vegetation, or anthropogenic sources, including aromatic hydrocarbons emitted from vehicles and industrial emissions [1, 2], undergo homogeneous and heterogeneous reactions [3, 4] in the complex atmospheric environment to form SOA. Considering its important role in regional haze formation, visibility

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degradation, and adverse health effects [2, 5], SOA has attracted widespread attention and research interest.

Due to the chemical complexity, the molecular tracer-based approach became a widely used method for providing direct insights into the chemical composition, source identification, and formation pathways of SOA [6, 7]. This method was derived from laboratory simulation studies [8, 9]. These experiments first simulated the atmospheric environment in a smog chamber, then introduced a certain amount of biogenic or anthropogenic precursor compounds, and after a specific reaction period, collected SOA products to determine the concentrations of certain characteristic components, which were also called SOA tracers. These tracers exhibited low volatility and high stability, serving as reliable chemical fingerprints for source attribution. Typical SOA tracers included isoprene-derived compounds (e.g., 2-methyltetrols), monoterpene oxidation products (e.g., pinic acid and pinonic acid), sesquiterpene-derived carboxylic acids (e.g., β-caryophyllinic acid), and aromatic SOA markers (e.g., phthalic acid and benzoic acid) [1, 10]. Based on the proportions of tracers obtained from simulation experiments, combining the specific concentrations of tracers in atmospheric samples, it is possible to estimate the concentration of related SOA in the atmosphere [11, 12].

Long-term field investigations, involving SOA tracer chemical compositions, spatiotemporal variations, and their correlations with other anthropogenic pollutants, are of profound importance, as they provide the groundwork for understanding the formation mechanism and source apportionment of SOA. In Nanjing, biogenic SOA was found to dominate in summer, whereas anthropogenic SOA formed from aromatics prevailed in winter, reflecting the influence of temperature and vegetation activity on biogenic VOC emissions [2]. In Jinzhong, a city in northern China, the significantly elevated aromatic tracers in $PM_{2.5}$ during winter were closely linked to residential heating [5]. In coastal regions such as Pingtan Island and the Pearl River Estuary, previous studies revealed dynamic SOA compositions under the alternating influence of continental and marine air masses, with biomass burning contributing notably during specific episodes [7, 10]. Previous studies focused mainly on typical urban environments with high pollution levels of particulate matter, including cities characterized by intense vehicle exhaust, such as Beijing and Shanghai [13, 14], and cities characterized by heavy industrial emissions, such as Zibo [15]. After more than a decade of atmospheric pollution control, particulate matter pollution across China has improved remarkably, and it is now far less severe than it was in the 2010s. Nowadays, focusing solely on particulate matter pollution is insufficient to characterize the local atmospheric pollution status.

Tai'an is a tourist city located in the central part of Shandong Province, and its atmospheric environmental pollution status showed distinctive characteristics. In summer, Tai'an experienced severe O_3 pollution, and the average summer O_3 concentration exceeded 180 μg m^{-3} during 2016-2021 [16]. Meanwhile, in winter, Tai'an suffered from haze pollution, which is consistent with the situation in most cities in northern China, where the $PM_{2.5}$ concentration in winter was the highest among all four seasons of the year. In this study, the observation campaign was carried out in Tai'an, and $PM_{2.5}$ samples were collected in summer and winter during 2021-2022. Four types and 17 species of SOA tracers in $PM_{2.5}$ were detected and analyzed. The concentration levels, seasonal variations, and characteristics under different types of pollution were revealed.

Material and Methods

Site and Sampling

The observation campaign was carried out at the Atmospheric Environment Monitoring Station in Tianpinghu Park (117°2′14″E, 36°12′44″N), Tai'an, Shandong Province. The station was located in the western suburb of Tai'an, with sparse human activities in the surrounding area. $PM_{2.5}$ samples were collected using a medium-flow sampler (HT-16A, Wuhan Tianhong Instruments, China) at a flow rate of 100 L min^{-1} onto a quartz fiber filter (φ = 88 mm, Whatman). The sampling duration was 24 h for each $PM_{2.5}$ sample, starting at 8:00 and ending at 8:00 a.m. the next day. Samples were sealed and stored in a refrigerator at -20ºC until analysis. Sample collection was performed in both summer and winter, specifically during June 21, 2021-August 20, 2021, and December 14, 2021-February 14, 2022, respectively. Four blank samples were simultaneously collected using the same method but under no flow. Due to some unfavorable weather conditions or electric failures, there were 54 and 58 effective $PM_{2.5}$ samples collected during the summer and winter campaigns, respectively.

Online Measurement and Chemical Analysis

Meteorological parameters, including ambient temperature (T, °C), relative humidity (RH, %), and wind speed (WS, m s^{-1}), were measured using an automatic meteorological station. Ambient O_3 and NO_2 were measured using a 49i O_3 analyzer and a 42i NO_2 analyzer (Thermo Environmental Instruments Inc., USA, C-series), respectively. A beta attenuation and optical analyzer (model 5030 SHARP monitor, Thermo Scientific) was used to monitor ambient $PM_{2.5}$. The SO_4^{2-} concentration in $PM_{2.5}$ was measured using ion chromatography (Dionex, 940 Professional, Metrohm, Switzerland).

Aliquots of $PM_{2.5}$ samples were cut into pieces (~0.5×0.5 cm) and extracted with a 10 mL

dichloromethane/methanol mixture (1:1, V:V). The extraction was performed under ultrasonication for 10 min and repeated three times. The extracted solvents were mixed together, filtered through a polytetrafluoroethylene filter (0.22 μm pore size), and dried under a high-purity nitrogen stream. Then, the extracts were derivatized with 100 μL N,O-bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) with 1% trimethylsilyl chloride and 20 μL pyridine, and heated under 70ºC for 1 h [6]. After cooling to room temperature, the extracts were mixed with 630 μL n-hexane (containing ketopinic acid as an internal standard). The extracts were finally injected into gas chromatography (GC, Agilent 6890N)/mass spectrometer (MS, Agilent 5975C) for analysis. A DB5-MS (30 m ×0.25 mm ×0.25 μm) was used as the capillary column, and helium was used as the carrier gas at a flow rate of 1.0 mL min^{-1}. The oven temperature program was as follows: 70ºC for 2 min, raised to 300ºC at a rate of 6ºC min^{-1}, and finally held for 20 min [6]. The MS was operated in negative electron ionization mode at 70 eV and scanned in the range of 50-550 m/z.

Four types of SOA tracers were investigated in this study, including isoprene tracers (SOA_I), monoterpene tracers (SOA_M), β-caryophyllene tracers (SOA_C), and aromatic hydrocarbon tracers (SOA_A). SOA_I consisted of 6 components: 2-methylthreitol, 2-methylerythritol, 2-methylglyceric acid (MGA), cis-2-methyl-1,3,4-trihydroxy-1-butene, 3-methyl-2,3,4-trihydroxy-1-butene, and trans-2-methyl-1,3,4-trihydroxy-1-butene. Among them, the first two were collectively referred to as 2-methyltetrols (MTLs), while the last three were collectively referred to as pentene-triols (C_5). SOA_M consisted of 9 components: pinic acid (PA), pinonic acid (PNA), 3-hydroxyglutaric acid (HGA), 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA), 3-acetylglutaric acid (AGA), 3-hydroxy-2,2-dimethylglutaric acid (HDMGA), 3-(2-hydroxyethyl)-2,2-dimethylcyclobutane carboxylic acid (DCA), 3-acetyladipic acid (AAA), and 3-isopropylglutaric acid (IGA). β-caryophyllenic acid (CPA) and 2,3-dihydroxy-4-oxopentanoic acid (DHOPA) represented SOA_C and SOA_A, respectively. Laboratory studies have shown that anthropogenic aromatic hydrocarbons can form a C_4 degradation intermediate under complex atmospheric environments [17], and the intermediate can further react to generate C_4 diacids. Field sampling results [18] showed that malic acid was the dominant C_4 diacid in particulate matter, indicating that malic acid could be a tracer of anthropogenic aromatic hydrocarbons. In addition, a biomass burning tracer, levoglucosan, and a butanoic diacid, malic acid, were also investigated. For quantification, PA, PNA, HGA, malic acid, and levoglucosan were determined using authentic standards. For the other components, due to the lack of commercial standards, SOA_I tracers were quantified using erythritol as a standard, SOA_M tracers were quantified using malic acid as a standard, CPA was quantified using PA as a standard, and DHOPA was quantified using citramalic acid [6, 19, 20], respectively.

Quality Control and Quality Assurance

Blanks were analyzed using the same method as samples, but none of the target components were detected. Authentic standards were spiked into solvent, dissolved into prebaked quartz filters, and finally detected to test their recovery. Results showed the recovery rates of PA, PNA, HGA, malic acid, and levoglucosan were 87±15%, 93±18%, 79±9%, 96±10%, and 82±25%, respectively. Ketopinic acid was added in each sample before the measurement [9], and its recovery reached 94±18%. The experimental results were not corrected for recovery rates.

Secondary Organic Carbon (SOC) Estimation Method

SOC was estimated based on the SOA-tracer method, which was established by Kleindienst and co-workers [9]. This method measured the fraction of some SOA tracers to SOC (f_{SOC}) from laboratory experiments conducted in a smog chamber. Then the SOC originating from the related precursors could be estimated by the Equation (1) shown below:

$$[SOC] = \sum_i [tri] / f_{SOC} \quad (1)$$

where [SOC] was the mass concentration of the corresponding SOA, Σ_i[tri] was the summed mass concentration of the measured i SOA tracers. Specific values of f_{SOC} for isoprene, monoterpenes, β-caryophyllene, and aromatics were 0.155±0.039, 0.231±0.111, 0.0230±0.0046, and 0.0079±0.0026, respectively [9].

Criteria Used to Distinguish between Pollution and Non-Pollution Days

The pollution conditions in Tai'an indicated that O_3 was the primary air pollutant in summer, while haze pollution was more severe in winter. According to the NAAQS Grade I criteria for O_3 (<100 μg m^{-3}), summer samples were grouped into O_3 pollution days and non-O_3 pollution days. Meanwhile, according to NAAQS Grade II criteria for $PM_{2.5}$ (<75 μg m^{-3}), winter samples were grouped into haze days and non-haze days.

Results and Discussion

Overview of SOA Tracers and SOC

The concentrations of all measured SOA tracers in this study are listed in Table 1. In summer, SOA_M were the dominant components, with a concentration as high as 41.1 ng m^{-3}. SOA_I had a minor concentration of 28.5 ng m^{-3}. SOA_C and SOA_A were quite low, both not exceeding 2.00 ng m^{-3}. In winter, SOA_M still dominated, and the concentration was at least three times higher than that of

Table 1. Concentrations of SOA tracers in this study (units: ng m^{-3}).

Components	Abbreviations	Summer (n = 54)		Winter (n = 58)	
		mean±std	min-max	mean±std	min-max
2-methylglyceric acid	MGA	8.17±2.66	2.73-16.8	1.54±0.46	0.33-2.62
cis-2-methyl-1,3,4-trihydroxy-1-butene	C_5	0.10±0.06	0.03-0.30	0.40±0.17	0.05-0.73
3-methyl-2,3,4-trihydroxy-1-butene		1.78±0.81	0.60-4.98	0.22±0.10	0.03-0.49
trans-2-methyl-1,3,4-trihydroxy-1-butene		2.17±0.86	0.57-4.75	0.23±0.09	0.07-0.42
2-methylthreitol	MTLs	4.78±1.70	1.84-8.89	0.46±0.17	0.17-1.08
2-methylerythritol		11.5±4.76	4.42-23.3	1.39±0.47	0.50-2.90
Sum of isoprene SOA tracers	SOA_I	28.5±7.49	13.7-45.7	4.23±0.88	1.51-6.19
Pinic Acid	PA	7.26±3.50	1.79-14.8	1.45±0.45	0.60-2.82
Pinonic Acid	PNA	10.3±4.12	3.63-22.2	2.63±0.89	1.10-5.32
3-hydroxyglutaric acid	HGA	7.74±2.77	3.21-16.8	2.23±0.70	0.81-4.37
3-(2-hydroxyethyl)-2,2-dimethylcyclobutane carboxylic acid	DCA	1.09±0.71	0.42-3.97	0.99±0.42	0.27-2.06
3-hydroxy-2,2-dimethylglutaric acid	HDMGA	0.79±0.25	0.36-1.51	2.17±0.72	1.19-4.54
3-acetylglutaric acid	AGA	3.10±1.22	1.43-7.86	0.66±0.32	0.25-1.76
3-acetyladipic acid	AAA	1.93±1.32	0.47-6.82	0.39±0.34	0.13-2.33
3-isopropylglutaric acid	IPA	3.51±2.23	1.50-11.3	1.12±0.55	0.42-3.32
3-methyl-1,2,3-butanetricarboxylic acid	MBTCA	5.37±1.71	2.57-11.2	2.17±0.75	1.12-4.71
Sum of monoterpene SOA tracers	SOA_M	41.1±11.2	22.2-75.9	13.8±2.97	8.36-23.1
b-caryophyllenic acid	CPA/SOA_C	1.94±0.72	0.73-4.84	2.01±0.67	0.83-3.61
2,3-dihydroxy-4-oxopentanoic acid	$DHOPA/SOA_A$	1.26±0.51	0.24-2.78	3.34±1.21	1.30-7.49

any other component (13.8 ng m^{-3}). The concentrations of the other three kinds of SOA in descending order were SOA_I, SOA_A, and SOA_C, all ranging between 2.00 ng m^{-3} and 5.00 ng m^{-3}. The much higher SOA_I and SOA_M concentrations in summer indicated a massive emission of plant-derived biogenic aerosols [6, 21]. Although SOA_A were minor components in both seasons, the concentration in winter was 2.65 times higher than that in summer. The much higher SOA_A concentration emphasized the greater contribution of anthropogenic sources to SOA in winter.

The concentration and distribution of estimated SOC are shown in Fig. 1a). The SOC concentration was 0.60 μg m^{-3} in both summer and winter, but significant differences were found in its distribution. In summer, SOC_I, SOC_M, and SOC_A were all at high levels, with concentrations varying between 0.16 μg m^{-3} and 0.18 μg m^{-3}. In winter, SOC_A had the highest concentration of 0.42 μg m^{-3}, which was more than twice the sum of the concentrations of the other three. The contribution of aromatic hydrocarbons was much more important to SOC than to SOA, indicating that aromatic hydrocarbons originating from anthropogenic activities had a great impact on SOC in Tai'an.

Characteristics and Seasonal Variation of SOA Tracers

SOA_I Tracers

For comparison, concentrations of SOA tracers in other studies were shown in Fig. 1b) and c). The sum of SOA_I tracers ranged from 13.7-45.7 ng m^{-3} with an average of 28.5 ng m^{-3} in summer. This value was much lower than that at other urban or suburban sites such as Beijing (137 ng m^{-3}) [1], Bengbu (47.2 ng m^{-3}) [22], and Zibo (45.4 ng m^{-3}) [15], at the same level as that in Jinzhou (27.6 ng m^{-3}), and higher than that at the coastal site of Fuzhou (19.8 ng m^{-3}) [6]. The comparison results highlighted that SOA_I in Tai'an was in a relatively low condition. Besides, the sampling site in this study was also located at the foot of Mt. Tai, but the concentration was approximately half of that at the summit of Mt. Tai (56.4 ng m^{-3}) [23], suggesting a lower emission intensity of isoprene at the foot of Mt. Tai. The distribution of the three categories of SOA_I tracers is shown in Fig. 2a). MTLs, which were considered as products formed through the low-NO_x channel, dominated the SOA_I tracers with an average concentration of 16.3 ng m^{-3} and they covered 57.2% of the total. MGA,

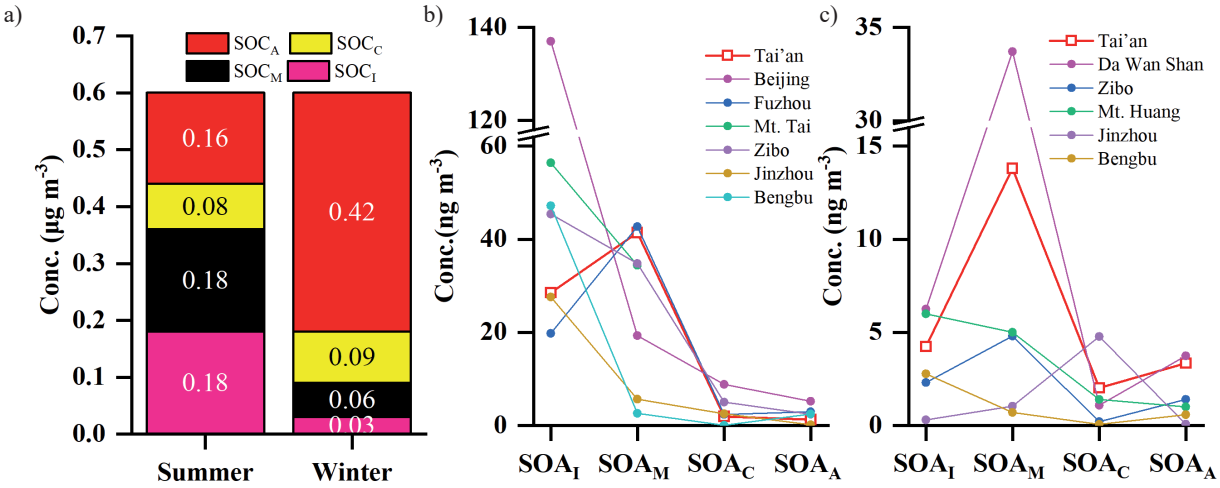

Fig. 1. a) Concentration and distribution of estimated SOC, and comparison of SOA tracers in this study and others in b) summer and c) winter.

which was considered a product formed through the high-NO_x channel, ranked second and accounted for approximately half the concentration of MTLs. C_5 were the components with the lowest content (4.1 ng m^{-3}), and they covered 1/2 the concentration of MGA. The dominance of MTLs in this study was consistent with previous summer studies [1, 24]. These two isomers showed a good correlation (R^2 = 0.875) and the ratio of 2-methylerythritol to 2-methylthreitol was 2.30 (Fig. 2b)), indicating their homology.

The sum of SOA_I tracers in winter was quite low (4.2 ng m^{-3}), and it was only approximately 1/7 of the summer value. This was true in all the other sites (Fig. 1c)) and was mainly because the reduced biological activity of plants in winter decreased the biogenic source precursors. The order of the three categories of SOA_I tracers in terms of concentration from high to low did not change compared to summer, but their proportions varied considerably. The proportion of MTLs decreased to 45.2% and the proportion of MGA increased to 35.7%. Considering the different formation pathways of MTLs and MGA in chamber experiments [25], the ratio of MGA/MTLs reflected the impact of NO_x on SOA_I formation. This value differed across sites and was usually higher in urbanized sites but lower in natural areas. It was 0.91 in winter and 0.57 in summer, respectively, indicating more severe anthropogenic pollution in winter. The relatively higher proportion of high-NO_x channel products was consistent with the more severe pollution level in winter, emphasizing that the contribution of formation channels to SOA_I tracers varies significantly among seasons.

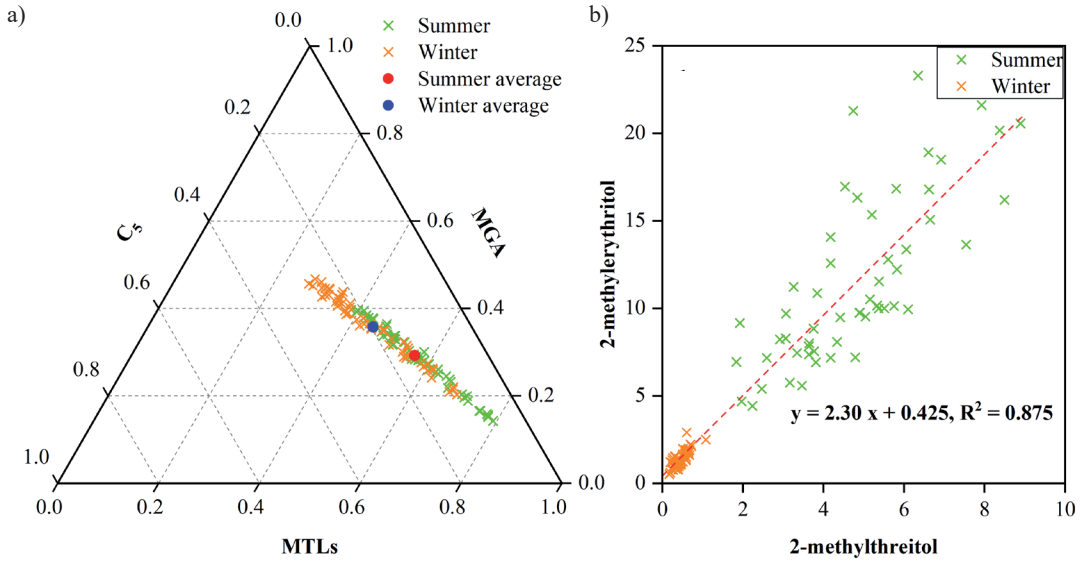

Fig. 2. a) Distribution of MTLs, MGA, and C_5 in SOAI tracers and b) correlation between MTLs.

SOA_M Tracers

The sum of SOA_M tracers ranged from 22.2-75.9 ng m^{-3} with an average of 41.1 ng m^{-3} in summer. It was at the same level as that at the coastal site of Fuzhou (42.7 ng m^{-3}) and was considerably higher than the values (<35 ng m^{-3}) in other sites, indicating the importance of monoterpene species to the formation of SOA in Tai'an. PNA, HGA, and PA were the three dominant components, each with a concentration larger than 7.0 ng m^{-3}. They had concentrations much higher than the other SOA_M tracers and contributed 61.1% of all SOA_M tracers. MBTCA, IPA, and AGA ranked next, with concentrations of 5.4 ng m^{-3}, 3.5 ng m^{-3}, and 3.1 ng m^{-3}, respectively. These three components contributed 29.0% of all SOA_M tracers. The last 4 components covered less than 10.0% of the total SOA_M tracers, and each had a concentration no larger than 2.0 ng m^{-3}. The sum of SOA_M tracers in winter was also low (13.8 ng m^{-3}), and it was about one-third of the summer value. But this was considerably higher than the concentrations reported in North China such as Zibo (4.8 ng m^{-3}) [15], Jinzhou (1.04 ng m^{-3}) [5], and Bengbu (0.70 ng m^{-3}) [22], further highlighting the contribution of monoterpene species to SOA.

The distribution pattern of specific SOA_M tracers differed considerably in winter compared with that in summer. PNA, HGA, HDMGA, and MBTCA became the four dominant components, each of which had a concentration larger than 2.0 ng m^{-3}, and they contributed 66.7% of all SOA_M tracers. All the SOA_M tracers exhibited the characteristic of higher concentrations in summer and lower concentrations in winter, with the sole exception of HDMGA, which showed the opposite trend. Its concentration in winter was 2.75 times higher than that in summer, making it a notable feature of this study in Tai'an. Due to the reduced level of plant biological activity in winter, the emissions of biogenic precursors decrease significantly. The overall concentration of SOA_M tracers declined in winter, which was mainly attributed to two factors. First, plant metabolic activities were weak in winter, resulting in low emissions of SOA precursors. Second, both temperature and ultraviolet intensity were low in winter, weakening the formation reactions of SOA_M tracers. For the first-generation products, PA and PNA, in addition to the decreased concentrations, their proportions also decreased. PA was found to show a more significant decrease in proportion than PNA. This was because of the different formation mechanisms of the two compounds. PA could be generated through only one Criegee intermediate, while PNA could be generated from two precursor Criegee intermediates [26]. The greater number of formation pathways resulted in considerable production of PNA even under unfavorable conditions. The aging degree of SOA has attracted researchers' attention, driven by the need to understand its role in regional pollution. Generally, the ratio of PA plus PNA to MBTCA (P/M) was used to characterize this parameter of SOA_M [1]. Smog chamber experiments showed that in fresh samples, P/M typically ranged from 1.15 to 3.21 [6, 27]. The average values of summer and winter samples were 3.48 and 2.04, respectively, indicating relatively fresh SOA in summer. This was consistent with the atmospheric condition in Tai'an that in summer, the atmosphere had better fluidity with more precipitation, which did not favor the accumulation of components. Meanwhile, strong sunlight and high O_3 concentration facilitated the conversion of precursors, thereby resulting in the formation of relatively fresh SOA. In contrast, the poor atmospheric fluidity in winter elevated the accumulation of pollutants, and the products of precursors had sufficient time to continue participating in relevant reactions, leading to the formation of relatively aged SOA.

Previous studies reported that the production of MBTCA varied considerably in α-pinene SOA and β-pinene SOA [27], whereas HGA did not. Thus, the ratio of HGA to MBTCA (HGA/MBTCA) became a parameter to distinguish the dominant monoterpene, and it was approximately 1.0 at sites that took α-pinene as the major precursor [28]. In this study, HGA/MBTCA were 1.48 and 1.13 for summer and winter, respectively. The results suggested that α-pinene was the major contributor to the precursors, and β-pinene contributed more to summer than to winter.

SOA_C and SOA_A Tracers

The SOA_C tracer, CPA, was basically the same in summer and winter, being 1.9 ng m^{-3} and 2.0 ng m^{-3}, respectively. This phenomenon was the same as in Bengbu [22]. But in Zibo [15], different results were reported that the seasonal variation of SOA_C exhibited lower concentrations in winter. The difference suggested that there may be other potential sources of CPA in Tai'an during winter. In summer, compared with SOA_I and SOA_M tracers, this concentration was much lower, indicating β-caryophyllene was a minor component compared with isoprene or monoterpene. But in winter, this concentration was quite considerable, reaching nearly 50% of the SOA_I concentration and 15% of the SOA_M concentration.

The SOA_A tracer, DHOPA, had a much higher concentration in winter than in summer, being 3.3 ng m^{-3} and 1.3 ng m^{-3}, respectively. In summer, the concentration was less than 50% of those reported in Beijing, Fuzhou, Zibo, and Bengbu, whereas in winter, the concentration was slightly lower than the concentration in Da Wan Shan Island [7], and at least 2.3 times higher than the concentrations in Zibo, Mt. Huang, Jinzhou, and Bengbu. As an anthropogenic source tracer, this result indicated the high contribution of intense anthropogenic activities to SOA in Tai'an during winter.

SOA Tracers under Pollution Days

Meteorological parameters, ambient components, and concentrations of SOA tracers for the four groups

of samples were listed in Table 2. The average O_3 concentrations of O_3 pollution days and non-O_3 pollution days were 126 μg m^{-3} and 77 μg m^{-3}, respectively, and the average $PM_{2.5}$ concentrations of haze days and non-haze days were 99 μg m^{-3} and 59 μg m^{-3}, respectively.

SOA Tracers during O_3 Pollution Days in Summer

Time series of SOA tracers in summer are shown in Fig. 3. SOA_I, SOA_C, and SOA_A showed slightly lower concentrations during O_3 pollution days than during non-O_3 pollution days, with increase rates not exceeding 10%. For specific components, except MLTs, the concentration differences of all the tracers between O_3 pollution days and non-O_3 pollution days were within 1 ng m^{-3}. The concentration of MLTs during O_3 pollution days was 4.1 ng m^{-3} lower than that during non-O_3 pollution days, which may be related to the susceptibility to oxidation of 2-methylthreitol and 2-methylerythritol. SOA_M showed a quite different pattern compared with the others, their concentrations during O_3 pollution days were 30.9% (10.4 ng m^{-3}) higher than those during non-O_3 pollution days. This emphasized the great impact of monoterpenes on SOA formation during O_3 pollution days in summer. PA and PNA increased most with 4.8 and 4.5 ng m^{-3}, respectively. IPA, MBTCA, and HGA ranked next with increases of 0.83 ng m^{-3}, 0.46 ng m^{-3}, and 0.28 ng m^{-3}, respectively. The other four SOA_M tracers increased much less (<0.05 ng m^{-3}), with individual ones even showing a slight decrease. The results indicated that the substantial presence of O_3 in summer led to the formation of more SOA_M. Since the increments of first-generation products were much higher than those of later-generation products, the SOA was much fresher during O_3 pollution days (P/M = 4.03) than during non-O_3 pollution days (P/M = 2.58).

Table 2. Meteorological parameters, ambient components, and concentrations of SOA tracers in the four groups of samples.

Components	Units	Summer		Winter	
		O_3 pollution (n = 37)	non-O_3 pollution (n = 17)	haze (n = 36)	non-haze (n = 22)
		mean±std	mean±std	mean±std	mean±std
Temp	ºC	27.9±1.6	26.7±1.8	3.4±2.0	0.7±2.6
RH	%	68.9±8.5	76.9±8.3	61.9±12.3	44.7±9.7
$PM_{2.5}$	μg m^{-3}	33±10	23±9	99±21	57±14
O_3	μg m^{-3}	126±21	74±15	32±12	43±15
NO_2	μg m^{-3}	16±7	11±7	44±10	32±11
MGA	ng m^{-3}	8.43±2.96	7.62±1.73	1.63±0.40	1.37±0.52
C_5	ng m^{-3}	4.21±1.59	3.73±0.98	0.90±0.24	0.75±0.30
MTLs	ng m^{-3}	15.0±5.53	19.1±6.53	1.75±0.56	2.03±0.64
SOA_I	ng m^{-3}	27.2±7.26	30.4±7.36	4.28±0.78	4.15±1.03
PA	ng m^{-3}	8.78±3.03	3.95±1.70	1.53±0.42	1.31±0.44
PNA	ng m^{-3}	11.7±3.82	7.18±2.87	2.78±0.89	2.38±0.83
HGA	ng m^{-3}	7.82±2.72	7.55±2.88	2.36±0.79	2.01±0.44
DCA	ng m^{-3}	1.07±0.65	1.13±0.81	1.04±0.45	0.90±0.36
HDMGA	ng m^{-3}	0.80±0.27	0.77±0.20	2.32±0.76	1.92±0.56
AGA	ng m^{-3}	3.07±0.93	3.19±1.69	0.78±0.33	0.46±0.17
AAA	ng m^{-3}	1.93±1.19	1.93±1.55	0.39±0.26	0.40±0.44
IPA	ng m^{-3}	3.77±2.59	2.94±0.88	1.11±0.44	1.13±0.69
MBTCA	ng m^{-3}	5.51±1.83	5.05±1.36	2.25±0.76	2.04±0.73
SOA_M	ng m^{-3}	44.1±10.7	33.7±9.61	14.6±2.71	12.6±2.95
CPA/SOA_C	ng m^{-3}	1.92±0.67	1.98±0.82	2.11±0.68	1.84±0.62
DHOPA/SOA_A	ng m^{-3}	1.22±0.41	1.36±0.67	3.62±1.27	2.88±0.93
Malic acid	ng m^{-3}	6.68±2.67	6.48±3.65	8.84±3.41	6.34±2.69
Levoglucosan	ng m^{-3}	17.4±9.20	20.1±8.60	193±95.3	133±57.2

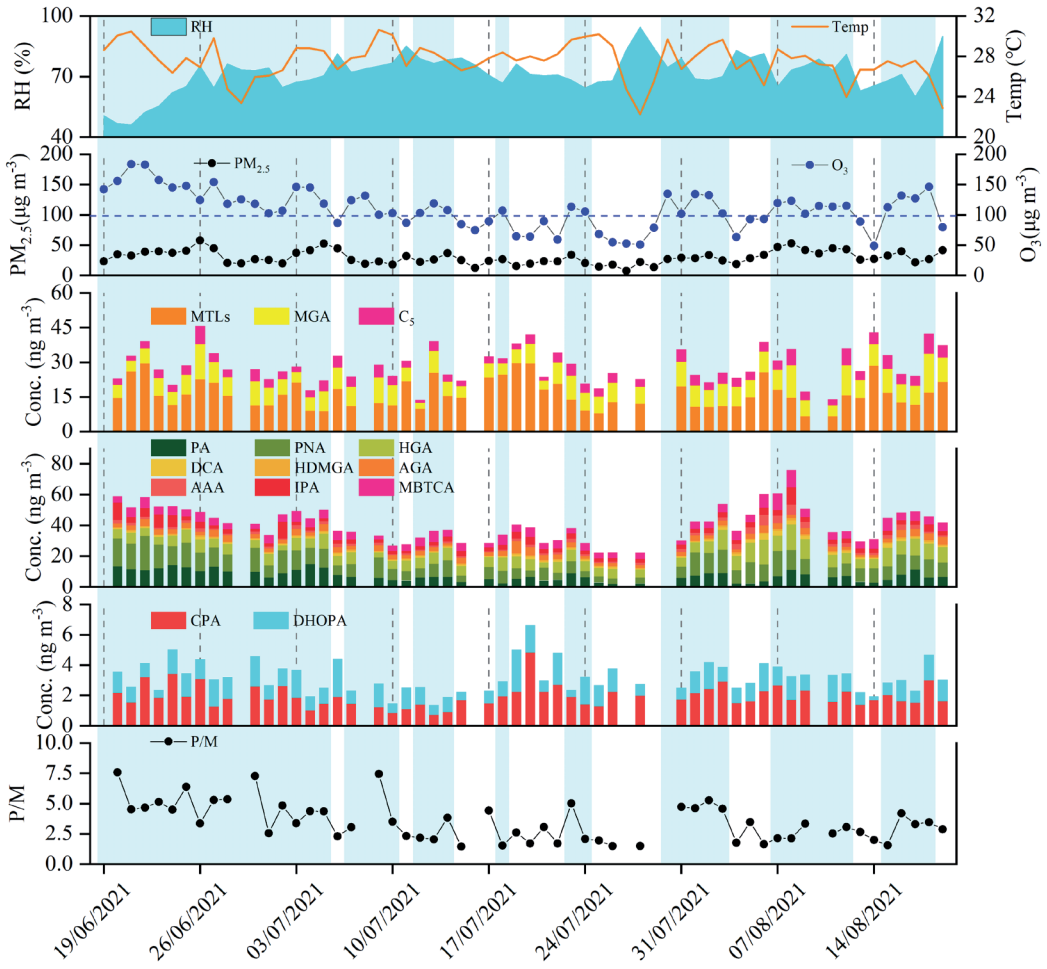

Fig. 3. Time series of SOA tracers in summer (the light blue area represents O_3 pollution days, and the horizontal blue dashed line represents the threshold for O_3 pollution).

SOA Tracers during Haze Days in Winter

Time series of SOA tracers in winter are shown in Fig. 4. SOA_I showed a slightly higher concentration during haze days than during non-haze days, with an increase rate of 3.1%. However, the variation of specific SOA_I tracers was far greater. The increase rates of MGA and C_5 were 19.0% and 20.0%, respectively, while the decrease rate of MLTs was 13.8%. The substantial increases and decreases in specific SOA_I tracers collectively resulted in the small variation of SOA_I. The increment of the high-NO_x product and the decrement of the low-NO_x product indicated a relatively higher NO_x condition during haze days compared with those during non-haze days. The result was also consistent with the higher NO_2 concentration during haze days (43 μg m^{-3}) compared with non-haze days (33 μg m^{-3}). There were some special haze days, including Dec. 22-23, Jan. 8-9, and Jan. 22, which were characterized by high RH (74.5%~89.0%) and very low values of MGA/MTLs (average of 0.60). The reason for this phenomenon was that under high-RH haze conditions, the HO_2· channel became the main chemical reaction for SOA_I formation, which formed more low-NO_x products and thus decreased the value of MGA/MTLs [29]. SOA_M, SOA_C, and SOA_A showed a similar concentration trend. They had higher concentrations during haze days than during non-haze days, with increase rates of 15.9%, 14.7%, and 14.7%, respectively. For SOA_M tracers, except AAA and IPA, which showed hardly any change in concentration, the increase rates of the others exceeded 10%. Under the relatively low O_3 concentration and more stable atmospheric conditions in winter, products from the ozonolysis reactions of monoterpene experienced long periods of aging (P/M = 2.04). The SOA was slightly fresher during haze days (P/M = 2.09) than that in non-haze days (P/M = 1.92), which may be attributed to the fact that the later-generation products were more easily affected by the complex components during haze days. DHOPA was found to have a positive correlation with $PM_{2.5}$ ($r = 0.369$, $P<0.01$), and its concentration remained at high levels when $PM_{2.5}$ concentration reached peaks. The results indicated that the complex atmospheric conditions during haze pollution improved the formation of DHOPA.

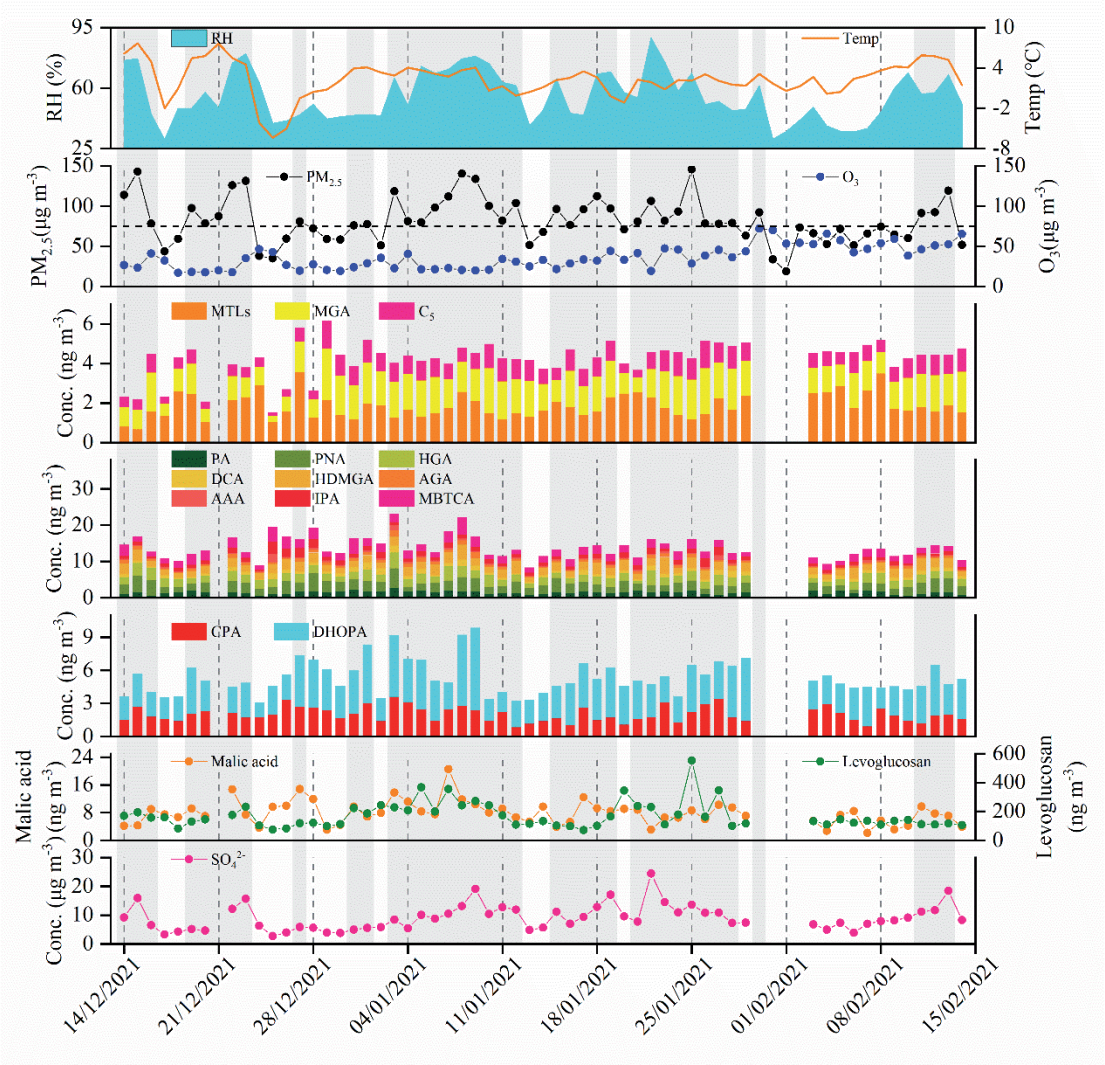

Fig. 4. Time series of SOA tracers in winter (the light gray area represents haze days, and the horizontal black dashed line represents the threshold for $PM_{2.5}$ pollution).

A special haze event (SHE), which started on Jan. 3, 2022, and ended on Jan. 12, 2022, was characterized by a high concentration of levoglucosan (average 240 ng m^{-3}), emphasizing the strong influence of biomass burning on this event. In addition to levoglucosan, malic acid and DHOPA were also found to have high concentrations during SHE. The average concentrations of malic acid and DHOPA during SHE were 10.7 ng m^{-3} and 4.9 ng m^{-3},respectively, which were significantly higher than their whole winter average of 7.9 ng m^{-3} and 3.3 ng m^{-3}, respectively. Notably, DHOPA reached its maximum concentration (7.5 ng m^{-3} on Jan. 9, 2022) during the entire observation period in SHE. These results indicated that haze pollution associated with biomass burning promoted the formation of anthropogenic SOA. SO_4^{2-} showed almost the same trend as RH, especially under high RH conditions. In high RH haze days, when RH reached peaks, SO_4^{2-} also reached peaks (>15 μg m^{-3}), consistent with the fact that high RH facilitated SO_4^{2-} formation. Previous studies reported that under high RH conditions, secondary inorganic formation promoted the aqueous-phase formation of SOA tracers [30, 31]. However, neither high concentrations of SOA tracers were found in the high RH haze days, nor was a significant positive correlation found between SOA tracers and SO_4^{2-}. The results indicated that the formation of secondary inorganic components had a minor influence on the formation of SOA tracers in this study.

Conclusions

SOA tracers in $PM_{2.5}$ samples in a relatively clean city were investigated in this study. SOA_M tracers exhibited the highest overall concentrations among the different tracer groups, and their concentrations were also at a high level compared with those reported in other studies. Biogenic SOA tracers accounted for the majority in summer, while anthropogenic SOA tracers had higher concentrations in winter.

Nevertheless, the corresponding SOC content remained the same in both seasons, with a value of 0.60 μg m^{-3}.

During O_3 pollution days in summer, SOA_M tracers showed a high increment of up to 30.9%, indicating the great contribution of ozonolysis reactions with monoterpene to SOA formation. During haze days in winter, the concentrations of SOA_I tracers originating from different formation pathways varied a lot, but the sum concentration of SOA_I tracers changed slightly. Meanwhile, SOA_M, $SOA_{C,}$ and SOA_A increased approximately 15.0% during haze days compared with during non-haze days. Whether in summer or winter, SOA was fresher during pollution days than during non-pollution days, but the reasons differed. During O_3 pollution days in summer, the substantial presence of O_3 produced more first-generation than later-generation products, while during haze pollution days in winter, later-generation products were consumed faster than first-generation products under complex atmospheric conditions. Specific haze events indicated that biomass burning promoted the formation of anthropogenic SOA, while the generation of secondary inorganic components had little impact on the formation of SOA in Tai'an.

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Conflict of Interest

The authors declare no conflict of interest.

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