JOURNAL OF ENVIRONMENTAL SCIENCES XX (2017) XXX–XXX

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JES JOURNAL OF ENVIRONMENTAL SCIENCES www.jesc.ac.cn

Potential of secondary aerosol formation from Chinese gasoline engine exhaust

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ARTICLE INFO

Article history:
Received 1 September 2016
Revised 17 February 2017
Accepted 22 February 2017
Available online xxxx

Keywords:
Port fuel injection
Gasoline engine exhaust
Secondary aerosol formation
Chamber simulation
Secondary organic aerosol

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 $PM_{2.5}$ (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

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http://dx.doi.org/10.1016/j.jes.2017.02.022
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(Jathar et al., 2014). These studies, however, were based on standards and usage data for gasoline engines and vehicles in Europe. Little information on secondary aerosol formation based on China's gasoline vehicle emissions is available in the literature. The complexity and uncertainty regarding the mechanisms of 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_2O_2 was also injected to generate sufficient OH exposure. Ambient sunlight was used to induce H_2O_2 to produce OH radicals. OH exposure in the chamber was calculated from the photolysis of H_2O_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_2O_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

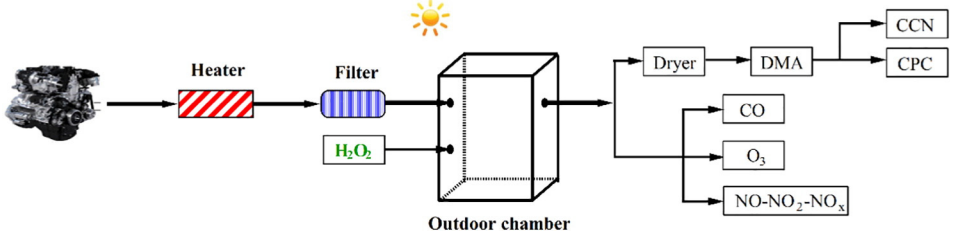

Fig. 1 – Schematic representation of the outdoor chamber set-up for the experiments. DMA: differential mobility analyzer; CPC: condensation particle counter; CCN: cloud condensation nuclei counter.

Please cite this article as: Du, Z., et al., Potential of secondary aerosol formation from Chinese gasoline engine exhaust, J. Environ. Sci. (2017), http://dx.doi.org/10.1016/j.jes.2017.02.022