Primary and secondary organic aerosol from vehicle engines

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Introduction

Organic aerosol (OA) is a major fraction of the submicron aerosol, which is known to influence climate and adversely affects health. OA consists of directly emitted primary OA (POA), and “secondary” OA (SOA). SOA is formed in-situ in the atmosphere via the reaction of volatile precursors. Vehicle exhaust is already a known source of POA and likely contributes to SOA formation in urban areas (Robinson \textit{et al.}, 2007; Weikamp \textit{et al}, 2007). However, the magnitude of this contribution is unknown.

The secondary organic aerosol formation of vehicle exhaust has recently been estimated by (i) analyzing ambient data from urban areas combined with fuel consumption data (Bahreini \textit{et al.}, 2012), or (ii) by examining the chemical composition of raw fuels (Gentner \textit{et al.}, 2012). Contradictory and thus somewhat controversial results in the relative SOA formation of diesel vs. gasoline vehicle exhaust were observed.

Experimental data from smog chamber studies can provide quantitative measurements of the relative SOA formation of different fuels and vehicle types, and can help elucidate the
impact of variable ambient conditions thereon. This information is crucial for our understanding of vehicular pollution and formulation of emission control strategies.

**Methodology**

We studied the SOA formation of passenger cars and trucks as a function of fuel type (gasoline, diesel) at different temperatures (T 22 vs. -7°C) and relative humidity (RH ~40 vs. ~90%). Vehicle exhaust, generated during regulatory driving cycles on chassis dynamometers (European Joint Research Centre Ispra, Italy), was injected from the tailpipe into the mobile PSI smog chamber (Platt et al., 2013) after a dilution of ca. 200 – 400x using heated silicon steel tubes (150°C) and a heated ejector diluter (150°C).

Particles were analysed using a high-resolution time-of-flight aerosol mass spectrometer (see DeCarlo et al., 2006 for further information on the instrument), scanning mobility particle sizer and aethalometers. Volatile organic compounds (VOCs) were analysed with a high resolution proton-transfer time-of-flight mass spectrometer, and gas-phase monitors were used to analyse CO, CO₂, CH₄, total hydrocarbons, NH₃ and other gases in the chamber.

The emitted or formed particle mass (g kg⁻¹ fuel) was calculated from a carbon mass balance [(OA / carbon of CO₂ and CO) * carbon content of fuel], analogous to Platt et al., 2013).

**Results and Discussion**

We observed that SOA formation is highly dependent on vehicle and fuel type (Fig. 1a). For gasoline cars, SOA mass exceeded POA and black carbon (BC) mass. At cold temperatures (-7°C) the primary particulate matter (mainly BC) was increased compared to standard temperature at 22°C. However, also the SOA mass was largely increased, leading to an increase in the SOA to POA+BC ratio also at cold driving and ageing conditions (-7°C vs. 22°C).

In contrast, relatively much lower SOA mass was observed for diesel vehicles (cars and trucks). For these vehicles, the total carbonaceous aerosol was dominated by BC and POA emissions. This is especially true for the tested trucks. Concerning the tested diesel car, the
application of a diesel particle filter (DPF) leads to very little primary particle mass (POA and BC). The small SOA mass, however, can be ascribed to a smaller fraction of VOCs emitted compared to the gasoline car.

Figure 1. -a- Carbonaceous aerosol mass (g kg\(^{-1}\) fuel) from gasoline and diesel vehicles at varied temperature and relative humidity (RH). -b- Organic aerosol (OA) formation (g kg\(^{-1}\) fuel) from a Euro 5 gasoline car in the smog chamber initiated with OH radicals (photochemistry).

Additionally, the emissions are significantly affected by ambient conditions: e.g. doubling the RH in the chamber resulted in a 3-fold higher SOA formation (Fig. 1ab). Despite the large
difference in the SOA mass, no distinct difference in the high resolution mass spectra of SOA was observed (gasoline car GC2, Fig. 2). In general, a large proportion of oxidized species (CHO$_1$ and CHO$_x$, x>1) was observed in the SOA fraction.

![Figure 2. High resolution m/z spectra of the SOA fraction (< 1000 nm particles). -a- RH ~40%, -b- RH ~90%.](image)

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**References**


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INTRODUCTION

Organic aerosol (OA) is a major fraction of the submicron aerosol, which influences climate and adversely affects health. OA consists of directly emitted primary (POA), and secondary OA (SOA), formed in-situ in the atmosphere via the reactions of precursors. Vehicle exhaust is not only a source of POA, but likely contributes to SOA in urban areas1,2. The formation of SOA from diesel and gasoline vehicle exhaust has recently been estimated3,4, but contradictory results were observed. Therefore, we addressed the SOA formation from diesel and gasoline vehicles in a smog chamber study.

METHODS

We studied the SOA formation of car and truck exhausts as a function of fuel type (gasoline, diesel), temperature (722, -7°C) and relative humidity (RH ~40, ~90%).

Exhaust was sampled at the tailpipe during regulatory driving cycles on chassis dynamometers (Joint Research Centre, Ispra), using heated silicon steel tubes and a heated ejector diluter (150°C), and injected into the PSI mobile smog chamber (200 – 400x diluted) (Fig. 1). Particles were analysed with scanning mobility particle sizer, high-resolution time-of-flight aerosol mass spectrometer, and aethalometer. Volatile organic compounds were analysed with a high-resolution proton-transfer-reaction time-of-flight mass spectrometer. Gas-phase monitors measured CO, CO2, CH4, total hydrocarbons, NH3 and other gases in the chamber. The emitted or formed aerosol mass (g kg-1 fuel) was derived from a carbon mass balance [(OA / carbon of CO2 and CO + carbon content of fuel)], Platt et al.5).

RESULTS & DISCUSSION

We observed that SOA formation is highly dependent on vehicle and fuel type. Additionally, it is significantly affected by ambient conditions: e.g. doubling the RH in the chamber resulted in a 3-fold higher SOA formation (Fig. 2 and 3). For gasoline cars, SOA mass exceeded POA and black carbon (BC) mass by far. The ratio of SOA to POA+BC was also largely increased at cold driving and ageing conditions (-7°C vs. 22°C). Comparatively much lower SOA mass was observed for diesel vehicles (cars and trucks), in which the total carbonaceous aerosol was dominated by black carbon and POA emissions.

Despite the large difference in the SOA mass, no distinct difference in the high resolution mass spectra of SOA was observed for the studied gasoline car (GC2), which requires further investigation. In general, a large proportion of oxidized species (CHOx and CHOx, x>1) was observed in the SOA fraction (Fig. 4).


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