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Short communication

Application of VUV-PIMS coupled with GC-MS in chemical characterization, identification and comparative analysis of organic components in both vehicular-derived SOA and haze particles

Peng Zhang ^{a, b, *}, Pengkun Ma ^{a, b}, Haixu Zhang ^{a, b}, Jinian Shu ^{a, b}, Bo Yang ^{a, b}, Zhen Li ^{a, b}^a State Key Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China^b University of Chinese Academy of Sciences, Beijing 100049, China

HIGHLIGHTS

- Haze particle and vehicular-derived SOA are first characterized using a newly built VUV-PIMS.
- VUV-PIMS of organic components in haze particle and vehicular-derived SOA show similar distributions.
- Some key organic components are identified to be carbonyl species after derivatization.
- 27.9%–51.7% particulate carbonyl species in heavy winter haze may result from the vehicular-derived SOA.

GRAPHICAL ABSTRACT

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ABSTRACT

Gasoline vehicle exhaust is a significant source of volatile organic compounds (VOCs) in megacities. In this study, chemical characterization of secondary aerosol particles from the oxidation of gasoline vehicular exhaust by O₃, OH, and NO₃ radicals and the airborne aerosol particles collected during a heavy haze episode (23–25 December 2015) in Beijing were elaborately investigated. The secondary organic aerosols (SOAs) collected from the exhaust and airborne aerosol particles were characterized with a newly built vacuum ultraviolet photoionization mass spectrometer (VUV-PIMS) after thermal desorption, and identified by gas chromatography mass spectrometry (GC-MS). The obtained photoionization mass spectra revealed that the SOAs from the oxidation of gasoline vehicular exhaust and airborne aerosol particles possess a series of common characteristic mass peaks at *m/z* 98, 112, 126, and 140. The components at *m/z* 98, 112, 126, 140 were further identified to be carbonyl species after PFBHA derivatization followed by GC-MS analyses. The carbonyl species from exhaust SOAs were found to be responsible for 51.7%, 57.5%, 36.3%, and 27.9% of the chemical components in haze particles at *m/z* 98, 112, 126, and 140, respectively, which indicates that these SOA components from the oxidation of gasoline vehicular exhaust are a major factor that affects the air quality in Beijing. Among the exhaust SOAs, the carbonyl species detected simultaneously in two (P(O₃/OH)) or three kinds of exhaust oxidation reactions (P(O₃/NO₃/OH)) make a significant contributions to these carbonyl species in haze particles (10.6% for *m/z* 98, 18.3% for *m/z* 112, 23.4% for *m/z* 126, and 20.5% for *m/z* 140). These results implies that the unsaturated VOCs (i.e. alkenes) from exhaust may be one kind of important SOA precursor and that their chemical

* Corresponding author. Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, China.

E-mail address: pengzhang@rcees.ac.cn (P. Zhang).

degradation in the atmosphere may have an important impact on urban air quality in heavy polluted cities such as Beijing, especially during severe winter haze weather.

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1. Introduction

Motor vehicles are becoming the fastest growing source of pollution in the megacities of China as vehicle use rapidly increases (Huang et al., 2015). A large amounts of volatile organic compounds (VOCs) in vehicle exhaust serve as important precursors to secondary organic aerosols (SOAs) (Gentner et al., 2012; Kleindienst et al., 2002; Liu et al., 2015; Nordin et al., 2013; Platt et al., 2013; Tkacik et al., 2014). Because exhaust-SOAs have been verified to be a significant fraction of PM_{2.5} and to possibly have a significant impact on air quality at various scales, vehicle exhausts are widely recognized to be a major source of haze formation in megacities (Bahreini et al., 2012; Gentner et al., 2012; Nordin et al., 2013; Platt et al., 2013; Presto et al., 2014; Weitkamp et al., 2007).

SOAs are formed by the photochemical reaction or ozonolysis of VOCs and by condensation of semi-volatile or nonvolatile products, followed by the partitioning of oxidation products to the particle phase. To identify the precursors and mass yield of SOAs caused by vehicle exhaust, numerous laboratory chamber experiments and field measurement studies have been conducted over the last few decades (Ensberg et al., 2014; Forstner et al., 1997; Gentner et al., 2012; Huang and Chao, 2015; Liu et al., 2015; Nordin et al., 2013; Platt et al., 2013; Tkacik et al., 2014; Weitkamp et al., 2008). Nordin et al. (2013) and Kleindienst et al. (2002) verified that 60%–85% of SOA formation could be attributed to the reaction products of light aromatic compounds (C₆–C₉), based on smog chamber studies of gasoline vehicle exhaust. Gentner et al. showed that diesel was responsible for 65%–90% of vehicular-derived SOAs, with substantial contributions from aromatic and aliphatic hydrocarbons (Gentner et al., 2012). Robinson et al. (2007), and Zhao et al. (2014), proposed that intermediate VOCs (C₁₂–C₂₂) in vehicle exhaust were also an important class of SOA precursors. Additionally, some recent studies have suggested that emissions of naphthalene, parts of polycyclic aromatic hydrocarbons, and nitrated polycyclic aromatic hydrocarbons from vehicle exhaust may also contribute to potential SOA formation as a result of their minor weight fractions in the fuels (Gentner et al., 2012; Healy et al., 2012; Jathar et al., 2013; Platt et al., 2013). However, many aspects of SOA composition in these exhaust-derived VOCs and IVOC are not yet well understood.

Through smog chamber experiments in recent years, significant advances have been made toward systematically characterizing and identifying SOA components caused by one or several single-ring light aromatic compounds (C₆–C₁₀) in the presence of OH radicals. Extensive studies have shown that SOAs are composed of species containing multiple functional groups of carbonyl, carboxyl and hydroxyl groups (Forstner et al., 1997; Jang and Kamens, 2001; Moise et al., 2015; Sato et al., 2012; Smith et al., 1999). However, because no actual aerosol measurements are performed and characterized in these recent studies, it remains unknown whether the proposed structure and distribution ratio of SOA components is consistent with that in haze particles. Moreover, SOA formation also occurs both during the day and night when O₃ and NO₃ radicals can react with olefins in exhaust. To the best of our knowledge, high alkene levels have been measured in Chinese gasoline oil (Zhang et al., 2013, 2015). More than 50 olefins have been observed and identified in vehicular exhaust (Gentner et al., 2013). These alkenes

(~15% in the mixing ratio of VOCs) provide nearly 75% of the reactivity of ambient VOCs (Shao et al., 2005). Another recent study showed that the formation of stabilized criegee intermediates (CIs), from the reaction between gasoline vehicle exhaust alkenes and O₃ in the presence of SO₂, would facilitate the production of sulfate and SOAs in the ambient atmosphere (Liu et al., 2016). However, the chemical characterization of SOA composition from the oxidation of gasoline vehicular exhaust has not been systematically studied for both ozonation reactions and exposure to the NO₃ radicals. It is therefore necessary to further investigate and characterize SOA composition from the vehicular exhaust by exposure to OH, NO₃ radicals and O₃. In order to address the significant impact of SOA formation on heavy haze days, it is also crucial to assess the consistency of these products with the major organic components in haze particles.

For these reasons, this study investigated SOA formation and characterization from vehicular exhaust by exposure to O₃, NO₃, and OH radicals in a smog chamber coupled with a newly built vacuum ultraviolet photoionization mass spectrometer (VUV-PIMS). The chemical composition of SOA particles was compared to actual haze particles collected during a heavy haze episode during a Beijing winter. Detailed experimental methods and results are reported in the following sections.

2. Experimental section

2.1. Experimental setup

All the experiments were carried out in a 1.2 m³ smog chamber at ~25 °C and 35% relative humidity (RH) under atmospheric pressure. 16 black light lamps (1.2 m-long, 365 nm 60 W Philips/10 R BL, Royal Dutch Philips Electronics Ltd, the Netherlands) surround the Teflon bag and are used as light source. One stainless steel fan was installed inside the reactor to guarantee well mixing of the introduced gas species and the oxidants within 60 s. A suite of instruments was used to characterize the gas- and particle-phase pollutants inside the chamber. A scanning mobility particle size (SMPS, TSI, Inc. classifier model 3081, CPC model 3010) was used to measure the size distributions and particle volume concentration. A newly laboratory-built VUV-PIMS was used to on-line monitor the gas-phase organic species and off-line characterizes SOA components. Detailed descriptions of VUV-PIMS have been presented elsewhere (Sun et al., 2015); only a brief description is presented as follows: VUV-PIMS consists of a radio frequency-powered VUV lamp, a VUV photoionizer, an ion-immigration region, and a reflection time-of-flight mass spectrometer. The mass resolution of VUV-PIMS is $\sim m/z$ 1000. An O₃ monitor (model 205, 2B Technologies) was used to measure O₃ concentration.

A UV lamp O₃ generator (NBF30/W) was employed to produce O₃ by passing a flow (0.6 L min⁻¹) of the oxygen/argon gas mixture through a UV lamp. The ozonolysis of exhaust was carried out in the presence of 3000 ppm cyclohexane (OH scavenger). NO₃ radicals were generated by the thermal decomposition of N₂O₅ within the chamber. N₂O₅ was synthesized according to the literature and kept in a glass trap in liquid nitrogen prior to use (Zhang et al., 2014, 2016). N₂O₅ was eluted by passing a stream of N₂ (~0.6 lpm) over N₂O₅ crystals held in a cooling bath (233 K). A digital refrigerated

circulator bath (−40–100 °C, DCW-4006, China) was used to maintain a constant temperature within the cooling bath. The concentration of NO₃ radicals was estimated to be ~62 ppbv according to the following equilibrium constant (Sander et al., 2006):

$$K_{eq} = \frac{[N_2O_5]}{[NO_2][NO_3]} = 3 \times 10^{-27} \exp(10990/T)$$

Hydroxyl radicals were generated by the irradiation of hydrogen peroxide (UV/H₂O₂) under 16 black light lamps (365 nm). 2 mL H₂O₂ (a 50% by weight aqueous solution of H₂O₂) was heated at 373 K and rapidly added into the chamber using a flow of purified air (~50 L min^{−1}). Average OH radicals level in the chamber was 2.6×10^7 molecule cm^{−3} based on the decay of 1,3,5-Trimethylbenzene. The concentrations of O₃, OH, and NO₃ radicals were higher than ambient concentrations in order to collect enough SOA particles in short time.

2.2. Experimental procedure

Given that the distribution ratio of VOCs in the exhaust from a motorcycle (HONDA, WH110T-A engine) was quite similar with some ubiquitous gasoline vehicles (i.e. Hyundai Elantra and Shanghai Volkswagen Skoda shown in Fig. S1), a motorcycle (HONDA, WH110T-A engine) running under idling conditions was used to generate gasoline vehicle exhaust. The motorcycle was fueled with gasoline (Chinese Grade 95#) and the engine was allowed to run for approximately 2.5 min before sampling. The entire raw exhaust was directly injected into the smog chamber through a stainless steel bellow. Prior to each experiment, the smog chamber was evacuated and filled with purified dry air at least five times to eliminate any residual hydrocarbon, O₃, or particles from the reaction in order to avoid carry-over problems. At the start of each experiment, the bag was filled approximately two thirds full of filtered air (i.e. leaving some of the volume free for exhaust injection for 40 s). Subsequent to exhaust injection, the chamber was filled close to maximum volume with pure air, ensuring more rapid mixing of the sample. The chamber was allowed to equilibrate for several minutes prior to characterization of the primary vehicular exhaust. After adding exhaust, O₃, OH, and NO₃ radicals were each introduced into the chamber, respectively, when the primary VOC concentrations and particle mass concentrations (0.5–1.5 μg m^{−3}) got stabilized in the chamber. SOA formation was observed immediately after these atmospheric oxidants injection. In this study, a three-channel sampler with pre-cleaned glass microfiber filters (47 mm diameter, 0.7 μm pore-size, Whatman) was used to collect SOA particles formed in the experiments and ambient aerosol samples during winter heavy haze days with exceedingly high PM_{2.5} levels (22–25 December 2015). 24-h ambient aerosol samples were obtained at an urban site in Beijing, near the Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences.

2.3. Analysis

The sampling time of SOA particles produced in chamber experiments was ~20 min. After the completion of sampling, one filter was used to characterize SOA components with VUV-PIMS through thermal desorption at 353 K and the other two filters were used to identify products via gas chromatography mass spectrometry (Agilent GC-MS, 6890 plus GC-5973 N MSD). The collected SOA particles were ultrasonically extracted using dichloromethane/methanol (3; 1, v/v) solution at room temperature, and then the extracts were filtered and further concentrated by gentle high purity nitrogen blow-down to about 0.5–1 mL. Each extract was split

into two fractions, one of which was derivatized with PFBHA (O-(2,3,4,5,6-pentafluorobenzyl)-hydroxyamine). The derivatization reactions converted polar organic compounds into less polar compounds, as carbonyl groups react with PFBHA to form oxime derivatives. Both the derivatized and underivatized fractions were analyzed using GC-MS. The GC-MS is comprised of a gas chromatographer (DB-5MS 30 m × 0.25 mm × 0.25 μm capillary column) and a mass spectrometer (quadrupole mass filter with a 70 eV electron impact ionizer). The 5 μL samples were introduced into the GC-MS system in the pulsed splitless mode. The temperature of the programmed temperature vaporizer was held at 270 °C. The initial oven temperature was set to 80 °C for 20 min, then step-by-step increased to 280 °C (by 3.5 °C min^{−1}) and held for 10 min. Helium (99%, Beijing Huayuan Gas Chemical Industry Co. Ltd.) was used as the carrier gas at a constant flow rate of 1 mL min^{−1}. The GC-MS total ion monitoring (TIM) and selected ion monitoring (SIM) were employed in this study.

3. Results and discussion

3.1. VUV-PI mass spectrum of VOCs and SOA formation

The VOCs in the smog chamber were detected on-line using VUV-PIMS. Fig. 1 shows the VUV-PIMS of VOCs from diluted gasoline vehicle exhaust (black line). The mass-to-charge ratio (*m/z*) of VOCs in gasoline vehicle exhausts mainly concentrated in a range between 78 and 134. These VOCs with high peak intensity (*m/z* 92, 106, 120, and 134) were identified to be single-ring light aromatics with the help of GC/MS analysis (Fig. S2) (Liu et al., 2015). A small amount of naphthalene (*m/z* 128) was also observed and identified in the vehicular exhaust. Additionally, we observed relatively strong protonated water clusters ((H₂O)₄H⁺) at *m/z* 73 (Sun et al., 2015). To better distinguish the VUV-PI mass spectra of saturated and unsaturated volatile organic compounds (e.g. alkenes) in gasoline exhaust, Fig. 1 showed the comparison of exhaust VUV-PI mass spectra in the presence of O₃ (Red line) and absence of O₃ (Blue line). In the presence of 500 ppbv O₃, the species with mass peaks at *m/z* 54, 56, 66, 68, 70, 80, 82, 84, 94, 96, 98, 104, 110, 116, 118, 130, and 132 were apparently consumed by O₃. These were there assigned as unsaturated volatile organic compounds (UVOCs). The UVOCs at *m/z* 56, 70, 84, 98, and 104 were assigned as mono-alkenes (C_nH_{2n}); *m/z* 54 and 68 were dialkenes (C_nH_{2n-2}); *m/z* 66 was cyclo-diolefins (C_nH_{2n-4}), and 82, and 96 were cycloalkenes (C_nH_{2n-2}). The above species have each been documented in the emission inventory of gasoline vehicular exhaust (<http://www.arb.ca.gov/testmeth/slb/sop102-103v2-2.pdf>). However, it should be noted that the UVOCs at *m/z* 80, 94, 110, 116, 118, 130, 132 were first observed using VUV-PIMS. Based on their molecular weights, the UVOCs at *m/z* 80 and 94 were assigned as cyclo-diolefins (C_nH_{2n-4}), *m/z* 110 was cycloalkenes (C_nH_{2n-2}), and *m/z* 116, 118, 130, 132 maybe alkenes with one benzene ring.

In this work, the concentrations of VOCs from exhaust would be much higher than what has been monitored in ambient atmosphere or used in other works, but the goal of these experiments was to further investigated chemical characterization of SOAs using VUV-PIMS than to simulate a typical atmospheric exposure. Given that VOCs in exhaust were rather complex, the detection limits of only small part of VOCs were calibrated. Thus, the detection limits of benzene (~300 counts ppbv^{−1}) and isoprene (~100 counts ppbv^{−1}) were employed to be the agencies of light aromatic hydrocarbons and unsaturated VOCs in exhaust, respectively. The initial concentrations of total light aromatic hydrocarbons (C₆–C₁₀) and unsaturated VOCs were estimated to be 2.3 ± 0.1 ppmv and 1.75 ± 0.05 ppmv, respectively. The evolution of SOA growth during the oxidation of exhaust by OH, NO₃ and O₃ was shown in

Fig. 1. VUV-PIMS of VOCs without (Blue) and with (Red) O_3 in diluted gasoline vehicle exhaust with an averaging time of 10 s. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. S3. After an initial period of aerosol growth, aerosol mass and volume were observed to stabilize with time. Compared with the OH radicals and O_3 experiments, the total SOA growth was minimum in the NO_3 radicals experiment. Recent studies have shown that NO_3 radicals produced less extremely low-volatility compounds and could contribute to particle growth in the presence of seed-particle, causing low aerosol mass yields (Draper et al., 2015; Perraud et al., 2012). We conclude that this idea may suitably explain the NO_3 -exhaust reaction observed in our experiment.

3.2. Chemical characterization of SOAs using VUV-PIMS

Chemical identification of SOAs was crucial for understanding the photo-oxidation and ozonolysis mechanisms of VOCs and the eventual formation of SOAs. The collected SOAs particles in haze and in experimental exhaust reactions were analyzed offline with VUV-PIMS after thermal desorption. The evolution of chemical composition for SOA under different temperature (353–393 K) were also conducted. The results show that the evolution of chemical composition for SOA is not essentially changed by temperature, which is consistent with one recent work by Cappa and Wilson (2011). Additionally, the experiment of background for vehicle exhaust only was also conducted. The VUV-PI mass spectra of exhaust background and O_3 /SOA after subtracting the exhaust background were shown in the Supporting Information (Fig. S5). It should be noted that only some water clusters (m/z 37, 55, and 73) and some particulate single-ring light aromatics (C8, C9, C10, and C11) were subtracted from the exhaust background. Thereby, we concluded that the contribution of background for vehicle exhaust on these major components in exhaust SOA could be ignored. Fig. 2 (A–D) shows the VUV-PIMS mass spectra of these collected SOA at 353 K. The products at m/z 58 and 72 were assigned to the two smallest yet most abundant dicarbonyls: glyoxal and methylglyoxal, following some previously reported research (Fu et al., 2008; Lim et al., 2013; Zhang et al., 2016; Zhao et al., 2012). Numerous cluster ions at m/z (69–72), (84–87), (94–102), (108–116), (122–130), and (136–144) were all observed in both the exhaust SOA and haze particles, which reflects the complexity and similarity of exhaust SOA. Notably, the products at m/z 98, 112, 126,

and 140 showed the most intensive signals in either exhaust SOA or haze particles. This phenomenon suggests that the atmospheric oxidation of gasoline exhaust by NO_3 , OH radicals, and O_3 may be an important source of specific SOA compounds with high yields in haze particles. Moreover, based on the comparison between PI mass spectrum of collected haze samples in the morning and in the evening (Fig. 2D), the signal of these major components intensifies in the evening apparently exceeded that in the morning by a factor of 3 when the $PM_{2.5}$ mass concentration increased from $870 \mu g m^{-3}$ to $1060 \mu g m^{-3}$. This implied that gasoline exhaust SOA chemistry is one significant factor in leading to rapid $PM_{2.5}$ mass growth in Beijing. Interestingly, the $PM_{2.5}$ mass concentration increased by approximately $300 \mu g m^{-3}$ on 23 December (Fig. S4), exceeding the measurement ($\sim 200 \mu g m^{-3}$) of 25 December (Fig. 2D). However, the increasing range of these major SOA components was one third of that on 25 December. We speculated that an increase of inorganic compounds (i.e., sulfate, nitrate, black carbon, etc.) dominated the $PM_{2.5}$ increase on 23 December, instead of the major SOA components.

Some previous studies on the photooxidation process of single-ring aromatic hydrocarbons speculated that these SOA components at m/z 96, 110, 124, and 138 were furaldehyde and heptadienal, at m/z 100, 114, and 128 were ketoaldehyde and dihydro-furandione, and at m/z 98, 112, 126, 140 were unsaturated ketoaldehyde and furandione (Jang and Kamens, 2001; Smith et al., 1999). These SOA components at m/z 96, 100, 110, 114, 124, 128, and 138 in the OH-exhaust SOA have a significant amount, after that at m/z 98, 112, 126, 140 (Fig. 2A). However, their peak intensities were far lower than that at m/z 98, 112, 126, 140 in haze particles (Fig. 2D). Thereby, we concluded that their contributions to haze formation are limited. Although the O_3 -exhaust SOA were formed under 3000 ppm cyclohexane, it could not be ruled out completely that OH and NO_3 radicals contribute to the reaction since a certain amount of OH and NO_3 radicals could be produced via alkene ozonolysis and the gas-phase reaction between O_3 and NO_x , respectively. Given that PI mass spectra alone provided limited compositional information and did not distinguish between different functional groups and isomers, the question of whether these major SOA components at m/z 98, 112, 126, and 140 formed in

Fig. 2. VUV-PIMS of SOA composition from the oxidation of gasoline exhaust by OH radicals (A), O_3 (B), NO_3 radicals (C), and the haze particles (D).

both the O_3 -exhaust reaction and the OH/ NO_3 -exhaust reaction required further investigation using GC-MS (see following section). Relative to the O_3 and OH radical reactions, concentrations and distributions of SOA components from NO_3 -exhaust were lower and apparently different, which implies that the SOA formation mechanisms have some important differences.

Additionally, it should be noted that a significant number of fragments at m/z 43 were observed in either exhaust-SOA or haze particles. Extensive studies have shown that the peaks at m/z 43 were dominated by $C_2H_3O^+$ fragments and were commonly associated with oxidized nonacid oxygenated species containing carbonyl groups (Jathar et al., 2013; Nordin et al., 2013). Therefore, it can be speculated that these major SOA components were some nonacid oxygenated species containing carbonyl groups.

3.3. Chemical identification of SOAs via GC/MS analysis

To further identify the major components at m/z 98, 112, 126, and 140, the SOA components were derivatized by PFBHA and analyzed using offline GC-MS. Fig. 3 shows the extracted total ion chromatogram of derivatized SOA components at m/z 98, 112, 126, and 140 from the haze particles and the vehicle exhaust reactions. The fragment of m/z 181 was ubiquitous in the EI mass spectra of SOA components at m/z 98, 112, 126, and 140 after derivatization (Fig. S6). The specific fragment mass at m/z 181 have been reported to be the major characteristic peak of derivatized compounds with the carbonyl functional group (Jaoui et al., 2014; Kalberer et al., 2000). This indicated that the observed compound in Fig. 3 contains at least a carbonyl group. The derivatized components at m/z 293, 307, 321, and 335 had a parent mass of m/z 98, 112, 126, and 140, respectively. A careful analysis of these derivatized products suggested that these SOA components in either exhaust SOA or haze particles have different structure isomers due to different retention times. The derivatized products at m/z 293, 307, 321, and 335 were some mono-functional derivatives. Further, some di-functional

derivatives at m/z 488 (parent mass m/z 98) and 502 (parent mass m/z 112) were also detected in haze particles, O_3 -exhaust SOA, and OH-exhaust SOA. We concluded that some of SOA components at m/z 98 and 112 were dicarbonyl compounds. It should be noted that part of mono-functional derivatives at m/z 98 and 112 in both OH-exhaust and O_3 -exhaust SOA and both OH-exhaust and NO_3 -exhaust SOA have the same retention time. In both OH- and O_3 -exhaust SOA, SOA component with m/z 293 at 38.39 and 54.67 min, with m/z 307 at 61.21 min, and with m/z 335 at 55.98 and 57.08 min have the same retention time. In both OH- and NO_3 -exhaust SOA, SOA component with m/z 307 at 58.81 min, with m/z 321 at 58.87 min, and with m/z 335 at 59.64 have the same retention time. These results imply that the oxidation of exhaust by O_3 , OH, and NO_3 radicals can produce some carbonyl species with the same molecular structure. Moreover, part of mono-functional and di-functional derivatives at m/z 98 and 112 in the OH-exhaust SOA and haze particles also have the same retention time with that in haze particles (i.e. m/z 293 at 56.17 min, m/z 307 at 56.58 min; m/z 502 at 66.55 min). This result further proved that the OH-exhaust SOA is one of important organic aerosol sources to haze pollution.

3.4. Contribution of carbonyl species from the exhaust SOA to that in haze particles

In order to further investigate how many kinds of carbonyl species in haze particles come from the oxidation of gasoline exhaust and their contribution to that detected in haze particles, derivatized samples of exhaust-SOAs and haze particles were reanalyzed via GC-MS selected ion monitoring (SIM) of molecular ions (dwell time 500 s). More information on the method to calculate the contribution of each kind of exhaust oxidation reaction has been provided in the Supporting Information. Fig. 4 shows the select ion chromatogram of derivatized products at m/z 293, 307, 321, and 335. By matching the retention times of these with that of haze particles, different carbonyl species (43 for m/z 98

Fig. 3. Total ion chromatogram of derivatized SOA components from the OH/exhaust reaction (A), O₃/exhaust reaction (B), NO₃/exhaust reaction (C), and the haze particle (D).

Fig. 4. Selected ion chromatogram of carbonyl species at m/z 98 (A), 112(B), 126(C), 140(D).

(39.4%), 49 for m/z 112 (45.4%), 27 for m/z 126 (27%), and 23 for m/z 140 (25.8%)) in the haze particles were identified to have resulted from exhaust-SOAs. Based on their relative abundance in haze particles, the contributions of carbonyl species from exhaust to haze particles were estimated to be 51.7% for m/z 98, 57.5% for m/z 112, 36.3% for m/z 126, and 27.9% for m/z 140, respectively (Fig. 5). These results implied that SOA components from the oxidation of gasoline vehicular exhaust represent a major factor affecting Beijing air quality. Additionally, it should be noted that some discrepancy between atmospheric particles and the exhaust SOA was observed; part of the carbonyl species in haze particles resulted from other sources, and their relative contributions were 48.3% for m/z 98, 42.5% for m/z 112, 63.7% for m/z 126, and 72.1% for m/z 140, respectively. This suggested that the actual haze particles were much more complicated than those formed via laboratory experiment and that contributions from carbonyl species with other sources cannot be ignored in heavy haze weather.

It should be noted that some carbonyl species could be detected simultaneously in two or three kinds of exhaust oxidation reactions. A possible explanation for this was that the species result from OH and NO_3 radical reactions, since a certain amount of OH and NO_3 radicals could be produced via alkene ozonolysis and the gas-phase reaction between O_3 and NO_x , respectively. Of course, different exhaust oxidation processes may also form some carbonyl species with the same molecular structure. Due to the complexity and diversity of SOA precursors in the exhaust and the uncertainty of formation mechanisms for exhaust SOA, it was extremely difficult to identify the specific sources of carbonyl species. In this work,

exhaust-dominated carbonyl species were divided into five groups as follows: $\text{P}(\text{NO}_3)$, products formed only in the NO_3 -exhaust reaction; $\text{P}(\text{OH})$, products formed only in the OH-exhaust reaction; $\text{P}(\text{O}_3/\text{OH})$, products formed in both O_3 - and OH-exhaust reactions; $\text{P}(\text{OH}/\text{NO}_3)$, products formed in both OH- and NO_3 -exhaust reactions; and $\text{P}(\text{O}_3/\text{NO}_3/\text{OH})$, products formed in O_3 -, NO_3 - and OH-exhaust reactions. The relative contributions of these carbonyl species from $\text{P}(\text{NO}_3)$, $\text{P}(\text{OH})$, $\text{P}(\text{O}_3/\text{OH})$, $\text{P}(\text{OH}/\text{NO}_3)$, and $\text{P}(\text{O}_3/\text{NO}_3/\text{OH})$ shown in Fig. 5 were notably different. The contributions of $\text{P}(\text{NO}_3)$ at m/z 98, 112, 126, 140 were higher than $\text{P}(\text{OH})$, which suggested that the NO_3 radical reactions of exhaust during the nighttime was also one of important factors to cause haze pollution. Given that aromatics and other saturated VOCs are not reactive to O_3 , thus the contributions of $\text{P}(\text{O}_3/\text{NO}_3/\text{OH})$ and $\text{P}(\text{O}_3/\text{OH})$ could be considered to be the contributions of unsaturated VOCs (i.e. alkenes). The total contributions of $\text{P}(\text{O}_3/\text{NO}_3/\text{OH})$ and $\text{P}(\text{O}_3/\text{OH})$ to haze particles are 10.6% for m/z 98 and 18.3% for 112, which are slightly lower than $\text{P}(\text{OH})$, $\text{P}(\text{NO}_3)$ and $\text{P}(\text{OH}/\text{NO}_3)$. These results indicated that contributions from the unsaturated VOCs in exhaust should not be ignored during haze formation. Moreover, the total contributions of $\text{P}(\text{O}_3/\text{NO}_3/\text{OH})$ and $\text{P}(\text{O}_3/\text{OH})$ to haze particles were 23.4% for m/z 126 and 20.5% for m/z 140, which was the highest. This further suggests that unsaturated VOCs in exhaust maybe also one kind of important SOA precursors and made an important contribution during the haze formation. Many recent studies have showed that reactivity of alkenes in gasoline vehicle exhaust can facilitate the production of sulfate and SOAs via inducing plentiful formation of stabilized criegee intermediate (CI) (Huang and Chao,

Fig. 5. The contribution of carbonyl species at m/z 98 (A), 112(B), 126(C), 140(D) from exhaust-dominated SOA in haze particles.

2015; Liu et al., 2016; Mauldin III et al., 2012; Sato et al., 2012; Welz et al., 2012). These unsaturated hydrocarbons (alkenes) with high content in gasoline vehicle exhaust showed a significant reactivity to O_3 , OH, and NO_3 radicals. Therefore, we speculated that the oxidation of alkene from exhaust may have a significant impact on urban air quality in heavy polluted cities such as Beijing, especially during severe haze weather (Nordin et al., 2013; Song et al., 2005).

4. Conclusions

Numerous laboratory experiments and field measurement conducted so far have shown that gasoline exhaust can play a significant role in the formation of severe haze, especially in heavily polluted cities such as Beijing. Despite these researches, our knowledge of the chemical characterization of exhaust SOA components and their contribution to haze particles remained poor. The investigation of the chemical characterization gasoline exhaust components in this study helped reveal the contribution of some major SOA components to the city haze.

Some major SOA components at m/z 98, 112, 126, and 140 formed in the oxidation of vehicle exhaust by O_3 , OH, and NO_3 radicals were first observed using VUV-PIMS. After derivatization by PFBHA followed by GC-MS analysis, these major components detected in the OH-exhaust, O_3 -exhaust and NO_3 -exhaust SOA were some carbonyl species containing at least one carbonyl group. Almost all of these carbonyl species formed in the oxidation of exhaust were detected in haze particles. The relative contributions of these carbonyl species from the exhaust to the haze particles were estimated to be 51.7% for m/z 98, 57.5% for m/z 112, 36.3% for m/z 126, and 27.9% for m/z 140, respectively, which implied that these SOA components represent a major factor in affecting Beijing air quality. Among these exhaust-dominated carbonyl species, $P(OH/O_3)$ and $P(O_3/NO_3/OH)$ also made a significant contributions to the carbonyl makeup of haze particles (10.6% for m/z 98, 18.3% for m/z 112, 23.4% for m/z 126, and 20.5% for m/z 140). This not only implied that alkenes from exhaust may be an important SOA precursor and that their chemical degradation in the atmosphere may have an important impact on urban air quality in heavy polluted cities such as Beijing, especially during severe haze weather. Additionally, a significant amount of carbonyl species in haze particles may have other pollution sources in addition to the oxidation of exhaust since P (other) at m/z 98, 112, 126, and 140 contributed to 48.3%, 42.5%, 63.7%, and 72.1%, respectively. These observations and conclusions indicate that further work is needed to look into other SOA precursors because of their large carbonyl species contribution. It will be very necessary to further deep-going investigating other important SOA components (i.e. organonitrate products formed in both the NO_x photochemistry and NO_3 reaction of exhaust) and their contribution as well as these carbonyls species.

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Appendix A. Supplementary data

Supplementary data related to this chapter can be found at <http://dx.doi.org/10.1016/j.atmosenv.2017.06.013>.

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