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Gasoline aromatic: a critical determinant of urban secondary organic aerosol formation

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Abstract

Gasoline vehicle exhaust is an important contributor to secondary organic aerosol (SOA) formation in urban atmosphere. Fuel composition has considerable potential impact on gasoline SOA production, but this impact is still taken little account in the emission regulations due to the poor understanding of the link between fuel components and SOA production. Here, we present an in-depth study to investigate the impact of gasoline aromatic content on SOA production through chamber approach. A significant amplification factor of 3 - 6 for SOA productions from gasoline exhausts was observed as gasoline aromatic content rose from 29% to 37%. Considerably higher emissions of both monocycle and polycyclic aromatic volatile organic compounds performed an essential role in the SOA production enhancement. Our findings indicate that gasoline aromatics have significant influence on ambient $PM_{2.5}$ concentration in megacities and highlight that more stringent regulation on gasoline aromatic content will achieve unexpected benefit on air quality in urban areas.

1 Introduction

Fossil fuel-powered vehicles, an important source of NO_x, volatile organic compounds (VOCs) and atmospheric particulate matter (PM), are always associated with the severe haze events, human health risks and climate forcing, particularly in urban areas (Guo et al., 2014;Huang et al., 2014;Parrish and Zhu, 2009;Kumar et al., 2014;Peng et al., 2016b;Kelly and Zhu, 2016;Liu et al., 2015a). Gasoline is the most widely used vehicle fuel and accounts for the largest total transportation energy consumptions

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in many countries (NBSC, 2015; EIA, 2015), e.g., U.S. and China. Among all the gasoline PM components, secondary organic aerosols (SOA) produced via atmospheric oxidation of VOC precursors in the exhaust have been proved by chamber experiments as a large fraction, if not the largest, of gasoline vehicular PM (Platt et al., 2014;Liu et al., 2015b;Gordon et al., 2014a;Jathar et al., 2014;Zervas et al., 1999;Jimenez et al., 2009). Moreover, ambient measurement also demonstrated that gasoline SOA were the largest source of vehicular carbonaceous PM in megacities such as Los Angeles (Bahreini et al., 2012). However, though increasingly stringent gasoline fuel standards, especially on sulfur content, have been implemented in the past decades in many countries to reduce the exhaust emissions, current gasoline fuel standards don't take enough account to the SOA production. This contradiction is mainly attributable to the poor understanding of the effects of fuel properties on the related SOA formation, and may ultimately lead to a policy bias on the control of vehicle emission regarding to the reduction of atmospheric pollution.

Aromatic hydrocarbons, unsaturated compounds with at least one benzene ring-like structure, account for 20% - 40% v/v of gasoline fuel. Aromatic VOCs (i.e., toluene, xylenes and trimethylbenzenes) react exclusively with the OH radical in the atmosphere, leading to the formation of a variety of low volatile species (e.g., benzoic acid) (Zhang et al., 2015), which will partition onto existing particle and be recognized as anthropogenic SOA. Therefore, the higher emission of aromatic VOCs will likely result in more SOA formation potential. Existing fuel-effect experimental and model studies have exhibited that high-aromatic fuel in gasoline fuel will lead to more emissions of primary PM as well as some aromatic VOCs (Karavalakis et al., 2015;Yinhui et al., 2016;Zervas et al., 1999;Agency, 2013), indicating the considerable potential impact of gasoline aromatic content on SOA production. Furthermore, though aromatic content in diesel fuel may have little impact on SOA formation (Gordon et al., 2014b), SOA production from gasoline vehicle is considered to be more sensitive to aromatic content than that from diesel vehicle (Jathar et al., 2013). However, till now, very few studies have successfully quantified the impact of gasoline aromatic content on SOA production and directly revealed the possible pathway.

In this study, an in-depth comprehensive research was conducted to investigate the link between gasoline fuel compositions, primary gas- and particle- phase emission, and corresponding SOA formation. Gasoline exhaust emissions were examined on two platforms under two different conditions. The first platform was the chassis dynamometer system equipped with a constant volume sampler (CVS). Vehicle

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exhausts after CVS was introduced into an outdoor environmental chamber and underwent aging under typical polluted urban condition to simulate the SOA formation in ambient atmosphere. The second platform was the experimental engine system on which emissions from a port gasoline injection (PFI) engine and a gasoline direct injection (GDI) engine were examined. SOA formation experiments from engine exhausts were carried out under strong oxidizability condition to obtain the highest SOA production potential. Most importantly, different gasoline fuels blended from different refinery streams were utilized in both platforms to probe the critical link among fuel components, VOCs emissions and related SOA production.

2 Materials and methods

2.1 Test fleet, cycle and engine.

In order to explore the SOA formation from gasoline vehicles with different standard stage and different working situation, both vehicle dynamometer PFI and PFI engine emission were tested in this work.

The chosen PFI vehicle belonged to a commonly used vehicle model in China, which certified to China IV emission standard (equivalent to Euro 4). The mileage of the test fleet was about 3000 km. The fleet was driven on a chassis dynamometer system (Burke E. Porter Machinery Company) using cold-start Beijing cycle in order to better simulate the actual driving situation in Beijing. Beijing cycle was about 17 min long, with highest speed about 50 km (Fig. S1). The temperature and the absolute humidity in the dynamometer room were kept at 23.0 ± 1.0° C and 8.4 ± 0.9 g m^{-3}, respectively, for all vehicle experiments (Table S1).

Vehicle exhaust underwent the first stage of dilution with filtered ambient air using a constant volume sampler (CVS) operated at 5.5 m^3 min^{-1} for all experiments. Approximately 5.3 L min^{-1} of diluted exhaust from the CVS was introduced into the 1.2 m^3 chamber to be further diluted with the clean air in the chamber (Fig. 1). The average dilution factor was approximately 20 in the CVS and was approximately 15 in the chamber. During the entire cycle, a light-duty gasoline vehicle emissions testing system (HORIBA, Ltd.) was used to measure the average and real-time concentration of THC, CO_2, CO, CO2 and NO_x.

The PFI and GDI engines were manufactured by a domestic Chinese automaker and equipped with turbocharger together with downsized displacement. The operation mode of the PFI engine for chamber

experiments was 2000 round per minute with 50% loading. After the engine became stable at this operating mode, the exhaust were introduced into the chamber passing through a heater (150° C) and a filter, with a flowrate of 5 L/min for 1 min. During the injection, the emission was transferred from the engine exhaust system into the chamber, successively. Particle number, mass and chemical composition, as well as VOCs in the exhaust were characterized at the same operating mode. Detail description of the engine experiments can be found in our previous study (Du et al., 2017) and all engine experiments used in this study are illustrated in Table S2.

2.2 Fuels

Three fuels (F1, F2 and F3) were utilized in this study to investigate the impacts of the gasoline fuel on SOA formation. A commercial Phase V gasoline (F1 fuel) with equivalent octane number of 93 was used as the base fuel. F1 fuel contains 30% aromatics and 4% olefin content (Table S3).

F2 fuel was blended from 80% of F6 fuel and 20% of refinery catalytic stream. Octane level and aromatic content (28.5%) in F2 fuel are very similar with that in F1 fuel, with the only difference to be the olefin content.

F3 fuel was blended from 80% of F2 fuel, 15–20% of refinery reformate stream and very small amount of o-octane and n-heptane to keep the same octane level. Compared with F2 fuel, F3 fuel contains similar olefin content (15%) but higher aromatic content (37%) (Table S3), but both F2 and F3 fuels meet the Phase V gasoline standard. Detail information about the fuels can be found in our previous paper (Yinhui et al., 2016).

On the basis of the aromatic contents, the F2 and F3 fuel can be well representative of the fuel normally used in the year around 2010 and after 2013 in Chinese market such as Beijing and Shanghai, respectively.

2.3 Chamber Simulation

The quasi-atmospheric aerosol evolution study (QUALITY) chamber was utilized were conducted to quantify SOA formation from both gasoline engine exhaust and gasoline vehicle exhaust. The 1.2 m^3 two-layer chamber was comprised of an inner layer of 0.13 mm PFA Teflon and an outer rigid 5.6 mm thick acrylic shell (Cyro Industries Acrylite, OP-4). Both of them allowed for efficient transmission of sunlight in UV ranges (Peng et al., 2016b). Pre-experiments have shown that wall loss decreased the particle number concentration by about 50% in about 2-3 hours, SO_2 and NO_x decreased to about 50%

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after 20 hours, while toluene and isoprene did not show obvious wall loss during a two-day experiment (Peng et al., 2016b).

Prior to each experiment, the QUALITY chamber was covered with two layers of anti-UV cloth to shield the chamber from sunlight and flushed by zero air for more than 15 hours to ensure a clean condition. In both vehicle and engine experiments, excess (1 ml 30%) H_2O_2 was also injected into the chamber via the makeup air flow as an extra hydroxyl radical (OH) source after adding the exhaust to perform. Chamber experiments were meanly conducted from moon to later afternoon, with inside temperature of 30 - 35 °C and of relative humidity (RH) of 40 - 60%. A suite of high time resolution state-of-the-art aerosol instruments were utilized to simultaneously measure the gas concentration and a comprehensive set of particle properties throughout the experiments, including concentrations of HONO, SO_2, NO_x, O_3, CO, CO_2 and several VOCs, the particle diameter, mass, chemical composition (Fig. 1).

During each chamber experiment, a suite of state-of-art instruments was utilized to characterize the evolution of gas- and particulate- phase pollutants intermittently (Table S4). Particle number distributions were measured with a scanning mobility particle sizer (SMPS) system, which was composed by one differential mobility analyzer (DMA, TSI, Inc., model 3081) and one condensation particle counter (CPC, TSI, Inc., model 3772). The mass concentration and size distribution of secondary species including organic aerosol (OA), sulfate, nitrate, ammonium and chloride, were measured by a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research, Inc.). The evolution of several volatile organic (VOCs) species were measured continually tracked by a proton transfer reaction mass spectrometer (PTR-MS, Ionicon HSL experiments). Meanwhile, VOCs in the chamber were also sampled by canisters every 1 hour during each experiment and analyzed by GC-MS/FID system (Wang et al., 2015). Hydroxyl radical (OH) levels in the chamber were inferred from the measured concentration ratios of toluene to benzene in this study (Yuan et al., 2013). Dedicated gas monitors, including the SO_2, NO_x, CO, CO_2 and O_3 monitors (Thermo), were utilized, and calibrated each experiment day. Zero airflow was connected to the chamber during experiment to make up the sampling airflow.

3 Results

3.1 Simulation of SOA formation from gasoline exhausts. The temporal evolution of gas- and particle-phase species during the chamber experiment was examined and is illustrated in Figure 2. The vehicle exhaust was diluted for about 20 times in CVS and additional 15 times in the chamber. The initial

concentration of NO_x, benzene and toluene in the chamber were 163 ppb, 5.6 ppb and 16.8 ppb, respectively, corresponding to the severe urban haze condition in the megacities (Guo et al., 2014). After the chamber was exposed to the sunlight, 99% of NO was converted to NO_2 within the first 10 min due to fast photolysis of H_2O_2 inside chamber. Then, the concentration of O_3 increased rapidly to approximate 400 ppb after 1 h exposure, and gradually decreased later in this experiment (Fig.2a).

Over the entire experiment, benzene and toluene experienced gentle decay in the concentrations, but with different decay coefficients (Fig. 2b). Aerosol evolution is always characterized by a photochemical-age-based parameterization method in ambient measurements as well as chamber experiments (Hu et al., 2013;de Gouw et al., 2005;Peng et al., 2016a). Therefore, in order compare our SOA production in different experiments (in which solar flux were different from each other), OH exposures are calculated based on the ratios of benzene and toluene concentrations, which react at different rates with OH radical (de Gouw et al., 2005). Besides, assuming that the OH concentration is 1.6×10^6 cm^{-3}, photochemical age is estimated to compare our results with the previous ambient measurements (Hu et al., 2013;Peng et al., 2016a).

New particle formation occurred inside the chamber within 10 min of exposure to the sunlight (Fig. 2c). These newly formed particles performed as seeds for the further formation of secondary species. A large quantity of secondary aerosols was then formed in the chamber, leading to the fast growth in the diameter of these particles to approximately 70 nm after 3h aging. The measurement of the particle compositions by a High time resolution ToF Aerosol Mass Spectrometer (AMS) reveals that the largest mass fraction of secondary aerosols in the chamber was SOA (approximately 96%, Fig. S2), indicating the critical role of the SOA for the secondary aerosol formation from gasoline exhausts. Because of the low aerosol loading (initially lower than 2 μg m^{-3}) and low relative humidity (40 - 50%) inside the chamber, heterogeneous reactions and aqueous phase processing were not important for the formation of SOA in this study (Zhang et al., 2015). Furthermore, the O:C ratio of SOA formed in the chamber stayed stable around 0.4 over the entire experiment, indicating that condensed phase reactions, i.e., aqueous or heterogeneous reactions, which produce high oxidized oligomers, was not significant in the chamber experiments in this study. These SOA, therefore, were likely formed via condensation of less volatile products oxidized through gas phase reactions of VOCs precursors with limited multigenerational chemistry (Robinson et al., 2007;Jimenez et al., 2009;Jathar et al., 2014). The AMS spectrum profile of gasoline SOA obtained in this study is highly correlated with the ambient SV-OOA in Beijing (R^2=0.99,

Fig. S3), further confirming the important contribution of gasoline emission on ambient $PM_{2.5}$.

SOA production per fuel consumption/mileage is calculated on the basis of SOA formation inside the chamber, dilution factors both in the CVS and inside the chamber, and fuel consumption/mileage for our working cycle. SOA mass concentration inside the chamber is corrected according to the particle wall loss curve (Fig. S4) as well as the dilution effect for both particles and gas precursors (Fig. S5). SOA production at the end of this experiment is calculated to be 80 mg kg-fuel^{-1}, or 6.7 mg km^{-1} (Fig. 2d). These values are 5 times higher than the emission factors of primary organic aerosols (POA) for the same vehicle at the same cycle.

3.2 Fuel impacts on SOA production. High-aromatic content gasoline leads to appreciably large enhancement on SOA production from both vehicle and engine experiments. As illustrated in Figure 3a, the final SOA production from gasoline vehicle exhaust ranged from 30 mg kg-fuel^{-1} to 98 mg kg-fuel^{-1} at the end of each experiment, comparable to the results from cold start experiments in previous studies (Gordon et al., 2014a;Jathar et al., 2014). Experiments using F3 fuel (with 36.7 % v/v aromatic content) exhibit the highest SOA production factors, followed by F1 fuel (with 29.8 % v/v aromatics content) and F2 fuel (with 28.5 % v/v aromatics content), successively. The average SOA production at after 12 photochemical-hours using F3 fuel was 76 mg kg-fuel^{-1}, equivalent to 3 times of that using F2 fuel, which has similar parameters with F3 fuel except the aromatic content. In addition, we observe noticeably large amount of the SOA formation in the first few photochemical hours in all experiments. The production rate of SOA can be as high as 5 - 13 mg kg^{-1} h^{-1}, indicating the existence of some semi-volatile species that could partition to particle phase after first generation oxidation (Keyte et al., 2013;Robinson et al., 2007).

SOA formation experiments from an experimental PFI engine exhaust were conducted under high oxidizing condition to obtain the SOA formation potential. As illustrated in Figure 3b, most of the SOA were formed within the first half an hour of each engine experiment and very little increase was observed over the following hours. The SOA formation potential from the engine exhaust using F3 fuel is 3.3 g kg-fuel^{-1} at this condition, equivalent to 5.6 folders of that using F2 fuel, which is 0.59 g kg-fuel^{-1} on average. The high emission of experimental PFI engine suggests that our engine exhaust experiment can represent the SOA production from gasoline vehicles with low treatment technics. Therefore, our results with two different experimental sets demonstrate the applicability of the enhancement of SOA formation using high-aromatic fuel, using either high or low after treatment technology, at either representative

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cycle condition or steady-state operating condition.

Though good reproducible is found for SOA production using either F2 or F3 fuels, there are inevitably several biases in the chamber simulation approach. For example, the SOA production in both vehicle and engine experiments might be underestimated due to loss of semi-volatile vapors to the chamber wall as well as the condensation of low organic vapor onto the particles that already lost on the chamber wall (Zhang et al., 2014). Also, the SOA production in engine experiments could be overestimated because the high concentration in the chamber might drive the gas-particle partitioning of the semi-volatile components into particle phase (Robinson et al., 2007). Nevertheless, the relative enhancement factor of SOA for different fuels is not largely influenced by these biases.

3.3 Aromatic emission and SOA production. To reveal the reason of this large amplification on SOA production owing to fuel constitution, gasoline PM and VOC emissions using F2 and F3 fuels were investigated and their emission factors (EFs) are illustrated in Figure 4. Huge differences in EFs among different gas- and particle-phase species were observed. For example, EFs of PM in both number and mass concentration using F3 fuel were only 20% larger than those using F2 fuel, consistent with previous studies(Administration.). Similar results are also obtained for most of the alkane VOCs as well as NO. On the contrary, the EFs for three types of species exhibit marked enhancement using high-aromatic gasoline fuel, i.e., SOA, aromatic VOCs and particle-phase Polycyclic Aromatic Hydrocarbons (PAHs). The EFs of each aromatic VOCs from the exhaust experimented an increase by 0.2 to 9.5 using high-aromatic gasoline fuel, with an enhancement factor for total aromatic VOCs of 3.3 and 2.7 in vehicle and engine experiments, respectively (Fig. 4). Coincidentally, the total particle-phase PAHs amplified for 1.8 times using high-aromatic gasoline fuel, with the amplification factor of each PAH species varied from 1.1 to 2.2. This reveals that the high-aromatic content fuel will favour the emission of all aromatic species from one cycle to seven cycles, including some aromatic semi-volatile organic components (SVOC).

There are two main routes of aromatic components into the exhaust, which are fuel aromatic survival and combustion-derived aromatics. Ethylene and acetylene are the key species for the combustion-derived aromatics. High concentration of ethylene and acetylene will accelerate the acetylene addition reaction, which will generate light aromatic VOC as well as PAHs in the engine(Frenklach, 2002;Wang and Frenklach, 1997). In this study, when the high-aromatic fuel was used, the concentrations of ethylene and acetylene from GDI engine before the three-way catalyst met an enhancement by a factor of 3.3 and 2.7, respectively (Fig. 4), suggesting that more acetylene and ethylene

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were formed from the dissociation of fuel aromatic contents.

SOA production (ΔOA*prediction*) from aromatic VOCs in the exhaust by multiplying the mass loss of each aromatic VOC precursor (Δi) by its SOA yield, *Yi* (Donahue et al., 2006):

$$\Delta OA_{predicted} = \sum_i (\Delta_i \times Y_i) \quad (1)$$

The SOA precursors here include benzene, toluene, C8-aromatics, C9-aromatics and styrene. SOA formation from C10-aromatics, alkenes and alkanes is found to be neglectable and are not taken account in SOA prediction in this study. The yields of VOCi under high NOx condition are used (Platt et al., 2013;Ng et al., 2007), due to the low initial VOCs/NOx ratios which ranged from 0.5 to 1.0.

Figure 5 exhibits the two typical experiments with observed and predicted SOA concentration as a function of photochemical age using F2 and F3 fuels, respectively. The predicted SOA in the end of the two experiments accounts for 46% and 30% of the observed SOA formation with toluene and C9-aromatics to be the largest contributors, consistent with the previous results (Gordon et al., 2014a;Platt et al., 2013;Nordin et al., 2013). Predicted SOA concentration using F3 fuel is about 90% higher than that using F2 fuel, suggesting the import role of single-ring aromatic VOCs on the enhancement of SOA formation using high-aromatic fuel. However, more than 50 % of the SOA concentration cannot be explained by gas-phase oxidation of these single-ring aromatic VOCs. This value is even large (up to 80%) in the first few photochemical hours in both experiments. In addition, much larger percentage of SOA using F3 fuel cannot be explained by the single-ring aromatic VOCs. This suggests the existence of some unspeicated organic vapors, most likely semi-volatile species, which are considered to have both large emission factor from vehicles and high SOA yield and might partition to particle phase after first generation oxidation (Chan et al., 2009;Liu et al., 2015b;Robinson et al., 2007;Jathar et al., 2014). Two-ring and three-ring gas phase PAHs, e.g., naphthalene and phenanthrene, which have been proved to have higher EFs using high-aromatic fuel (Chan et al., 2009), are a majority of these unspeicated organic vapors and may play a crucial role for the enhancement of SOA production using high-aromatic fuel.

4 Discussion

Our results exhibit the critical impact of gasoline aromatics on urban SOA formation. We observed an amplification factor of 3-6 on SOA formation using high-aromatic gasoline, which is mainly caused by the high emission of one-ring aromatic VOC as well as SVOC such low-molecular PAHs. This enhancement of SOA formation, meanwhile, is found not only using a new vehicle with new after

treatment technology at a representative cycle condition, but also using experimental engine with not well-performed after treatment at steady-state operating condition, suggesting the extensive applicability.

Moreover, photo-oxidation of aromatics leads to significant production of small dicarbonyls, i.e., glyoxal and methylglyoxal, which have high SOA yield via aqueous reactions (Zhang et al., 2015). If this aqueous SOA pathway is taken account, the influence of fuel on SOA formation will be much more remarkable. More work is needed to evaluate the aqueous pathway of SOA formation from gasoline exhaust.

Currently, aromatic content in gasoline fuel is increasing continuous in China, where more stringent standard on gasoline sulfur content are undertaking and the oil refining procedure are changing to meet the new standard. For example, we found the average aromatic content for gasoline fuel in the market meeting Beijing Ⅲ, Ⅳ and Ⅴ standards were 23.4%, 28.5% and 36.3%, respectively. Hence, the enhancement in SOA formation exerted by the increase of aromatic content in gasoline fuel from 29% to 37 % in this study can well represent the extra SOA formation due to the gasoline standard change in Beijing. Neglect of this side effect of fuel standard change may partially offset the tremendous endeavors on vehicle emission control by the local government. From another perspective, our findings provide a new direction in controlling air pollution from vehicles, which is to decrease the aromatic content in the gasoline fuel. This may request more hydrogenation catalysis instead of catalytic reforming in the petroleum refining procedure. Compared with the vehicle restriction regulation that met the shrill opposition voice from the society and the elimination of polluted vehicles that brought large amount of expenses, this direction might be more acceptable, efficient and economical. Additionally, current vehicle emission evaluation system, which mainly measures the emissions of PM, THC, NOx and CO, will fail to tell the consequences of using the high-aromatic gasoline fuel, as these species do not increase much when high-aromatic fuel is using (Fig. 4). Aromatic VOCs, especially the SVOC, should be considered in future vehicle emission evaluation.

Furthermore, this influence of gasoline aromatic content on air quality is not only adoptable in China. Strikingly, the current standard on gasoline aromatic content are not stringent enough in most of the countries and regions in the world, where fuel standards with very high maximum gasoline aromatic content (ranging from 35% to 42% in different countries) are implemented, even including some developed countries and regions, i.e., Europe, Japan, Australia. Our findings highlight the necessity of a more stringent regulation on gasoline aromatic content in the next renewal of the gasoline standard.

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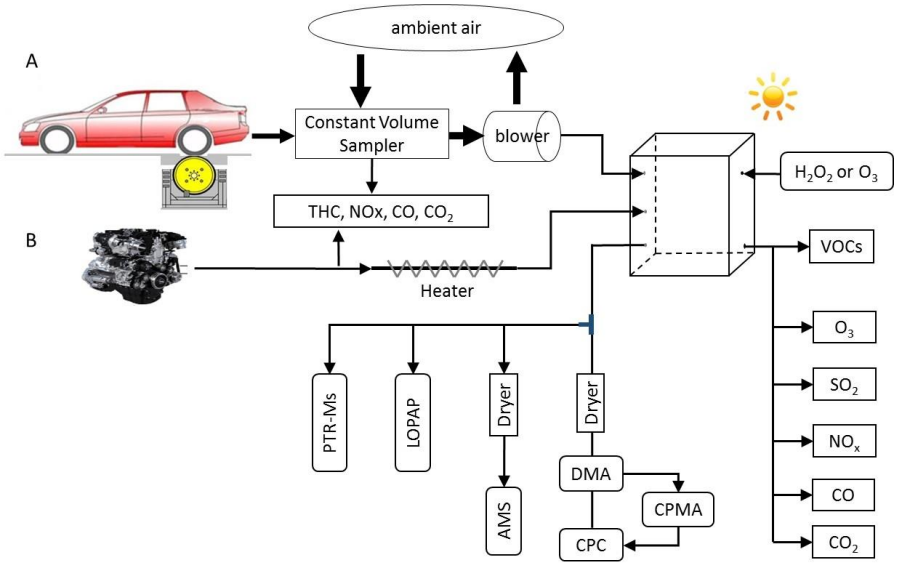

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453 **Figure 1.** Schematic diagram of chamber experiments.

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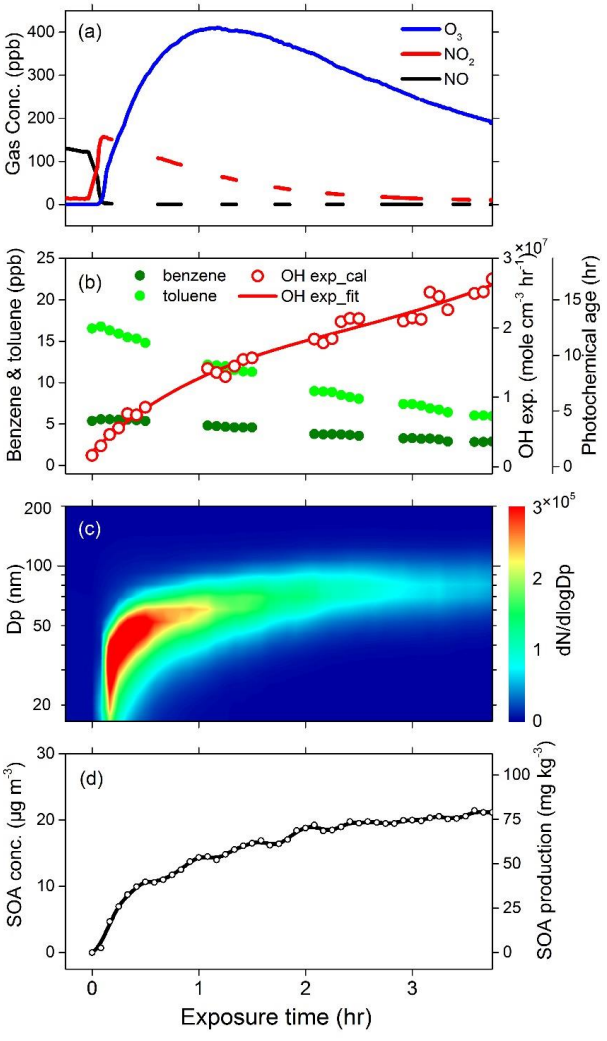

Figure 2. Evolution of gas-phase species (a, b), particle size distribution (c), and SOA concentration and production (d) during a typical chamber experiment (V2). OH exposure and photochemical age are calculated based on the ratios of benzene and toluene concentrations, assuming that OH concentration is 1.6×10^6 mole cm^{-3}. The SOA mass concentration is obtained by intergrading size distribution of particles inside the chamber on the basis of measured particle density. The measured SOA mass concentration is corrected according to the particle wall loss curve as well as the dilution effect for both particles and gas precursors.

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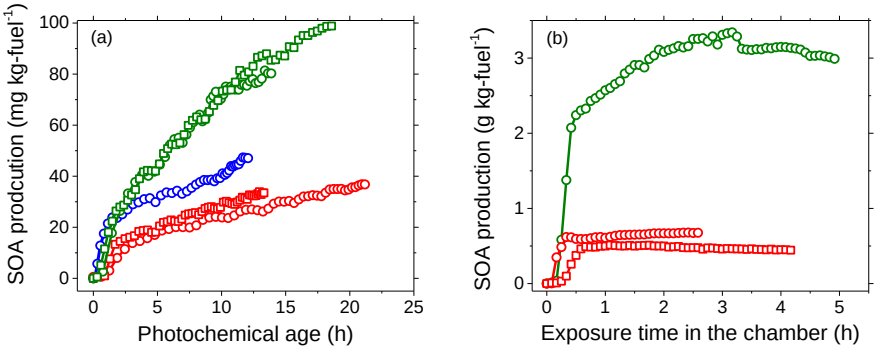

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465 **Figure 3.** SOA production in the vehicle experiments as a function of photochemical age (a) and in the
466 engine exhaust experiments as a function of exposure time (b). The blue, red and green symbols represent
467 experiments using the F1, F2 and F3 fuels, respectively. The green squares, green circles, red squares,
468 red circles and blue circles (a) represent the experiments V1, V2, V3, V4 and V5 shown in Table S1,
469 respectively. The green circles, red squares and red circles (b) represent the experiments E1, E2 and E3
470 shown in Table S2, respectively.

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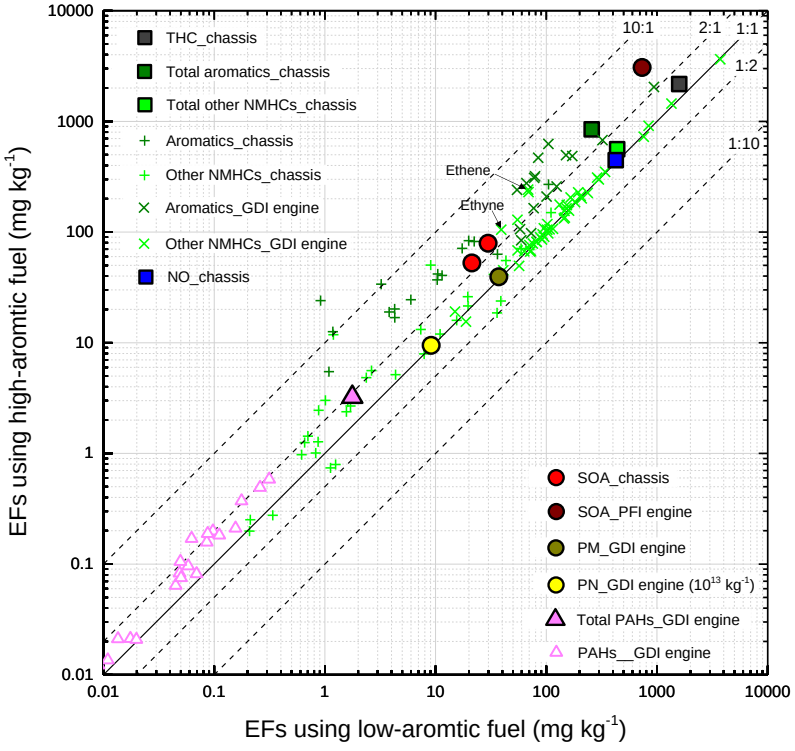

Figure 4. Comparison of emission factors (EFs) of gas- and particle species using high-aromatic fuel (F3 fuel) to those using low-aromatic fuel (F2 fuel). The symbols in the figure represent as following: the red circles: SOA productions after 6 and 12 photochemical hours; the wine circle: SOA production potential in PFI engine experiments; the light and dark yellow circle: total particle number and mass EFs for GDI engine; the hollow and solid purple triangle: EFs of each Polycyclic Aromatic Hydrocarbons (PAH) and total PAHs EFs for GDI engine; the dark gray, dark green and light green solid square: EFs of total hydrocarbons (THC), total aromatics and total other non-methane hydrocarbons (NMHCs) in the vehicle experiments, respectively; dark green and light green crosses: EFs of aromatics and other NMHCs species, respectively; blue solid square: EF of NO. The black line denotes that the ratio of EFs using aromatic-rich fuel over aromatic-poor fuel is 1:1, and dashed lines stand for the ratios of 10:1, 2:1, 1:2, and 1:10, respectively. Note that the PAHs and VOCs data for the GDI engine were measured before the three-way Catalyst (TWC).

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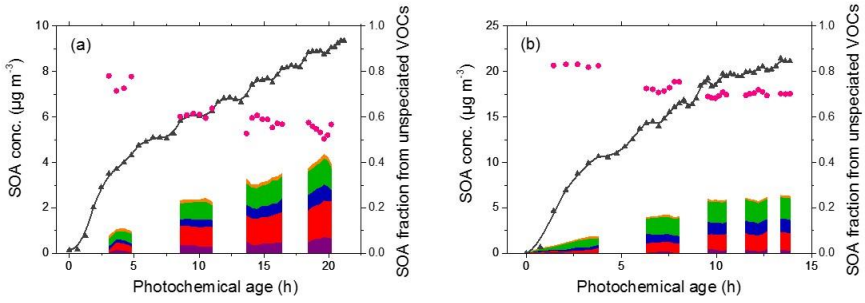

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486 **Figure 5.** Observed and predicted SOA concentration, and SOA fraction from unspeciated VOCs as a
487 function of photochemical age in typical chamber experiments using F2 (a) and F3 (b) fuels. Black line
488 and triangles represent the corrected SOA concentrations in the chamber experiments. The purple, red,
489 blue, green and yellow areas represent the predicted SOA from the oxidation of benzene, toluene, C8-
490 aromatics, C9-aromatics and styrene, respectively. The pink circles represent the SOA fractions that
491 cannot predicted by the one-ring aromatic VOC precursors.

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493