Potential of secondary aerosol formation from Chinese gasoline engine exhaust

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Abstract

Light-duty gasoline vehicles have drawn public attention in China due to their significant primary emissions of particulate matter and volatile organic compounds (VOCs). However, little information on secondary aerosol formation from exhaust for Chinese vehicles and fuel conditions is available. In this study, chamber experiments were conducted to quantify the potential of secondary aerosol formation from the exhaust of a port fuel injection gasoline engine. The engine and fuel used are common in the Chinese market, and the fuel satisfies the China V gasoline fuel standard. Substantial secondary aerosol formation was observed during a 4–5 hr simulation, which was estimated to represent more than 10 days of equivalent atmospheric photo-oxidation in Beijing. As a consequence, the extreme case secondary organic aerosol (SOA) production was 426 ± 85 mg/kg-fuel, with high levels of precursors and OH exposure. The low hygroscopicity of the aerosols formed inside the chamber suggests that SOA was the dominant chemical composition. Fourteen percent of SOA measured in the chamber experiments could be explained through the oxidation of speciated single-ring aromatics. Unspeciated precursors, such as intermediate-volatility organic compounds and semi-volatile organic compounds, might be significant for SOA formation from gasoline VOCs. We concluded that reductions of emissions of aerosol precursor gases from vehicles are essential to mediate pollution in China.

Introduction

After a tremendous increase in recent years, the total quantity of vehicles in China reached 269 million in 2015, comprising the second largest vehicle population in the world (National Bureau of Statistics of China, 2015). Vehicles emit large amounts of particulate matters and gaseous pollutants, such as carbon monoxide, nitrogen oxides and volatile organic compounds (VOCs). Primary particles from vehicles have been reported to contribute 5%–10% of PM2.5 (particulate matter with diameter less than 2.5 μm) in megacities in China (Huang et al., 2014). Gaseous pollutants from vehicles are precursors to secondary aerosols through gaseous- and/or aqueous-phase oxidation in the atmosphere (Gentner et al., 2012).

Previous smog chamber studies of exhaust from light-duty gasoline engines/vehicles have demonstrated that the amount of secondary aerosol formed from the oxidation of gaseous precursors exceeds that of primary aerosols emitted directly.
Skeptical scholars have combined factor analysis with 14C analysis to explore VOC mechanisms (Hallquist et al., 2009; Guo et al., 2012). Some fundamental factors regarding secondary aerosol formation have led to the poor understanding of the contribution of light-duty gasoline vehicles to ambient PM$_{2.5}$.

Secondary aerosols, mainly organics, nitrate, sulfate and ammonium, account for large fractions of PM$_1$ in many mega cities of China: 51%–80% in Beijing, 72%–84% in Shanghai and 77%–83% in Guangzhou (Huang et al., 2010, 2012). They drive severe haze pollution events to a large extent. However, the sources of secondary aerosols are not well-known, due to the lack of understanding of their composition and formation mechanisms (Hallquist et al., 2009; Guo et al., 2012). Some scholars have combined factor analysis with $^{14}$C analysis to distinguish fossil and non-fossil sources of secondary organic aerosol (SOA) (Szidat, 2009). Fossil SOA, mainly from traffic and coal burning, has been found to contribute about 45%–65% of SOA in Beijing (Huang et al., 2014), indicating the significant contribution of vehicles to SOA in urban areas.

In this study, a series of chamber experiments was conducted to investigate secondary aerosol formation from gaseous pollutants in gasoline engine exhaust. The port fuel injection (PFI) gasoline engine and fuel tested both have major market share in China. Diluted gaseous pollutants were injected into an outdoor chamber and photo-oxidized to examine secondary aerosol formation. This study was conducted to link vehicle source emissions with ambient particle matter, with the aims of evaluating the potential of secondary aerosol formation from gasoline engine exhaust in the ambient atmosphere, improving the general understanding of secondary aerosol formation mechanisms, and promoting reconceptualization of the role of gasoline vehicle emissions in atmospheric aerosol pollution.

### 1. Materials and methods

#### 1.1. Experimental set-up

Primary emissions of gaseous pollutants and particles were measured at the engine tailpipe using the gas analyzer AVL Combustion Emissions Bench II (CEB II, AVL, Austria). Particle samples from the engine tailpipe were analyzed by a balance and organic carbon/elemental carbon analyzer (OC/EC analyzer, Sunset Lab, USA), and primary emission factors were calculated accordingly.

The secondary aerosol formation simulation experiments were carried out in the outdoor chamber in September 2014 in Beijing. The two-layer outdoor chamber has a volume of 1.2 m$^3$. The inner layer is made of 0.13 mm perfluoroalkoxy (PFA) Teflon and the outer layer is a 5.6 mm thick rigid acrylic shell (OP-4 Acrylite, Cyro Industries, USA). Ambient sunlight is used to generate reactions in the chamber, in an environment similar to the real atmosphere. OP-4 Acrylite and PFA Teflon allow efficient ultraviolet (UV) transmission in the UV-B (280–315 nm) and UV-A (315–400 nm) ranges, leading to the penetration of about 60% of UV light through the two-layered wall into the chamber.

Four chamber experiments were performed with a PFI engine and fuel with 28.5% aromatic hydrocarbons, complying with China V gasoline fuel standard. The engine functioned at 2000 r/min and 50% loading. The experimental conditions are listed in Table 2.

Prior to each experiment, the chamber was cleaned by flushing with zero air for about 35 hr and illuminating with sunlight, to create a pristine environment. It was then covered with two layers of anti-UV cloth to block sunlight. Engine exhaust was injected into the chamber through a heater. Samples were heated up to 200°C, to reduce VOC loss. The particles in the exhaust were filtered, to ensure that the initial particle concentration was <100 particles/cm$^3$. Excess (1 mL, 30%) H$_2$O$_2$ was also injected to generate sufficient OH exposure. Ambient sunlight was used to induce H$_2$O$_2$ to produce OH radicals. OH exposure in the chamber was calculated from the photolysis of H$_2$O$_2$, using actinic flux spectra recorded by a multi-channel spectrometer with a photodiode array (Carl Zeiss MicroImaging GmbH, Germany). The related theory and details of physical and chemical processes were described by Stark et al. (2007). Assuming the 24 hr mean concentration of 10$^6$ OH molecules/cm$^3$ in Beijing (Lu et al., 2013), the OH exposure at the end of the experiments simulated an almost extreme case of oxidation, corresponding to more than 10 days in the atmosphere. Fig. 1 is a schematic illustration of the outdoor chamber, and the injection and measurement set-up.

After the injection of gaseous pollutants and H$_2$O$_2$, a 15-minute period was allowed to ensure sufficient mixing, and primary emissions in the dark chamber were then characterized. The anti-UV cloth was then removed to initiate photo-oxidation, this timepoint was referred to as $t = 0$ hr (Fig. 2). All experiments were conducted from about 13:00 to 17:00 with differing sunlight intensity.

High time resolution instruments were used to characterize gaseous and particulate-phase samples inside the chamber. VOC samples were collected from the gasoline engine exhaust

![Fig. 1 – Schematic representation of the outdoor chamber set-up for the experiments. DMA: differential mobility analyzer; CPC: condensation particle counter; CCN: cloud condensation nuclei counter.](image-url)
using canisters, under the same mode used for the chamber experiments, and analyzed in the laboratory using gas chromatography/flame ionization detection and gas chromatography–mass spectrometry (GC/FID–GC/MS, Agilent Technologies, USA).

1.2. Instrumentation

To track the evolution of secondary aerosol formation in the chamber, the properties of gaseous pollutants and particles were measured simultaneously with on-site instruments. These properties included gas concentration, particle size distribution, particle mass and particle hygroscopicity. Table 1 lists the main instruments used in the experiments.

1.2.1. Gaseous pollutant measurements

The concentrations of CO, NOx (including NO and NO2) and O3 were monitored during the aging process using CO analyzer, NO-NO2-NOx analyzer, and O3 analyzer respectively.

GC/FID–GC/MS was used to measure the main VOC concentrations. The custom-built two-column system consisted of a gas chromatograph with a flame ionization detector and a quadrupole mass spectrometer with a preconcentration system (Entech 7100A, Entech Instruments, USA). One column measured C2–C4
where $\kappa$ was calculated using Eqs. (1) and (2): Petters and Kreidenweis (2007), the hygroscopicity parameter measured by SMPS was fixed, and SS was then adjusted activated particles (sent to the CCNc, to count the number concentration of particle number distribution. The peak diameter of particle number distribution was calculated with consideration of number size distribution and density.

The parameter $\kappa$ was used to characterize the hygroscopicity of individual aerosol constituents, even complex aerosols in the atmosphere, based on the “$\kappa$-Kohler theory.” If the particles’ chemical composition changed, by chemical reactions or mixture with other compounds, $\kappa$ changed (Petters and Kreidenweis, 2013). In addition, $\kappa$ could be calculated as the volume-weighted average of each component’s $\kappa_i$ (Petters and Kreidenweis, 2007):

$$\kappa = \sum_i \kappa_i$$

where $\kappa_i$ and $\xi_i$ are the hygroscopicity parameter and volume fraction, respectively, of component $i$. Thus, $\kappa$ partly indicates the volume-apportioned chemical composition of secondary aerosols.

### 2. Results and discussion

#### 2.1. Primary emissions

The concentrations of gaseous emissions of CO, NOx, and total hydrocarbon (THC) at the engine tailpipe were about 1167, 664 and 415 ppm C (the compound’s carbon number times its volume fraction), respectively. The emission factor of non-methane organic gas (NMOG) was 2.2 g/kg-fuel, a little higher than “LEV1” gasoline vehicles (manufactured 1995–2003) in Gordon’s study. The total speciated VOCs emissions constituted 78% of THC, as determined by GC/FID–GC/MS. Speciated light aromatic precursors, including benzene, toluene, and C2–C4 benzenes, were classical gaseous SOA precursors (Table 3). The mass fraction of aromatic hydrocarbons accounted for about 19% of the total speciated VOCs, more than the 20%–25% for idling vehicles documented by Nordin et al. (2013), and slightly lower than the 22%–38% observed by Liu et al. (2015) for PFI vehicles. The aromatic hydrocarbon fraction of VOCs from PFI engine exhaust in this study was within the range of previous reports.

Under the mode of 2000 r/min and 50% loading, the PM$_{2.5}$ emission factor was $3.8 \pm 0.4$ mg/kg-fuel, with primary organic aerosol (POA) of $1.5 \pm 0.2$ mg/kg-fuel. The primary emission factors measured in this study are within 20% of emission factors reported in previous studies (Gordon et al., 2013, 2014a).
Our engine emitted fewer primary particles than did PFI vehicles and engines manufactured earlier, as newer engines must meet more stringent emission standards. Different testing modes may also lead to discrepancies in these measurements.

2.2. Secondary formation of gaseous pollutants from engine exhaust

The evolution of gas and particle phases in the outdoor chamber during experiment 1 is illustrated in Fig. 2. After exposure to ambient sunlight, H$_2$O$_2$ generated OH radicals. NO was converted continuously to NO$_2$, generating O$_3$ formation (Fig. 2a) (Nordin et al., 2013). In all experiments, new particle formation was observed within 15 min. The significant growth of particle diameter and mass concentration indicated substantial secondary aerosol formation (Fig. 2b and c).

Due to high initial concentrations of gaseous pollutants and OH in experiments 1, 2, and 3, wall-loss-corrected secondary aerosol mass concentrations increased rapidly after exposure to sunlight (Wall-loss correction is shown in Appendix A. Supplementary data). In experiment 1, the mass concentration increased from 6 to 170 $\mu$g/m$^3$ in the first 30 min (Fig. 2b). The peak diameters and the mass concentrations of secondary aerosols reached maxima within 1 hr, and remained stable in the following hours. These results indicate that secondary aerosol formation achieved extreme potential in the first hour. On the other hand, the rate of secondary aerosol formation was lower in experiment 4, in which less H$_2$O$_2$ was injected, and the particle mass concentration continued to increase until the end of the experiment (Fig. 2f).

The hygroscopicity parameter $\kappa$ of 120 nm particles was 0.104 with 0.2% SS. As the concentration of SO$_2$ was low (<15 ppb in the chamber), we assumed that secondary aerosols consisted mostly of internally mixed ammonium nitrate and organics. The $\kappa$ values of ammonium nitrate and organics (0.67 and 0.10, respectively) were applied to Eq. (3) to determine their volume-weighted averages (Svenningsson et al., 2006; Prenni et al., 2007). Organics were likely the dominant contributors to secondary aerosols formed from gaseous pollutants from gasoline engine exhaust, accounting for about 93% of these aerosols, with ammonium nitrate contributing the remaining 7%. The density of secondary aerosols was thus set as the density of organics, 1.2 g/cm$^3$ (Turpin and Lim, 2001).

To represent the ability of secondary aerosols to form from gaseous pollutants in gasoline engine exhaust (i.e., the mass of secondary aerosols formed from gas in a unit of exhaust air), we applied Eq. (4):

$$M = \frac{(M_{\text{max}} - M_0) V_c}{V}$$  \hspace{1cm} (4)

where $M$ (mg/m$^3$) is the potential of secondary aerosol formation from gaseous pollutants in exhaust, $M_{\text{max}}$ (mg/m$^3$) is the maximum particle mass concentration in the chamber during the experiments, $M_0$ (mg/m$^3$) is the initial particle mass concentration in the chamber, $V_c$ is the volume of the chamber (1.2 m$^3$), and $V$ (m$^3$) is the volume of exhaust air injected into the chamber.

The results of experiments 1, 2 and 3 regarding the potential of secondary aerosol formation were consistent (Table 2). The
calculation of the potential of secondary aerosol formation excluded the result of experiment 4, as it was conducted with less H$_2$O$_2$ and the maximum mass concentration had not been reached at the end of experiment. After about 4 hr photo-oxidization, the average ultimate secondary aerosol mass concentration in the chamber reached 140 ± 30 μg/m$^3$. The potential of secondary aerosol formation reached 33 ± 6 mg/m$^3$ in exhaust, with SOA accounting for 30 ± 6 mg/m$^3$. The potential of SOA production was 426 ± 85 mg/kg-fuel.

In this study, we tried to obtain the extreme case potential of SOA production from PFI gasoline engine exhaust, with high initial gaseous pollutant concentrations and a strong oxidation environment in the chamber. However, some rather than all gaseous pollutants participated in SOA formation, because part of them was sampled by the instruments. Thus, the potential of SOA formation appears to be underestimated in this study. In addition, the semi-volatile vapors also involve some uncertainties in SOA production estimation. The loss of semi-volatile vapors to the chamber walls leads to substantial underestimation of SOA formation, by a factor of 1.1–4.1 (Zhang et al., 2014). On the other hand, the initial gas concentrations with less dilution in the chamber might lead to gas–particle partitioning into more particulate-phase during oxidation (Donahue et al., 2006).

By summarizing the chamber experiments and flow reactor simulations relative to gasoline vehicles and in-use vehicles, we find much higher SOA production in this study than in others (Fig. 3). There are two explanations for such high SOA production. First, compared with “LEV1” gasoline vehicles under the cold-start Unified Cycle driving schedule reported by Gordon et al. (2014a), the gasoline engine under 2000 r/min and 50% loading in our study emitted more VOCs per kg-fuel, contributing to higher SOA production. Second, the OH exposure in this study (equivalent to more than 10 days) was much higher than for other chamber results in most previous studies. It was reported that SOA production increased as a function of photochemical age (Tkacik et al., 2014), and our SOA production remained within the trend among other results as illustrated in Fig. 3. Tkacik et al. (2014) found that SOA production decreased after 2.7 days of OH exposure, which they attributed to a transition from functionalization- to fragmentation-dominated reaction mechanisms. In contrast, we observed no decrease in SOA production, even at more than 10 days OH exposure. This difference may be because the potential aerosol mass reactor used in Tkacik’s study simulates 9 days in approximately 100 sec, with an oxidation environment greatly exceeding that of ambient air, leading to potential differences in reaction mechanisms. The contribution of intermediate-volatility organic compounds (IVOCs) and semi-volatile organic compounds (SVOCs) due to high initial gas concentrations may be another explanation.

The SOA production potential from gasoline engine obtained in this study is comparable with those from scooters and diesel vehicles without aftertreatment, but much higher than diesel vehicles with aftertreatment (Platt et al., 2014; Gordon et al., 2014b). Our result can represent emission from widely used gasoline vehicles with lower-tech aftertreatment. Considering the much larger population of gasoline vehicles in Chinese megacities such as Beijing, with over 3000 gasoline vehicles per square kilometer, this high potential implies the significant impact of gasoline emission on air quality, properly the largest among all kinds of traffic emissions in urban areas.

### 2.3. SOA mass closure of gasoline exhaust

The second organic aerosol yield $Y$ was defined as the ratio of the wall-loss-corrected measured SOA mass at the end of the experiments ($\Delta$OA) to the mass of SOA precursors ($\Delta$VOC) (Donahue et al., 2006; Odum et al., 1996), which was calculated by Eq. (5):

$$Y = \frac{\Delta \text{OA}}{\Delta \text{VOC}}$$

![Fig. 3 – Fuel-based secondary organic aerosol (SOA) production in the present chamber study and in flow reactor studies. The times of equivalent photochemical age are marked on the x-axis labels.](image-url)
SOA production ($\Delta$OA$_{predicted}$) from the exhaust was predicted using Eq. (6):

$$\Delta$OA$_{predicted} = \sum (\Delta_i \times Y_i)$$

where $\Delta_i$ is the change in VOC concentration and $Y_i$ is the SOA yield of VOC. The concentration of VOCs, including benzene, toluene, C2–C4 benzene in exhaust, were used to estimate the SOA production.

SOA formation from the photo-oxidation of VOCs was highly sensitive to the NO$_x$ conditions (Song et al., 2005; Ng et al., 2007a). Ng et al. (2007b) performed chamber experiments to examine SOA formation under high NO$_x$ conditions, with NO$_x$ concentrations of about 1 ppm at the inception of photo-oxidation. Some researchers consider VOCs/NO$_x$ = 0.3 to represent a high NO$_x$ condition (Metzger et al., 2008), and VOCs/NO$_x$ > 6 to represent a low NO$_x$ condition (Borrás and Tortajada-Genaro, 2012; Platt et al., 2013). In this study, the initial NO$_x$ concentrations were 1.9–2.8 ppm, and the VOCs/NO$_x$ ratio was about 0.5. Therefore, the SOA formation by gaseous pollutants from FF engine exhaust in the chamber occurred under high NO$_x$ conditions.

Table 3 lists SOA yields and predicted SOA concentrations of benzene, toluene, and C2–C4 benzenes, including 16 compounds measured by off-line GC–MS. High NO$_x$ SOA yields for benzene, toluene, and m-xylene were taken from Ng et al. (2007b), and the SOA yield of m-xylene was used for C2–C4 benzenes (Platt et al., 2013). As the known SOA yields of alkanes and alkenes are much lower than those of aromatics, they were not taken into account in the SOA prediction.

The predicted SOA contributions from these VOC species are compared with SOA measured in the chamber experiments in Fig. 4. Benzene and toluene were the main precursors to SOA, in terms of concentration and yield. Predicted SOA from single-ring aromatics accounted for about 14% of the SOA production observed in the chamber experiments. This result is comparable to the 2%–12% reported by Nordin et al. (2013). Therefore, total SOA formation could not be explained by traditional speciated SOA precursors (single-ring aromatics and mid-weight VOCs), and this was also found in other fuel combustions, including wood and diesel (Weitkamp et al., 2007; Grieshop et al., 2009).

In our study, SOA from unspeciated precursors accounted for about 86% of the total measured SOA formed from exhaust of light-duty gasoline vehicles. The huge gap between predicted and measured SOA was due to the contributions of unspeciated IVOCs and SVOCs, such as branched and cyclic alkanes, and complex aromatic hydrocarbons (Robinson et al., 2007). They likely had higher molecular weights or were more polar, and thus were not captured in the GC/MS analysis in this study. Given the high initial concentrations and high SOA yield, naphthalene may be an important unspeciated precursor of SOA production, with an estimated 5%–52% contribution to SOA mass (Nordin et al., 2013; Liu et al., 2015), which is much higher than those of single-ring aromatics (Odum et al., 1997; Chan et al., 2009). When we assumed an average 29% contribution of naphthalene, the ratio of predicted to measured SOA reached about 43% in this study, comparable with the results of previous studies (Fig. 4). The SOA mass closure study indicates that unspeciated SOA precursors, including some IVOCs and SVOCs, appear to contribute the majority of SOA formation, much more than traditional SOA precursors.

Another possible explanation for the gap is the discrepancy of SOA yield under high and low NO$_x$ conditions. The SOA yield was much higher under low NO$_x$ conditions than under high NO$_x$ conditions (Odum et al., 1996; Ng et al., 2007b). During 4–5 hr photo-oxidation, the NO$_x$ condition changed from high to low (Johnson et al., 2004). Thus, the SOA yields under high NO$_x$ conditions used to predict SOA formation will lead to underestimation in SOA prediction.

3. Conclusions

A series of experiments using an outdoor chamber was conducted to investigate secondary aerosol formation from gaseous pollutants in FF engine exhaust. A widely

<table>
<thead>
<tr>
<th>Species</th>
<th>Emitted VOCs (ppb)</th>
<th>Yield</th>
<th>Predicted SOA (µg/(m³ exhaust))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1277</td>
<td>0.28</td>
<td>1141</td>
</tr>
<tr>
<td>Toluene</td>
<td>3761</td>
<td>0.11</td>
<td>1557</td>
</tr>
<tr>
<td>C2-benzene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>689</td>
<td>0.08</td>
<td>239</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>165</td>
<td>0.08</td>
<td>57</td>
</tr>
<tr>
<td>m/p-Xylene</td>
<td>512</td>
<td>0.08</td>
<td>178</td>
</tr>
<tr>
<td>Styrene</td>
<td>18</td>
<td>0.08</td>
<td>6</td>
</tr>
<tr>
<td>C3-benzene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,3,5-Trimethylbenzene</td>
<td>359</td>
<td>0.08</td>
<td>141</td>
</tr>
<tr>
<td>1,2,4-Trimethylbenzene</td>
<td>84</td>
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<tr>
<td>1,2,3-Trimethylbenzene</td>
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<td>o-Ethyltoluene</td>
<td>250</td>
<td>0.08</td>
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<tr>
<td>m-Ethyltoluene</td>
<td>667</td>
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<td>262</td>
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<tr>
<td>p-Ethyltoluene</td>
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<td>0.08</td>
<td>114</td>
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<tr>
<td>n-Propylbenzene</td>
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<td>59</td>
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<td>i-Propylbenzene</td>
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<tr>
<td>C4-benzene</td>
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<tr>
<td>o-Diethylbenzene</td>
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<td>51</td>
</tr>
<tr>
<td>m-Diethylbenzene</td>
<td>34</td>
<td>0.08</td>
<td>15</td>
</tr>
</tbody>
</table>

VOC yields were taken from Ng et al. (2007b).
used PFI engine and fuel were employed to reflect the exhaust of current gasoline vehicles with lower-tech aftertreatment in Beijing.

Substantial secondary aerosol formation occurred in the chamber during about 4–5 hr photo-oxidation, under conditions of high initial concentrations of gaseous pollutants and a strong oxidizing atmosphere. The experiments represented more than 10 days of oxidation in summer in Beijing. Secondary aerosols were composed predominantly of organics, as indicated by the hygroscopicity parameter $\kappa$. The potential of SOA production reached $33 \pm 6 \text{ mg/m}^3$ in exhaust, and $426 \pm 85 \text{ mg/kg-fuel}$. SOA production significantly exceeded POA in this case, consistent with the findings of many previous studies.

The high NO$_x$ SOA mass yield was used to predict SOA formation for the mass closure study. Compared with the formed SOA observed in the chamber experiments, the use of traditional speciated SOA precursors evidently leads to the underestimation of SOA mass. IVOCs and SVOCs may be important candidate contributors to SOA formation.

This study revealed that the potential of secondary aerosol formation from gaseous pollutants in PFI gasoline engine exhaust greatly exceeds primary emissions. Thus, gasoline vehicles contribute significantly to aerosol loading in the ambient air, and have further impacts on air quality and human health. Strict control of gas precursors of secondary aerosols, such as the reduction of VOCs and NO$_x$ emissions, should be considered.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jes.2017.02.022.

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