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Effect of measurement protocol on organic aerosol measurements of exhaust emissions from gasoline and diesel vehicles



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HIGHLIGHTS

- Differences in the measured concentrations of organic carbon (OC) are observed.
- The differences are mainly due to different times elapsed during sampling.
- Semi-volatile organic compounds (SVOC) are not at equilibrium for short elapsed times.
- Gas-phase fraction of emitted SVOC leads to an underestimation of emitted OC.
- Estimated gas-phase SVOC suggest an underestimation of gas + particle SVOC by 60%.

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ABSTRACT

Exhaust emissions of semi-volatile organic compounds (SVOC) from passenger vehicles are usually estimated only for the particle phase via the total particulate matter measurements. However, they also need to be estimated for the gas phase, as they are semi-volatile. To better estimate SVOC emission factors of passenger vehicles, a measurement campaign using a chassis dynamometer was conducted with different instruments: (1) a constant volume sampling (CVS) system in which emissions were diluted with filtered air and sampling was performed on filters and polyurethane foams (PUF) and (2) a Dekati Fine Particle Sampler (FPS) in which emissions were diluted with purified air and sampled with on-line instruments (PTR-ToF-MS, HR-ToF-AMS, MAAP, CPC). Significant differences in the concentrations of organic carbon (OC) measured by the instruments are observed. The differences can be explained by sampling artefacts, differences between (1) the time elapsed during sampling (in the case of filter and PUF sampling) and (2) the time elapsed from emission to measurement (in the case of on-line instruments), which vary from a few seconds to 15 min, and by the different dilution factors. To relate elapsed times and measured concentrations of OC, the condensation of SVOC between the gas and particle phases is simulated with a dynamic aerosol model. The simulation results allow us to understand the relation between elapsed times and concentrations in the gas and particle phases. They indicate that the characteristic times to reach thermodynamic equilibrium between gas and particle phases may be as long as 8 min. Therefore, if the elapsed time is less than this characteristic time to reach equilibrium, gas-phase SVOC are not at equilibrium with the particle phase and a larger fraction of emitted SVOC will be in the gas phase than estimated by equilibrium theory, leading to an underestimation of emitted OC if only the particle phase is considered or if the gas-phase SVOC are estimated by equilibrium theory. Current

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European emission inventories for passenger cars do not yet estimate gas-phase SVOC emissions, although they may represent 60% of total emitted SVOC (gas + particle phases).

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1. Introduction

Organic compounds emitted from gasoline and diesel vehicles are found in both the gas and particle phases (Schauer et al., 1999, 2002). We define volatile organic compounds (VOC) as compounds that only exists in the gas phase, in opposition to intermediate volatility organic compounds (IVOC) and semi-volatile organic compounds (SVOC) that may partition between the gas and particle phases (Robinson et al., 2007; Donahue et al., 2012). Here, the term SVOC refers to both IVOC and SVOC. May et al. (2013a, b) examined the volatility of organic compounds in exhaust emissions of gasoline and diesel vehicles and showed that a large fraction of organic compounds is semi-volatile. Gentner et al. (2012) reported significant fractions of unburned fuel in the gas phase in exhaust emissions from both gasoline and diesel vehicles. The unburned fuel is a major source of gas-phase SVOC in exhaust emissions. This large fraction of SVOC leads to a significant mass of gas-phase organic compounds in the exhaust emissions, which may not be quantified properly during standard emission tests that focus solely on the particulate fraction. Because SVOC emissions are currently missing from most emission inventories (Denier van der Gon et al., 2015), air-quality models, which simulate the fate of organic compounds in the atmosphere, tend to under-estimate organic carbon concentrations (Couvidat et al., 2012).

To obtain concentrations of pollutants in the exhaust emissions that are within the measurable range of the instruments, the exhaust emissions must be diluted with air. Dilution leads to cooling of the hot exhaust emission and, therefore, results in an increase in condensation of SVOC (Hildemann et al., 1989). However, after the temperature of the diluted emissions has reached an ambient level, increasing dilution further can lead to evaporation of SVOC by phase equilibrium (Lipsky and Robinson, 2006; Fujitani et al., 2012). Because of changes in the partitioning of SVOC, the measured emission rate of particulate organic carbon (OC) changes with dilution whereas the emission rate of elemental carbon (EC) does not vary with dilution because of its non-volatility. From the work of Robinson et al. (2007) for a diesel truck, Couvidat et al. (2012) estimated that at ambient concentrations (a few $\mu\text{g}/\text{m}^3$ typical of the exhaust concentrations measured after dilution), the gas/particle ratio of SVOC, which is defined here as the ratio of the SVOC concentration per unit volume of air in the gas and particle phases, could be around 4.

The mass transfer by condensation or evaporation between the gas and particle phases is a dynamic process (Meng and Seinfeld, 1996; Sartelet et al., 2006; Couvidat and Sartelet, 2015). The gas/particle ratio evolves with time and the time scales depend on the particle sizes. Albriet et al. (2010) showed that the concentrations of organic aerosols evolve greatly in the first few meters following exhaust from a vehicle tailpipe, i.e., on short time scales. Therefore, the gas/particle ratio of SVOC could depend strongly on the sampling system (length of the sampling line, dilution factor, elapsed time between emission and measurement, etc) used to measure SVOC in the exhaust emissions.

Because of their semi-volatile properties, measurements of SVOC are difficult. For example, SVOC may condense on or evaporate from filters depending on the atmospheric conditions, e.g., temperature, leading to uncertainties in measuring organic

particles. In this study, measurements of exhaust emissions were performed using a chassis dynamometer and vehicles typical of the French fleet in circulation. The concentrations of SVOC measured using different instruments (filter sampling by dilution with a constant volume sampler (CVS) and on-line instruments (e.g., aerosol mass spectrometer)) are compared to understand the discrepancies in OC concentrations between the filter sampling and the on-line measurements.

First, the measurements conducted with the filter sampling and the on-line instruments are described. Second, gas/particle ratios of SVOC are estimated from chemical speciations obtained from the filter sampling measurements. Third, discrepancies in the measurements of EC/OC between the filter sampling and the on-line measurements are presented. Finally, using the on-line measurements as initial conditions, SVOC concentrations in the gas and particle phases are simulated to understand the time scales involved in the dynamic evolution of SVOC. The simulation results are compared to measurements with the filter sampling to characterize and explain the major sources of discrepancies in the measurements performed with the different instruments.

2. Measurement set-up

2.1. Instruments

Vehicles were operated on a chassis dynamometer and exhaust emissions were measured using a CVS system in which emissions were diluted with filtered air and sampled on quartz filters and polyurethane foams (PUF). The CVS system was used to dilute exhaust emissions with filtered ambient air (4 filters in series including M6-F7-F9, M5, F7 EN-779-2012 filters, a HEPA H13 EN 1822-2009 filter, and a cylindrical cartridge of charcoal scrubber). Dilution factors ranged from about 20 to 80. Particulate matter (PM) and SVOC were sampled out from the dilution tunnel with a servo-controlled system designed by Serv'Instrument for this study. PM was collected on quartz filters (Pallflex™, diameter 47 mm) at flow rates depending on both the emission levels of tested vehicles and subsequent analyses (from 5 to 30 L/min for EC/OC measurements and from 30 to 50 L/min for chemical speciation). Quartz filters were pre-baked at 500 °C for 8 h before being used. SVOC were collected onto PUF. PUF were also conditioned before being used. Test blanks were collected following the same procedure (including driving cycle durations). The dilution time between emissions and the measurements was about 5 s. However PM and SVOC accumulated on filters and PUF respectively during the cycle durations (about 15 min). Samples were stored at -18 °C in aluminium foil and sealed in polyethylene bags until analyses. The analysis of EC/OC was carried out by the thermo-optical Sunset Lab analysis method according to the EUSAAR protocol (Jaffrezou et al., 2005; Cavalli et al., 2010). Then, the chemical speciation of gas-phase SVOC and organic particles (alkanes) were performed by the Gas Chromatography–Mass Spectrometry (GC–MS) method (Piot, 2011).

Another platform of measurements, independent from the CVS, was also used. The exhaust emissions were diluted with purified air using a Dekati Fine Particle Sampler (FPS-4000) directly connected to vehicle tailpipes. In case of very high exhaust emissions

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