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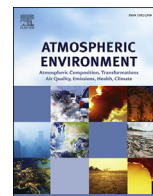


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## Effect of measurement protocol on organic aerosol measurements of exhaust emissions from gasoline and diesel vehicles



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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  $-18\text{ }^\circ\text{C}$  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 (Jaffrezo 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

(emissions from the diesel car without particle filter), additional dilution using Pallas diluter was used to maintain the concentration levels of emissions within the measuring range of the on-line instruments, i.e., typical of those encountered in the atmosphere: between 10 and 50  $\mu\text{g}/\text{m}^3$ . The dilution factors using FPS and Pallas diluter ranged from 10 to 1530 depending on the vehicle emission levels. Then, the diluted exhaust emissions were measured using the on-line instruments of the MASSALYA platform ([http://lce.univ-amu.fr/massalya\\_en.html](http://lce.univ-amu.fr/massalya_en.html)):

- Scanning Mobility Particle Spectrometer (SMPS): functioning CPC (Condensation Particle Counter) mode counting particles of diameter larger than 2 nm.
- Multi Angle Absorption Photometer (MAAP): measurement of black carbon (BC) (temporal resolution of 30 s).
- High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS): analysis of the non-refractory fraction of submicron aerosols, e.g., organic and inorganic aerosols (temporal resolution of 2 min).
- Proton Transfer Reaction Time-of-Flight Mass Spectrometer (PTR-ToF-MS): analysis of volatile organic compounds (VOC) (temporal resolution of 2 s).

## 2.2. Vehicle types and driving cycles

The vehicles were selected to represent the major vehicle classes in the French fleet in circulation according to the following criteria (André et al., 2014):

- European emission standards or Euro classes (see <http://ec.europa.eu/environment/air/transport/road.htm>)
- Motorization: diesel or gasoline
- Engine capacity: big, medium, small engine displacements (defined as vehicles with the following capacities: above 2 L, from 1.4 to 2 L, below 1.4 L, respectively)
- Presence or not of an after-treatment system

The data suggest that with regard to the Euro classes, Euro 3 and Euro 4 vehicles accounted in 2011 for a large part of the fleet, followed by Euro 5 and Euro 2 vehicles (see Table 1).

André et al. (2014) also estimated that annual traffic driving distances of diesel vehicles represented in 2011 about 70% of the fleet of passenger cars. Diesel vehicles with medium engine displacement (1.4–2.0 L) accounted for 78% of the diesel vehicles. In 2013, diesel vehicles equipped with a particulate filter accounted for 39% of the diesel vehicles (André, 2013). For gasoline vehicles, vehicles with small displacement (less than 1.4 L) accounted for about 62% of the gasoline vehicles. Therefore, we chose two diesel vehicles and one gasoline vehicle to represent the French fleet in circulation as follows:

- Gasoline Euro 2 with small displacement, < 1.4 L (E2G)
- Diesel Euro 4 with medium displacement, 1.4–2 L (E4D)
- Diesel Euro 5 with medium displacement, 1.4–2 L (E4DF)

We tested a Euro 4 diesel vehicle equipped with a particulate filter instead of a Euro 5 diesel vehicle. The main effect of Euro 5 compared to Euro 4 is to reduce PM emissions from 25 mg/km to 5 mg/km. The tested Euro 4 diesel vehicle equipped with a particulate filter meets Euro 5 standard for PM emissions even though it does not meet Euro 5 standard for nitrogen oxides ( $\text{NO}_x$ ) emissions.

Tested vehicles are loaned private vehicles (rental vehicles may not be representative of the national fleet because their mileage

may be low). The E2G vehicle is a 1.3 L Ford Ka (1999) with a mileage of 82,000 km. The E4D vehicle is a 1.5 L Renault Kangoo (2005) with a mileage of 146,000 km. The E4DF vehicle is a 1.9 L Audi A3 (2009) with a mileage of 73,800 km. All vehicles were operated using commercialized diesel and gasoline fuels.

The ARTEMIS European driving cycles (urban, rural-road and freeway), which are designed to be representative of actual driving conditions in Europe, were used for this study (André, 2004). The urban cycle represents driving conditions in urban areas (repeated accelerations), while the rural-road cycle represents driving conditions on main roads in suburban and rural areas outside cities (flowing conditions) and the freeway cycle represents high-speed driving conditions (average speed > 90 km/h). With a focus on urban areas, the ARTEMIS urban and rural-road cycles are chosen here. According to André (2004), 25–30% of trips start with a cold engine (engine temperature below 30 °C) in Europe, regardless of their driving cycle (urban, rural-road, and freeway). As most trips are urban (70%), influence of the cold start on the urban cycle is examined here. To summarize, the following driving cycles were performed in this study:

- ARTEMIS urban cycle with hot start (HotUrban)
- ARTEMIS urban cycle with cold start (ColdUrban)
- ARTEMIS rural-road cycle with hot start (Road)

Because on-line instruments are used here, we tried to reduce the variability of vehicle operations during measurements by repeating part of the ARTEMIS cycles. By doing so, the average speed of the ARTEMIS cycles as well as the acceleration and deceleration phases were kept during measurements. For the ARTEMIS urban cycle, a “heavy-traffic” part is chosen (mean speed of 20 km/h) and for the ARTEMIS rural-road cycle, a “steady-speed” part is chosen.

## 3. Gas- and particle-phase emissions of SVOC

### 3.1. Measurements

Gas- and particle-phase SVOC emission factors were measured from PUF and filter samples, respectively, collected from the tunnel of the CVS system. Alkane and aromatic SVOC were identified for the gas phase, however, only the measured emission factors of alkanes are available for the particle phase (Polo, 2013). Therefore, the gas/particle ratios of alkanes C11 to C40 are presented here. For the urban cycle with cold start, the measured emission factors of the alkanes are shown in Fig. 1 for both the gas- and particle-phases. Although particle-phase SVOC emission factors are low for the E4DF vehicle, the gas-phase SVOC emission factors are high.

Gas/particle ratios of alkanes are estimated from the filter sampling, as shown in Table 2. For all cycles, they are the lowest for the E4D vehicle and the highest for the E4DF vehicle. For the E4D vehicle, the gas/particle ratios vary between 0.7 (for the urban cycles) and 1.1 (for the rural-road cycle), in good agreement with previous studies (e.g., Schauer et al., 1999). For the E2G vehicle, they vary between 9 (for the rural-road cycle) and 35 (for the urban cycle with a hot start). For the E4DF vehicle, they vary between 52 (for the rural-road cycle) and 208 (for the urban cycle with a cold start).

### 3.2. Theoretical estimation of gas/particle ratios

Because of long elapsed times of sampling, the gas-phase SVOC concentrations associated with the filter sampling may be assumed to be at thermodynamic equilibrium with the particle-phase concentrations. In that case, they can be estimated as follows (Pankow, 1994):

**Table 1**  
Distribution (%) of traveled kilometers by passenger cars for the year 2011 in France (André et al., 2014).

Type	Engine displacement	Pre-Euro	Euro 1	Euro 2	Euro 3	Euro 4	Euro 5	Total
Diesel	<1.4 l	0.1	0.1	0.0	2.5	3.4	0.9	7.0
	1.4–2.0 l	1.2	2.8	5.9	16.5	21.3	5.9	53.6
	>2.0 l	0.4	0.6	1.1	1.8	3.1	0.9	7.9
	Total	1.7	3.5	7.0	20.8	27.8	7.7	68.5
Gasoline	<1.4 l	1.9	2.6	4.4	3.4	5.8	1.5	19.6
	1.4–2.0 l	0.8	1.0	2.8	2.1	3.4	0.9	11.0
	>2.0 l	0.1	0.1	0.2	0.0	0.4	0.1	0.9
	Total	2.8	3.7	7.4	5.5	9.6	2.5	31.5
Total		4.5	7.2	14.4	26.3	37.4	10.2	100

$$A_g^{CVS} = \frac{A_p^{CVS}}{K_p M_o^{CVS}} \quad (1)$$

where  $A_g^{CVS}$  and  $A_p^{CVS}$  are the concentrations of a SVOC species in the gas and particle phases, respectively ( $\mu\text{g}/\text{m}^3$ ),  $K_p$  is the partitioning coefficient ( $\text{m}^3/\mu\text{g}$ ) of the species and  $M_o^{CVS}$  is the total concentration of organics present in the particles ( $\mu\text{g}/\text{m}^3$ ).

The particle-phase concentrations of SVOC ( $A_p^{CVS}$ ) are estimated from the measured emission factors as follows:

$$A_p^{CVS} = \frac{F_{OC}^{CVS} df}{V} \quad (2)$$

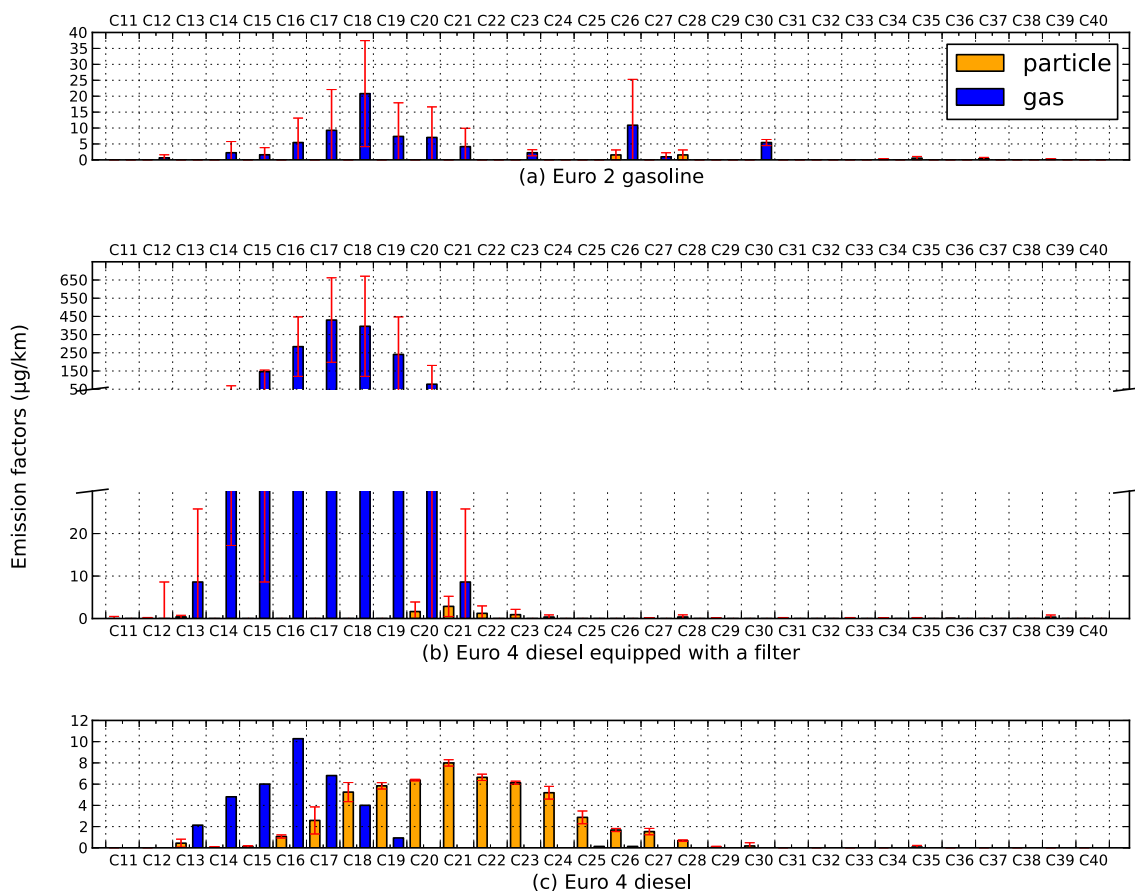
where  $F_{OC}^{CVS}$  ( $\mu\text{g}/\text{km}$ ) is the measured emission factor for OC,  $f$  is the

mass ratio between organic matter (OM or particle-phase SVOC) and OC. It is assumed to be equal to 1.2, as indicated by Schauer et al. (2008).  $d$  (km) and  $V$  ( $\text{m}^3$ ) correspond to the total distance traveled and the total volume of exhaust gas at the tail pipe during the cycle, respectively.

To simplify the calculation, all the alkanes are lumped here into one surrogate species. This lumping is necessary to conduct the simulations that are presented in section 5. As only one species is used in the gas-phase SVOC estimations, we have  $M_o^{CVS} = A_p^{CVS}$ . Therefore, Equation (1) becomes

$$A_g^{CVS} = \frac{1}{K_p} \quad (3)$$

Thus the gas-phase SVOC concentrations are inversely



**Fig. 1.** Emission factors of gas- and particle-phase alkanes from C11 to C40 sampled onto PUF (gas) and quartz filters (particles) with the filter sampling for the tested vehicles and the ColdUrban cycle. If data are available for a single measurement, the error bars (red lines) are not included. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Table 2**  
Gas/particle ratios of alkanes measured by the filter sampling and estimated by assuming thermodynamic equilibrium (using particle-phase concentrations measured by the filter sampling). For the on-line measurements, ratios are estimated from mass conservation and are recalculated taking into account the differences (a factor of 2.5) in dilution factors between the two sampling trains.

Vehicle type	E2G			E4D			E4DF		
	Road	ColdUrban	HotUrban	Road	ColdUrban	HotUrban	Road	ColdUrban	HotUrban
Measurement (CVS <sup>a</sup> )	9	24	35	1.1	0.7	0.7	52	208	88
Estimation (CVS <sup>a</sup> )	19	5	10	0.4	0.3	0.1	37	114	50
Estimation (MAS <sup>b</sup> )	174	30	172	22	16	81			
Dilution correction (MAS <sup>b</sup> )				9	6	32			

<sup>a</sup> Filter sampling.

<sup>b</sup> On-line measurement.

proportional to the partitioning coefficients. The partitioning coefficients  $K_p$  for each of these species are estimated according to Pankow (1994) by the following equation:

$$K_p = \frac{8.202 \times 10^{-5} T}{MW_i p_i^0 \times 10^6} \quad (4)$$

where  $T$  is the temperature (K),  $MW_i$  is the molar mass of species  $i$ , and  $p_i^0$  is the saturated vapor pressure (atm). The saturated vapor pressures are estimated based on Haynes (2014) reports temperatures at which the vapor pressure reaches specified pressure values (1 Pa–100 kPa). For the alkane species used here (C17 to C19), the lowest reported temperatures range from 51.5 °C (C<sub>17</sub>H<sub>36</sub>) to 71.1 °C (C<sub>19</sub>H<sub>40</sub>). Therefore, some extrapolation was needed to estimate saturated vapor pressures at 298 K. Calculated values of  $K_p$  are listed in Table 3.

The selection of the surrogate species to represent all SVOC species is based on the measured profiles of alkanes (Fig. 1) and Albriet et al. (2010). The selection is conducted in three steps. First, we select three to four species with the highest total emission factors of the gas plus particle phases. Second, we calculate their partitioning coefficients and then gas-phase SVOC concentrations using Equations (3) and (4). In this step, we compute gas/particle ratios with the particle-phase concentrations of SVOC from the filter sampling and the theoretically estimated gas-phase concentrations of SVOC. Finally, we compare these computed gas/particle ratios with the measured gas/particle ratios presented in Table 2 and we select the surrogate species to be the one that gives the best agreement with the measurements. The species selected are C<sub>18</sub>H<sub>38</sub> for the E2G vehicle, C<sub>19</sub>H<sub>40</sub> for the E4D vehicle and C<sub>17</sub>H<sub>36</sub> for the E4DF vehicle. The OM/OC ratio values are about 1.18 for these three species.

As shown in Table 2, the theoretically estimated gas/particle ratios are of the same order of magnitude as the measurements performed with the filter sampling (whereas these measured ratios span more than two orders of magnitude). For the older diesel E4D vehicle, the gas/particle ratios are under-estimated, as they range between 0.1 and 0.4 (0.7–1.1 for the measurements). For the E4DF vehicle, they are also slightly under-estimated, as they range between 37 and 114 (52–208 for the measurements). For the E2G vehicle, the gas/particle ratio is over-estimated during the Road driving cycle (19 vs 9), whereas they are under-estimated during the urban driving cycles (5 vs 24 for ColdUrban and 10 vs 35 for HotUrban).

#### 4. Comparison of EC/OC measured with the Dekati FPS and the MASSALYA platform

##### 4.1. EC/OC analysis

The EC/OC analysis by the filter sampling produces emission

**Table 3**  
Properties of the surrogate species used in the simulations.

Vehicle	Species	MW <sub>i</sub> (g/mol)	$p_i^0$ (atm)	$K_p$ (m <sup>3</sup> /μg)
E2G	C <sub>18</sub> H <sub>38</sub>	254	$5.88 \times 10^{-7}$	$1.63 \times 10^{-4}$
E4D	C <sub>19</sub> H <sub>40</sub>	268	$2.72 \times 10^{-7}$	$3.35 \times 10^{-4}$
E4DF	C <sub>17</sub> H <sub>36</sub>	240	$1.32 \times 10^{-6}$	$7.71 \times 10^{-5}$

factors of EC and OC for each vehicle and driving cycle presented in section 2.2. Because of high uncertainties in the EC and OC emission factors measured with the filter sampling for the E4DF vehicle due to the very low particle-phase concentrations, the analysis is presented only for the E4D and E2G vehicles.

The E4D vehicle emits much larger amounts of PM than the E2G vehicle. Fig. 2 presents the emission factors of EC and OC for the ColdUrban cycle. The differences between the vehicles are significant: up to 7 times larger for OC, 300 times larger for EC.

The EC/BC ratio is necessary to estimate EC concentrations from the BC concentrations, which are measured by MAAP. There are a number of comparative studies for the concentrations of EC and BC. However, the EC/BC ratio is not consistent among them. Some studies reported that EC concentrations are larger than BC concentrations in urban regions (Allen et al., 1999; Babich et al., 2000), however others reported lower EC concentrations than BC concentrations (Jeong et al., 2004; Husain et al., 2007; Ram et al., 2010). Therefore, we assume that the EC/BC ratio is equal to unity in this study.

The ratio between OM, which is measured by AMS, and OC is assumed to be equal to 1.2 following Schauer et al. (2008).

Table 4 compares the EC/OC ratios measured by the two sampling trains (filter sampling and on-line measurement). Note that for the on-line measurement, the EC/OC ratios are computed from the BC/OM ratios. The ratios are significantly different for all vehicles. The ratios obtained by the on-line measurements are larger than those obtained by the filter sampling, which implies that OC is lower in the on-line measurements since EC should be similar in both sampling systems. For the E2G vehicle, ratios between the two sampling trains suggest, therefore, that the SVOC emissions in the particle phase (i.e. OC) measured by the on-line measurements are significantly lower than those measured by the filter sampling. In other words, if the gas-phase concentrations of SVOC were measured by both sampling systems, they would be higher with the on-line measurements. The reason for this difference may lie in the elapsed times between emission and measurements. The elapsed times in the filter sampling are longer than those in the on-line measurements (about 15 min for the filter sampling and less than 5 s for the on-line measurements). Our hypothesis is that the longer elapsed time in the filter sampling favors the condensation of SVOC onto the particle phase and leads to higher concentrations of OC measured by the filter sampling compared to the on-line measurements.

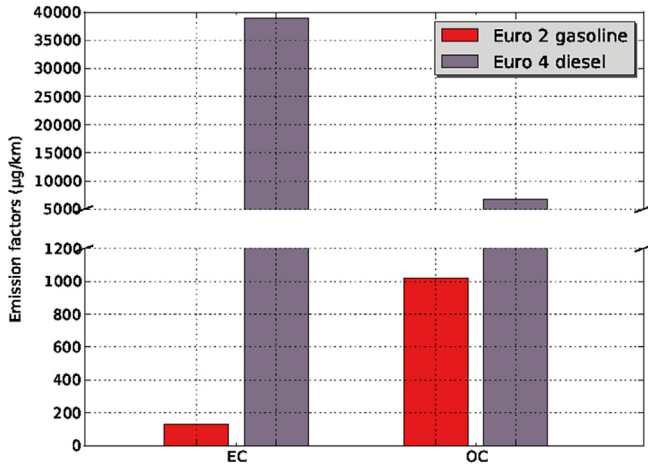


Fig. 2. Emission factors of EC and OC for the tested vehicles during the ColdUrban cycle.

#### 4.2. Comparisons of concentrations

In order to compare the gas- and particle-phase SVOC concentrations from both systems, the EC and OC emission factors reported from the filter sampling are converted into concentrations, since the MAAP and AMS of the on-line measurements provided BC and OM concentrations, respectively.

This conversion was presented for the particle-phase concentrations of SVOC in section 3.2. Similarly to that, the EC emission factors are converted to concentrations as follows:

$$A_{EC}^{CVS} = \frac{F_{EC,n}^{CVS} d}{V} \quad (5)$$

where  $F_{EC,n}^{CVS}$  ( $\mu\text{g}/\text{km}$ ) is the emission factor for EC.

First of all, the concentrations of EC and BC are compared for the purpose of validation: as EC and BC are inert components, the concentrations obtained from the filter sampling and the on-line measurements should be the same. The concentrations of EC and BC for the E2G vehicle are in good agreement for the ColdUrban cycle. The concentrations of EC by the filter sampling are not available for the HotUrban and Road cycles. However, the concentrations of EC and BC for the E4D vehicle differ by a factor of two for the Road and ColdUrban cycles. For the filter sampling with the CVS system, because the total volume including emission exhaust and dilution air is constant, the dilution factor evolves during the driving cycle. These time variations of the dilution can lead to discrepancies between the measured concentrations of EC by the filter sampling and BC by the on-line measurement, which uses constant dilution factors. Furthermore, the EC/BC ratio is uncertain as discussed in section 4.1.

A correction factor is used to take into account these discrepancies in the experiments of this study. This correction factor is defined so that the concentrations of EC by the filter sampling

matches the concentration of BC by the on-line measurement as follows:

$$f_{ec} = A_{BC}^{MAS} / A_{EC}^{CVS} \quad (6)$$

The correction factor is then applied to the estimation of the concentration of OC by the filter sampling as follows:

$$A_{p,corr}^{CVS} = \frac{F_{OC}^{CVS} df}{V} f_{ec} \quad (7)$$

The concentrations estimated for each vehicle and driving cycle are presented in Fig. 3.

For the E2G and E4D vehicles, the differences between the concentrations in the particle-phase SVOC estimated by the filter sampling and the on-line measurements are significant. The concentrations of particle-phase SVOC measured by the filter sampling ( $A_{p,corr}^{CVS}$ ) are up to 68 times larger than those measured by the on-line measurements ( $A_p^{MAS}$ ). These differences can be attributed to three main causes.

- As mentioned above, the condensation of SVOC is greater with the filter sampling as the elapsed time between emission and measurements is longer. The EC/OC analysis performed by the filter sampling requires longer times (approximately 15 min) than the on-line measurements, because of the loading of the filters. This difference in the elapsed times may lead to a different fraction of SVOC in the particle phase because of the dynamics of condensation/evaporation (see section 5).
- Different dilution factors can lead to differences in gas/particle phase equilibrium (see section 4.3).
- There are uncertainties in the measurements and particularly in the EC/OC distribution, which is operationally defined and can vary depending on the instruments. In particular, the emission factors for EC and OC with the filter sampling for the E2G and E4DF vehicles were significantly variable in a repeated sampling. The results presented here were obtained by averaging the samplings.
- Adsorption of gas-phase SVOC onto filters may lead to an increase in the concentrations of particle-phase SVOC measured by the filter sampling. However, it is difficult to quantify the adsorption of SVOC onto filters (Liu et al., 2009).

For the on-line measurements, gas-phase concentrations were not measured. However, they can be estimated from the particle-phase concentrations and the filter sampling, using the conservation of the total mass (gas + particle) between the two sampling trains as follows:

$$A_p^{MAS} + A_g^{MAS} = A_{p,corr}^{CVS} + A_g^{CVS} \quad (8)$$

where  $A_g^{MAS}$  and  $A_g^{CVS}$  are the gas-phase SVOC concentrations for the on-line measurements and the filter sampling, respectively.

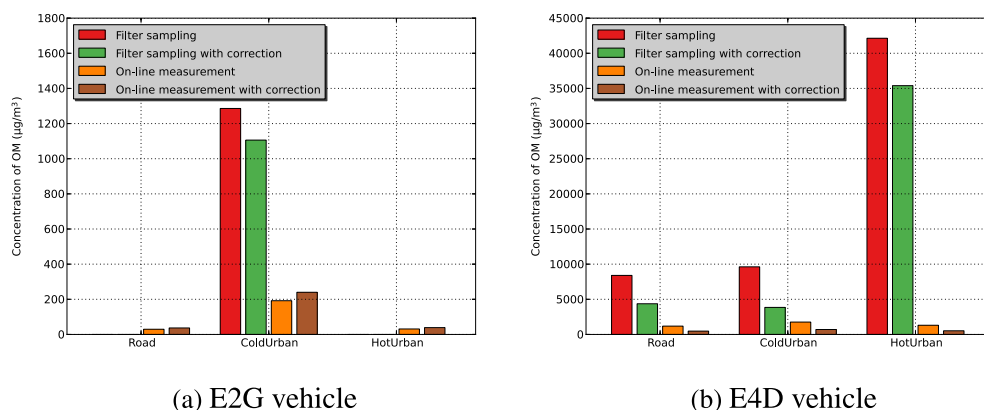
Fig. 4 summarizes how gas-phase SVOC concentrations are estimated and the relations between the two sampling trains.

The gas/particle ratios estimated from the on-line

Table 4

EC/OC ratios in the emissions measured by the filter sampling and the on-line measurements. For the on-line measurements, the EC/OC ratios are computed from the BC/OM ratios.

Vehicle type	E2G			E4D			E4DF		
	Road	ColdUrban	HotUrban	Road	ColdUrban	HotUrban	Road	ColdUrban	HotUrban
Filter sampling	–	0.13	–	6.6	5.8	0.46	–	–	–
On-line measurement	0.92	0.60	0.78	61	32	31	1.2	1.3	0.46



**Fig. 3.** Measured or estimated concentrations of OM for tested vehicles and driving cycles. The red and green bars represent the concentrations by the filter sampling before/after the correction using the correction factor defined in Equation (6), respectively. The orange and brown bars represent the concentrations by the on-line measurement before/after the correction using the dilution correction factor defined in section 4.3, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

measurements in Table 2 are systematically higher than those from the filter sampling, suggesting that thermodynamic equilibrium is not yet achieved in the on-line measurements. In section 5, the dynamic evolution of gas/particle partitioning is presented to explain the differences in the SVOC gas/particle ratios observed between the two sampling trains.

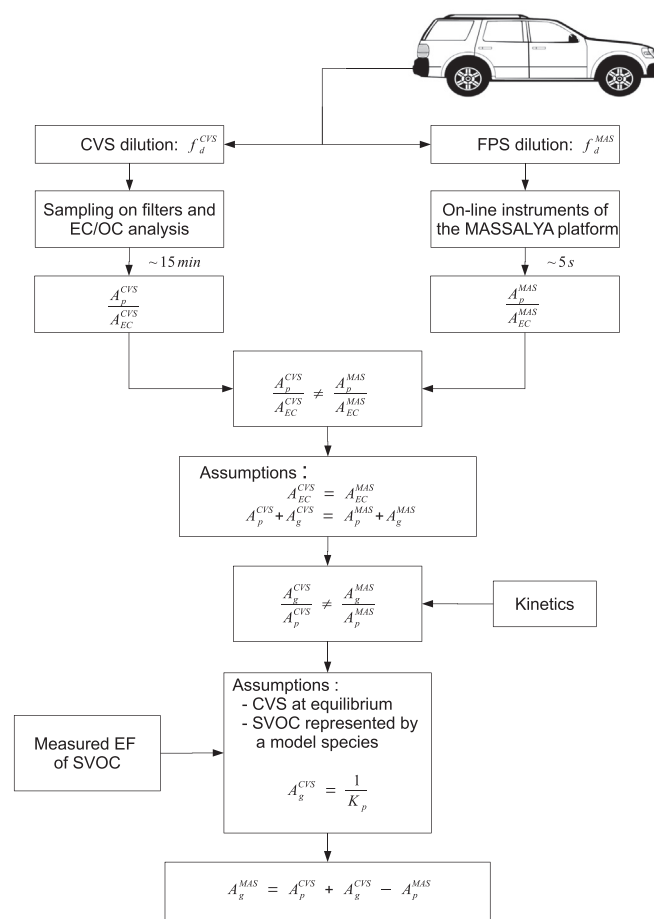
#### 4.3. Effect of dilution

As shown in Table 5, the dilution factors used in the two sampling trains differ depending on the experiments. These differences may explain some of the discrepancies between the two sampling trains for OC. Robinson et al. (2007) showed that organic particle emission factors may vary greatly with the dilution factor for diesel vehicles. The averaged dilution factors of the filter sampling are low for all experiments: they vary between 23 and 79. For the on-line measurements, the dilution factors are also low for the E2G vehicle (30–65). However, they are high for the E4D vehicle: between 890 and 1530. For the E2G vehicle, the dilution factors of the two sampling trains are of the same order of magnitude. However, for the E4D vehicle, the dilution factors are very different: the dilution factors of the on-line measurements are 23–49 times greater than those of the filter sampling.

To estimate the effect of dilution factors on gas/particle partitioning of SVOC, the on-line measurements were repeated using different dilution factors for the E2G vehicle (6, 10, and 15) and the E4D vehicle (660, 1000, 1300, 1750, and 2000). The concentrations of BC and OM were measured using the different dilution factors. To examine the effect of the dilution factor, the measured concentrations of diluted BC and OM are compared to concentrations at the tailpipe, i.e., concentrations before dilution. The concentrations before dilution are estimated by multiplying the value of the dilution factor and the measured diluted concentrations:

$$A_{\text{BC}}^0 = A_{\text{BC}}^d f_d \quad (9)$$

where  $A_{\text{BC}}^d$  is the diluted concentration of BC,  $A_{\text{BC}}^0$  is the concentration of BC before dilution at the tailpipe and  $f_d$  is the dilution factor. Estimated concentrations of BC before dilution are expected not to vary with dilution because BC is not volatile. However, the estimated concentrations of BC before dilution increase with the dilution factors for the E4D vehicle and decrease for the E2G vehicle. This is due to measurement artefacts and uncertainties in the value of the dilution factor. Therefore, the dilution factors were



**Fig. 4.** Schematic representation of the estimation of gas-phase SVOC concentrations for the two sampling trains.

corrected so that the estimated concentrations of BC before dilution do not vary with dilution. The correction is done using the measurements performed with the lowest dilution factor as reference (6 for the E2G vehicle and 660 for the E4D vehicle). The corrected dilution factors are listed in Table 6 (corrections range from 17 to 30%).

Then, concentrations of OM before dilution are calculated using



**Table 5**  
Dilution factors used for both the filter sampling and the on-line measurements.

Vehicle type	E2G			E4D			
	Driving cycle	Road	ColdUrban	HotUrban	Road	ColdUrban	HotUrban
Filter sampling		23	43	40	60	74	79
On-line measurement		30	65	31	1170	1530	890

**Table 6**  
Dilution factors with/without correction.

Vehicle type	E2G			E4D				
Dilution factor	6	10	15	660	1000	1300	1750	2000
Corrected dilution factor	6	11.7	19.3	660	919	1159	1391	1687

these corrected dilution factors. Unlike BC, they do vary with dilution because of condensation/evaporation of organics. To remain constant with dilution, the concentrations of OM before dilution should be calculated as follows:

$$A_p^o + \Delta A_p = A_{pd}^{d,corr} \tag{10}$$

where  $A_p^o$  and  $A_{pd}^d$  corresponds to the OM concentrations at the tailpipe and the diluted concentrations of OM, which were measured by AMS, respectively.  $\Delta A_p$  represents the conversion between the gas and particle phases of SVOC by dilution and  $f_d^{corr}$  is the corrected dilution factor.

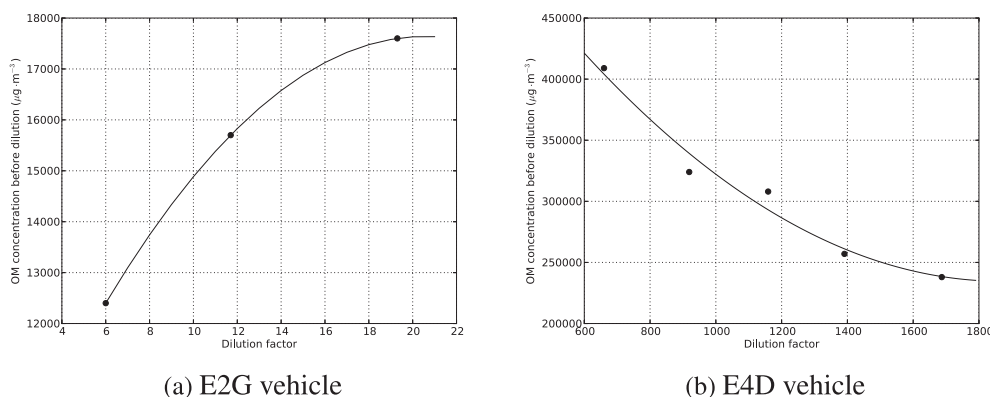
Fig. 5 presents the calculated concentrations ( $A_p^o + \Delta A_p$ ) of OM before dilution for two vehicles. In this figure, because the concentrations  $A_p^o$  at the tailpipe do not vary with dilution, the differences in the concentrations between different dilution factors represent  $\Delta A_p$ , i.e., the effects of condensation/evaporation during dilution on the measured concentrations.

For the E2G vehicle, the concentrations of OM increase with dilution. Increasing the dilution by a factor of 2 (between 6 and 12) leads to an increase in OM concentration by a factor of almost 1.3. However, the increase in OM concentration is less as the dilution increases. This increase may be due to the cooling of the exhaust emissions by low dilution (Hildemann et al., 1989). As shown in Fig. 5a, decreasing the dilution factor of 20 by a factor of 2 leads to a decrease in OM concentrations of about 20%. Therefore, if the same dilution were used for the two sampling trains of this study, the OM concentrations of the on-line measurements would be lower than estimated and the differences between the concentrations of the two sampling trains in the particle phase would be greater than estimated here, by at most 20%.

On the other hand, for the E4D vehicle (see Fig. 5b), the concentrations of OM decrease with dilution as reported by Robinson et al. (2007). This decrease may be due to a higher fraction of SVOC in the gas phase when the dilution factor is higher, in agreement with previous studies for diesel vehicles (Lipsky and Robinson, 2006; Fujitani et al., 2012). Increasing the dilution factor by a factor of 3 from 600 to 1800 leads to a decrease in OM concentrations by a factor of about 1.8. This is in agreement with the work of Robinson et al. (2007) for diesel vehicles. However, the dilution factors of the on-line measurements are 23–49 times higher than those of the filter sampling. According to Robinson et al. (2007), if the same dilution were used for the two sampling trains (i.e., if dilution factors of the on-line measurements were 23–49 times lower than they are), OM concentrations of the on-line measurements would be about 2.5 times higher than they are. But large differences between the OM concentrations estimated for the two sampling trains would still subsist: the OM concentrations of the on-line measurements are between 240 and 1450 times lower than those of the filter sampling. To take into account the effect of the differences of dilution factors between the two sampling trains, the estimated OM concentrations of the on-line measurements are multiplied by 2.5 and accordingly the gas/particle ratios of Table 2 are divided by 2.5.

**5. Dynamic evolution of SVOC concentrations**

In the previous section, we showed that the thermodynamic equilibrium between the gas and particle phases may not yet be achieved, for the on-line measurements of exhaust emissions. However, gas and particles are likely to have reached thermodynamic equilibrium for the filter sampling, because of the longer times elapsed between emission and measurements (about 15 min). Here, the dynamic changes of the SVOC concentrations after emission are simulated. The concentrations measured by the on-line measurements are taken as initial conditions, as the elapsed time of the on-line measurements is low (less than 5 s).



**Fig. 5.** Calculated concentrations of OM before dilution.

**Table 7**  
Measured mean diameters and calculated kinetic mass transfer rates.

Vehicle type	E2G			E4D			E4DF		
	Road	ColdUrban	HotUrban	Road	ColdUrban	HotUrban	Road	ColdUrban	HotUrban
Mean diameter (nm)	62	60	58	71	74	72	87	61	136
Mass transfer rate (s <sup>-1</sup> )	0.22	1.16	0.23	48.7	38.3	29.6	0.02	0.02	0.005

### 5.1. Description of the gas/particle mass transfer model

The partitioning between gas and particles and the particle-phase concentrations of SVOC  $A_p$  evolve with time following the dynamic equation of condensation/evaporation (e.g., Couvidat and Sartelet, 2015).

$$\frac{dA_p}{dt} = k \left( A_g - \frac{A_p}{K_p M_o} \right) \quad (11)$$

The kinetic mass transfer rate  $k$  is defined as follows:

$$k = 2\pi d_p D_{air} N f(Kn, \alpha) \quad (12)$$

where  $d_p$  is the particle mean diameter (m),  $D_{air}$  is the diffusivity of the condensing species in air ( $0.14 \times 10^{-4} \text{ m}^2/\text{s}$ ), and  $N$  is the number concentration of particles ( $\#/m^3$ ). The function  $f(Kn, \alpha)$  depends on the Knudsen number ( $Kn$ ) which can be calculated using  $\lambda$ , the mean free path in air (68 nm at 100 kPa and 293 K).

When mass transfer occurs from the surrounding gas to atmospheric particles, the diameter of particles is crucial to define the transfer regime between the kinetic regime (particle diameters lower than  $\lambda$ ) to the continuum regime (particle diameters greater than  $\lambda$ ). If  $\lambda \approx d_p$ , the mass transfer lies in the transition regime and the following equation may be used to describe the mass transfer (Dahneke, 1983; Seinfeld and Pandis, 1998):

$$f(Kn, \alpha) = \frac{1 + Kn}{1 + 2Kn(1 + Kn)/\alpha} \quad (13)$$

where  $Kn = 2\lambda/d_p$ . The accommodation coefficient  $\alpha$ , which accounts for imperfect surface accommodation, is taken equal to 0.1 following Saleh et al. (2013). For the E4D vehicle, because of large concentrations of EC, equilibrium is achieved very fast. Thus the  $\alpha$  value does not influence much the simulation results.

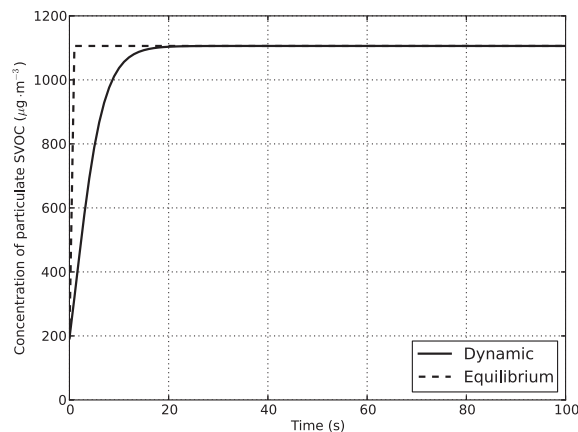
The particle mean diameter  $d_p$  is estimated from the total mass concentration of particles and the number of particles measured by the MASSALYA platform (SMPS), as shown in Table 7. For the E2G vehicle, the mean diameter is estimated to be about 60 nm for all cycles, which is consistent with previous studies (e.g., Seigneur, 2009). For the E4DF and E4D vehicles, the mean diameters are larger than for the E2G vehicle; in particular, for the HotUrban cycle of the E4DF vehicle (58 nm for E2G vs. 136 nm for E4DF).

The estimated kinetic mass transfer rates  $k$  are presented in Table 7. The large differences among the mass transfer rates of the three vehicles result mostly from the differences in particle number concentrations present in the emission exhaust.

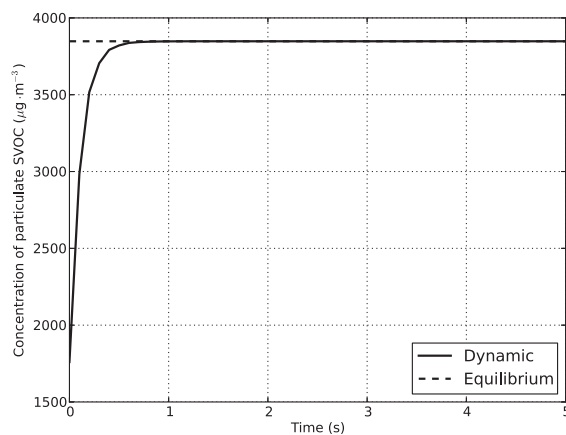
### 5.2. Description of the aerosol model

The Size Resolved Aerosol Model (SIREAM) (Debry et al., 2007) coupled to the Secondary Organic Aerosol Processor (SOAP) (Couvidat and Sartelet, 2015) was used here to model aerosol dynamics. In this model, particles consist of:

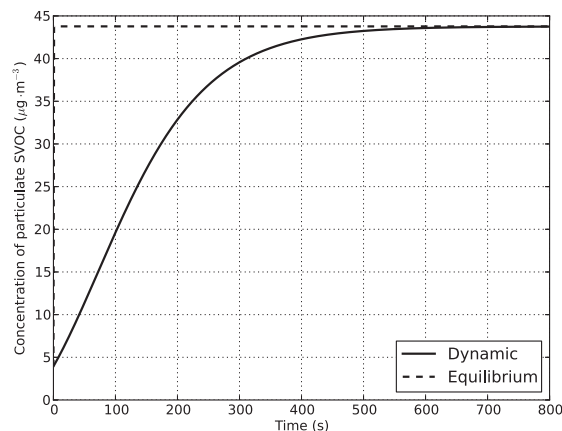
- Inert species: mineral dust and EC



(a) E2G



(b) E4D



(c) E4DF

**Fig. 6.** Modeled concentrations of particle-phase SVOC using the equilibrium (dotted line) and dynamic (solid line) approaches for the three vehicles and ColdUrban driving cycle.

- Inorganic species: sulfate, ammonium, nitrate, sodium, and chlorine
- Organic species: primary and secondary organic aerosols.
- Liquid water

SIREAM treats nucleation, coagulation, condensation, and evaporation. Nucleation and coagulation are neglected in this study in order to focus on the mass transfer of SVOC from gas to particle by condensation/evaporation. The condensation of SVOC occurs on pre-existing particles. Evaporation may occur upon dilution of the exhaust emissions, particularly for ultrafine particles which are subject to the Kelvin effect. SIREAM provides three methods to solve condensation/evaporation: a completely dynamic method where the evolution of concentrations between the gas and particle phases is dynamically resolved (see section 5.1), an equilibrium approach where it is assumed that thermodynamic equilibrium between the gas and particle phases is instantaneous, and a hybrid approach that combines the two approaches depending on particle sizes or characteristic times to reach equilibrium. The dynamic and equilibrium methods are compared here.

### 5.3. Modeling results

The dynamic evolution of aerosols was simulated using SIREAM for the three vehicles. The concentrations of PM (EC, OM, and inorganic aerosols) measured by the on-line measurements are used as initial conditions for the simulations. For the E4D vehicle, the OM concentrations are corrected by a factor of 2.5 to take into account the influence of dilution. The gas-phase SVOC concentrations are estimated as described in section 4.2 for the on-line measurements. For the E4DF vehicle, gas-phase SVOC concentrations cannot be estimated because of the lack of CVS measurements. The ratios of particle-phase SVOC concentrations between the filter sampling and the on-line measurements of the E4D vehicle are used to estimate the particle-phase SVOC concentrations for the E4DF vehicle. The ratios vary from 2 for the ColdUrban cycle to 27 to the HotUrban cycle.

Fig. 6 shows the temporal evolution of particle-phase SVOC concentrations using the dynamic and equilibrium approaches to compute condensation/evaporation. In the equilibrium approach, gas- and particle-phase SVOC are instantaneously at equilibrium by definition. In the dynamic approach, the particle-phase SVOC concentrations increase toward equilibrium, as condensation takes place. A characteristic time is defined as the time to reach equilibrium (within 1%). The characteristic times vary from less than 1 s to about 8 min using the dynamic approach depending on vehicles and cycles. These characteristic times explain why the measurement techniques lead to differences between the concentrations measured by the two sampling trains. For the on-line measurements, the times elapsed between emission and measurement are lower than the characteristic times of condensation for the E2G and E4DF vehicles. Thus, the SVOC concentrations in the particle phase are significantly lower than those at equilibrium and in the comparison for the E2G and E4DF vehicles, the greater time elapsed between emission and measurement (~ 15 min, following dilution) for the filter sampling leads to larger concentrations of particle-

phase SVOC.

These modeled characteristic times correspond to the analytic characteristic times obtained from the mass transfer rates (see Table 7). For the E2G vehicle, the characteristic time of the ColdUrban cycle is much lower than those of the HotUrban and Road cycles. Because particle sizes are not significantly different among the driving cycles, this lower time for the ColdUrban cycle is due to higher number concentrations of particles measured by the on-line measurements (ColdUrban:  $2 \times 10^6 \text{ \#m}^{-3}$  vs HotUrban:  $4 \times 10^5 \text{ \#m}^{-3}$ , Road:  $3.7 \times 10^5 \text{ \#m}^{-3}$ ), as the mass transfer rate (the characteristic time) is proportional (inversely proportional) to the particle number concentration. For the E4D vehicle, very low characteristic times (less than 1 s) are obtained for all driving cycles due to the large particle number concentrations in the emissions. The highest characteristic times are obtained with the E4DF vehicle because of the low particle number concentrations.

For all three vehicles, this work shows that the concentrations estimated from the on-line measurements are not at thermodynamic equilibrium between the gas and particle phases.

## 6. Discussion

For on-road gasoline and diesel vehicles, measured emissions at the exhaust may depend on the instruments being used for dilution and measurements. For example, this work shows that the EC/OC ratios differ depending on whether the measurements are made on-line (HR-ToF-AMS and MAAP) with a short time elapsed between emission and measurement (a few s) or by filter and PUF sampling with a longer elapsed time (~15 min).

The concentrations of gas-phase SVOC were estimated from the measurements of alkane concentrations performed with filter and PUF sampling in the CVS system in both the gas and particle phases. The partitioning between the gas and particle phases is reasonably well explained for alkanes by lumping all of them into one surrogate species and assuming thermodynamic equilibrium between the gas and particle phases. For the on-line measurements, where only particle-phase SVOC were measured, gas-phase SVOC were estimated assuming mass conservation. The gas/particle ratio of SVOC varies with the cycle (road, cold urban, hot urban), but larger variations are observed depending on the vehicle. On average, the gas/particle ratio of SVOC is lower for the diesel vehicle (about 0.8) and is higher for the gasoline vehicle (about 23) and the diesel with a particle filter (about 116). COPERT emission factors (<http://emisia.com/copert>), which are typically used in Europe to develop emission inventories for air quality, do not take into account those gas-phase SVOC. Because COPERT factors are usually estimated using a filter sampling system, this study provides an estimation of the gas-phase SVOC emissions for air-quality modeling purposes. For example, following Table 1, let us assume that 31.5% of traveled kilometers are traveled by gasoline vehicles ( $d_{\text{gasoline}}$ ), 60.8% by diesel vehicles ( $d_{\text{diesel}}$ ), and 7.7% by Euro 5 diesel vehicles or Euro 4 diesel vehicles with a particle filter ( $d_{\text{diesel-PF}}$ ). The gas/particle ratio of SVOC emissions for passenger cars in France can then be estimated using the emission factors ( $F_{\text{OC}}^{\text{CVS}}$ ) and the gas-particle ratios (GPR) measured in this study for the 3 types of vehicles:

$$\frac{\text{Gas - phase SVOC emissions}}{\text{Particle - phase SVOC emissions}} = \frac{GPR_{\text{E2G}} * F_{\text{OC, E2G}}^{\text{CVS}} * d_{\text{gasoline}} + GPR_{\text{E4D}} * F_{\text{OC, E4D}}^{\text{CVS}} * d_{\text{diesel}} + GPR_{\text{E4DF}} * F_{\text{OC, E4DF}}^{\text{CVS}} * d_{\text{diesel-PF}}}{F_{\text{OC, E2G}}^{\text{CVS}} * d_{\text{gasoline}} + F_{\text{OC, E4D}}^{\text{CVS}} * d_{\text{diesel}} + F_{\text{OC, E4DF}}^{\text{CVS}} * d_{\text{diesel-PF}}} \quad (14)$$

By further assuming that 30% of trips are rural-road trips, 70% are urban trips, and 30% of urban trips are with a cold start, the gas/particle ratio of SVOC emissions for passenger cars in France is estimated to be on average about 1.5. This result implies that current European emission inventories underestimate SVOC emissions from passenger cars by about 60%, since they only account for their particulate fraction (i.e., 1/2.5).

The gas/particle ratios measured with the on-line measurements are greater than those measured with the filter sampling, suggesting that concentrations of gas/particle may not be at thermodynamic equilibrium for the on-line measurements. The dynamic evolution of SVOC particle concentrations was simulated with an aerosol model with concentrations estimated from MASSALYA measurements as initial conditions. Depending on vehicles and road cycles, thermodynamic equilibrium between gas and particles may take up to 8 min to be reached. A time elapsed between emission and measurement shorter than this characteristic time to reach equilibrium can lead to lower concentrations in the particle phase than those that would be estimated assuming thermodynamic equilibrium, because the equilibrium between gas and particles has not yet been reached. These results suggest that it is essential to take into account the time elapsed between emission and measurements to properly estimate the gas/particle ratio in the emission exhausts of vehicles tested on a chassis dynamometer.

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