



Emissions of organic aerosol mass

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# Emissions of organic aerosol mass, black carbon, particle number, and regulated and unregulated gases from scooters and light and heavy duty vehicles with different fuels

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## Abstract

A sampling campaign with seven different types of vehicles was conducted in 2009 at the vehicle test facilities of the Joint Research Centre (JRC) in Ispra (Italy). The vehicles chosen were representative of some categories circulating in Europe and were fueled either with standard gasoline or diesel and some with blends of rapeseed methyl ester biodiesel. The aim of this work was to improve the knowledge about the emission factors of gas phase and particle-associated regulated and unregulated species from vehicle exhaust. Unregulated species such as black carbon (BC), primary organic aerosol (OA) content, particle number (PN), monocyclic and polycyclic aromatic hydrocarbons (PAHs) and a selection of unregulated gaseous compounds, including nitrous acid (N<sub>2</sub>O), ammonia (NH<sub>3</sub>), hydrogen cyanide (HCN), formaldehyde (HCHO), acetaldehyde (CH<sub>3</sub>CHO), sulfur dioxide (SO<sub>2</sub>), and methane (CH<sub>4</sub>), were measured in real time with a suite of instruments including a high-resolution aerosol time-of-flight mass spectrometer, a resonance enhanced multi-photon ionization time-of-flight mass spectrometer, and a high resolution Fourier transform infrared spectrometer. Diesel vehicles, without particle filters, featured the highest values for particle number, followed by gasoline vehicles and scooters. The particles from diesel and gasoline vehicles were mostly made of BC with a low fraction of OA, while the particles from the scooters were mainly composed of OA. Scooters were characterized by super high emissions factors for OA, which were orders of magnitude higher than for the other vehicles. The heavy duty diesel vehicle (HDDV) featured the highest nitrogen oxides (NO<sub>x</sub>) emissions, while the scooters had the highest emissions for total hydrocarbons and aromatic compounds due to the unburned and partially burned gasoline and lubricant oil mixture. Generally, vehicles fuelled with biodiesel blends showed lower emission factors of OA and total aromatics than those from the standard fuels. The scooters were the main emitters of aromatic compounds, followed by the gasoline vehicle, the diesel vehicles and the HDDV.

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## 1 Introduction

Vehicles are still a significant source of air pollution in Europe even though the introduction of new technologies has led to substantial reductions (H.E.I., 2010). Gasoline vehicles emit mostly carbon monoxide (CO), hydrocarbons (HC) and nitrogen oxides ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ), while diesel vehicles without aftertreatment devices emit relatively small amounts of CO and HC but large amounts of  $\text{NO}_x$  and particulate matter (PM) (H.E.I., 2010). In southern Europe and in some Asian countries, the urban traffic scenario of many cities is characterized by the presence of a high density of two-wheel motor vehicles, which are important sources of PM and HC (Picini et al., 2005; Adam et al., 2010).

$\text{NO}_x$ , volatile and semi-volatile organic compounds (VOCs and SVOCs) are precursors for photooxidants, such as ozone and peroxyacetyl nitrate, and secondary aerosol formation in ambient air (Finlayson-Pitts and Pitts, 1997; Atkinson and Arey, 2003; Robinson et al., 2007). Aerosols can have a direct radiative forcing (scattering and absorption of solar and infrared radiation) and an indirect radiative forcing (alteration of cloud properties and precipitation patterns) (IPCC, 2013).

In urban environments, there is evidence that adverse non-carcinogenic and carcinogenic effects might be associated with exposure to diesel particulate matter (DPM) (E.P.A., 2002; Pope and Dockery, 2006). The organic aerosol (OA) can be an important constituent of PM and it can contain toxic or carcinogenic chemicals including polycyclic aromatic hydrocarbons (PAHs) (Rogge et al., 1993; Schauer et al., 1999). Different studies have tried to correlate the toxicity of DPM with its chemical constituents like organic and elemental carbon (Mar et al., 2000; Metzger et al., 2004).

Aromatic hydrocarbons and in particular PAHs are a very important class of organic compounds from the health perspective, which are emitted from virtually all combustion sources. Specific PAH congeners may be used as tracers for motor vehicle exhaust (Cass, 1998; Schauer et al., 1999; Picini et al., 2005). Aromatic hydrocarbons are present in unburned petroleum and lubricating oil and they are often produced dur-

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ing combustion processes. Various conditions affect the aromatic hydrocarbon composition in the exhaust, such as fuel composition, fuel to air ratio, engine combustion temperature, or fuel injection timing (Lima et al., 2005; Lim et al., 2007).

Concerning diesel and gasoline vehicles, European regulations have continuously introduced more stringent limits for different exhaust pollutants (CO, NO<sub>x</sub>, PM, etc). Moreover the European Commission has added a particle number limit to its Euro 5/6 emission standards for light-duty diesel vehicles (Co-decision Regulation EC 715/2007 and Comitology Regulation EC 692/2008). For two-wheel motor vehicles, the European Directive 97/24/EC (Euro 2) introduced a substantial reduction of CO and a lower limit for the sum of HC and NO<sub>x</sub>. A new regulation is expected in the coming years (Euro 3 and Euro 4).

Fuel improvements, especially sulfur content reduction, was one way to reduce vehicle emissions (Thompson et al., 2004a). To reduce fossil fuel dependence and emissions, and to respect the more stringent regulations, in particular for PM, other fuels like bio-fuels (i.e. biodiesel) have been introduced. Biodiesel are fatty acid methyl or ethyl esters made from vegetable oils or animal fats that can be used in diesel engines. Various studies have shown that the use of biodiesel reduces the emissions of HC, CO and PM and the improvements are mainly due to the higher oxygen content of the fuels compared to diesel fuel (Mayer et al., 2005; Lapuerta et al., 2008; Di et al., 2009; Karavalakis et al., 2009).

The introduction of newer technologies and the use of aftertreatment devices, to comply with newer regulations, have effectively reduced the emissions from motor vehicles. Three-way catalytic converters (TWC) reduce emissions of CO, HC, and NO<sub>x</sub> by more than 90 %, while for diesel vehicles the use of abatement devices is needed to get lower emissions of NO<sub>x</sub> and PM (Walker, 2004; Fino, 2007; H.E.I., 2010). Catalytic converters were also adapted at the tailpipe of two-wheel motor vehicles to comply with the Euro 2 emission standard. Nevertheless, scooters remain a considerable source of pollutants (Ntziachristos et al., 2005; Prati and Costagliola, 2009; Adam et al., 2010).

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In order to develop inventories for gaseous or particulate motor vehicle emissions, emission factor values (EF) are needed (i.e. the amount of a pollutant emitted per kilometer or per unit of fuel burned). Current methods for deriving emission factors range from measurement of single vehicles, to vehicle fleets using dynamometers, roadways or tunnels or estimates based on remote sensing of fuel consumption (e.g. Morawska et al., 2008).

A lot of studies have been conducted in order to provide insight into the origin of the vehicle emissions and to establish effective vehicle emission control strategies. For instance, Yanowitz et al. (1999) measured the regulated emissions from heavy duty diesel vehicles, Shah et al. (2004) measured mass and organic matter, Thompson et al. (2004a, b) measured particle number, and Lev-On et al. (2002) unregulated pollutants like PAHs. Regulated and unregulated emissions from passenger car have been characterized by many researchers (e.g. Ntziachristos et al., 2004; Bosteels et al., 2006; Caplain et al., 2006; Karlsson, 2004; Devos et al., 2006; Heeb et al., 2008). Some studies have also compared different vehicle categories for regulated pollutants and particle number emissions (e.g. Ntziachristos et al., 2003). Recently size resolved and chemically resolved characterization of the non-refractory part of the emitted particulates was measured from in-use vehicles (Canagaratna et al., 2004). However, according to our knowledge, there are no studies that measured simultaneously regulated and unregulated pollutants for different types of vehicles to the extent shown here until 2009 when the measurements were performed.

The aim of this work was to improve the knowledge about the emission factors of a comprehensive set of gas phase and particle-associated regulated and unregulated species for different classes of vehicles. A sampling campaign with seven different types of vehicles was conducted in 2009 at the vehicle test facilities of the Joint Research Centre (JRC) in Ispra (Italy). The vehicles chosen were representative of vehicle categories circulating in Europe in 2009, comprising a Euro III heavy duty diesel vehicle, a Euro 3 diesel passenger car, Euro 4 diesel passenger cars, a Euro 4 gasoline car, a Euro 3 diesel van, and Euro 1 and Euro 2 scooters. They still comprise a major

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fraction on the road. All vehicles were tested using the European legislative driving cycles, steady state cycles and speed ramp sequences. Vehicles were fueled either with standard gasoline or diesel, and eventually some of them were also run with blends of rapeseed methyl ester biodiesel. Results on regulated emissions will be presented together with results from unregulated emissions.

In particular, the black carbon and the primary organic aerosol content of particulate matter were investigated with a multi-angle absorption photometer (MAAP) and an Aerodyne high resolution time of flight aerosol mass spectrometer (HR-ToF-AMS), respectively. Particle number was measured with a condensation particle counter (CPC) and monocyclic and polycyclic aromatic hydrocarbons by a REMPI (resonance enhanced multi-photon ionization) instrument coupled with a ToF (time-of-flight) mass spectrometer. Nitrogen species ( $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{NH}_3$  and  $\text{HCN}$ ), oxygenated small compounds (formaldehyde, acetaldehyde), sulfur dioxide and methane were monitored by a high resolution Fourier transform infrared spectrometer (HR-FTIR). The data may serve as reference for emission ratios of various compounds for different type of vehicle emission that are often used for the interpretation of ambient data and are difficult to find in the literature.

## 2 Materials and methods

### 2.1 Vehicles and fuels

The following vehicles were tested: a Euro III heavy duty diesel vehicle (HDDV(EIII)), a Euro 3 diesel light duty passenger car (Diesel-P(E3)), a Euro 3 diesel light duty van (Diesel-V(E3)), a Euro 4 diesel light duty passenger car (Diesel-P(E4)), a Euro 4 gasoline light duty passenger car (Gasoline-P(E4)), a Euro 1 scooter (Scooter(E1)) and a Euro 2 scooter (Scooter(E2)). The technical characteristics of the vehicles are summarized in Table 1. The HDDV(EIII) was not equipped with any aftertreatment device, while the diesel and gasoline vehicles were equipped with a diesel oxidation catalyst

(DOC) and a three-way-catalyst (TWC), respectively. The Scooter(E1) had an oxidation catalyst, while the Scooter(E2) featured a secondary air injection system (SAS) and an oxidation catalyst.

The experiments were conducted with commercial diesel and gasoline fuels. The sulfur content in the diesel fuels was either less than 50 ppm or less than 10 ppm (Tables 1 and S1). Some experiments were performed with 10 % and 30 % rapeseed methyl ester (RME) biodiesel fulfilling the EN14214 biodiesel standard added to the commercial diesel fuel. Two-stroke scooters with 50 cm<sup>3</sup> displacement engines were tested with a conventional gasoline-lubricant (2 %) mixture. The gasoline fuel complied with the certified reference fuel CEC RF-02-99 oxy 0.8-1.2 according to Directive 97/24/EC and 98/70/EC. Mineral oil was used for the Scooter(E1), while semi-synthetic oil was used for Scooter(E2). The effect of the alternative fuel (30 % biodiesel blend) on the emission factors of all investigated compounds are summarized in Table S2.

## 2.2 Sampling system

The tests were performed on the Vehicle Emission Laboratory (VELA) chassis dynamometers of the Institute for Environment and Sustainability (IES) of the EC-JRC Ispra, Italy. Three different laboratories were used: two for the passenger cars, one for the two-wheel motor vehicles and a new test facility for the HDDV(EIII) (Giechaskiel et al., 2007a; Adam et al., 2011). A typical schematic diagram of the experimental systems is shown in Fig. 1.

A full flow dilution tunnel with constant volume sampler (CVS) was used to dilute the exhaust according to the European legislation for passenger cars and scooters. Most instruments were connected to the dilution tunnel directly or with one or two ejector diluters (Dekati Ltd, Tampere, Finland) in series depending on the emissions levels. The flow of the dilution air in the dilution tunnel and the number of diluters used for each experiment are reported in Table S1 in the Supplement, together with other information about every single test (type of cycle, engine temperature, type of fuel). The dilution ratio provided by each diluter was ~ 1 : 12. For the experiments with two-wheel motor

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vehicles, a cyclone (50 % cut-point diameter of 20  $\mu\text{m}$ ) was added between the tailpipe and the dilution tunnel in order to protect the instruments connected to the CVS from oil droplets. The REMPI-TOF and the FTIR were directly connected to the tailpipes of the vehicles (see instrumentation below).

## 2.3 Instrumentation

### 2.3.1 High resolution time of flight aerosol mass spectrometer (HR-ToF-AMS)

An Aerodyne high resolution time of flight aerosol mass spectrometer (HR-ToF-AMS) was used during this campaign for real-time measurements of the submicron non refractory aerosol components such as organic aerosol (OA), sulfate ( $\text{SO}_4$ ), and nitrates.

A detailed description of the instrument is given in DeCarlo et al. (2006), while the basic principles are reported in Chirico et al. (2010). Table 2 summarizes the instruments used and the compounds they measured.

The flow calibration, the servo position check, the lens alignment and the size calibration were performed at the beginning of the campaign, while the ionization efficiency (IE) calibration was performed at the beginning and once every week. The baseline, the  $m/z$  and single ion calibrations were performed every day. The averaging time was 5 s in V mode (3 s in MS mode and 2 s in PToF mode).

Data analysis was performed in Igor Pro 6.03A (Wavemetrics, Lake Oswego, OR) using the AMS Analysis Toolkit Squirrel v.1.44. The AMS fragmentation table (Allan et al., 2004) was modified to account for the contribution of the gas phase species to  $m/z$  44, 29 and 16–20. For organic signals at  $m/z$  28 and 18 the fragmentation table suggested by Aiken et al. (2008) was used. Gas phase corrections were made by HEPA filtered air sampled at the end of each test with the vehicle engines at idle mode. The temporal fluctuation of the diluted  $\text{CO}_2$  concentration was measured during each run and taken into account to estimate the temporal contribution of the organic aerosol at  $m/z$  44. A particle collection efficiency of unity was assumed to estimate the aerosol mass concentration.

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### 2.3.2 Carbon dioxide analyzer

Carbon dioxide (CO<sub>2</sub>) was measured with a differential, non-dispersive, infrared (NDIR) gas analyzer (LI-7000, LI-COR Biosciences). A two-point calibration in the range 0–560 ppm was performed with 560 ppm CO<sub>2</sub> gas bottle standard and CO<sub>2</sub>-free air bottle before the campaign. The instrument was run with 1 s time resolution.

### 2.3.3 Multi-angle absorption photometer (MAAP)

Black carbon (BC) concentrations in PM<sub>1</sub> were measured with a MAAP (Model 5012, Thermo) equipped with a PM<sub>1</sub> size cut. The BC content of the aerosols was quantified by measuring the optical absorption of light at 630 nm by particles collected on a glass fiber filter, correcting for the scattering effects of the filter and particles (Petzold and Schönlinner, 2004). A mass specific absorption cross section of 6.6 m<sup>2</sup> g<sup>-1</sup> at 630 nm was used to convert the absorption measurement into a BC mass concentration. The instrument was run with 1 s time resolution.

### 2.3.4 Condensation particle counter (CPC)

A condensation particle counter (CPC, model 3022A, TSI) was used to measure the particle number concentration. Particles are guided through a chamber where the particles are enlarged by condensation of supersaturated butanol vapor into droplets of about 10 µm and are optically detected. The instrument has 50 % detection for 7 nm particles and 90 % detection for 15 nm particles. The maximum concentration that can be measured by the instrument is  $9.99 \times 10^6$  particles cm<sup>-3</sup>. The instrument was run with 5 s time resolution.

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### 2.3.5 Resonance enhanced multi-photon ionization time-of-flight mass spectrometer (REMPI-TOFMS)

Monocyclic aromatics and PAHs were measured by a REMPI (resonance enhanced multi-photon ionization) instrument coupled with a ToF mass spectrometer. This technique is a sensitive on-line method for the detection of gaseous aromatic compounds. A heated sampling system with PM filter (200 °C, 4 L min<sup>-1</sup>) was orthogonally connected to the tailpipe of the vehicles. The transfer line consisted of a deactivated silica capillary (length 1.5 m; inner diameter i.d. = 0.32 mm; *T* = 220 °C) by which a constant volume of exhaust was continuously drawn into the instrument (flow rate 8 mL min<sup>-1</sup>; residence time < 1 s). This enabled to analyze undiluted and non-aged exhaust.

The principle of REMPI-TOFMS was already described in detail (Mühlberger et al., 2001) therefore, only a brief description is given here: fundamental Nd:YAG laser pulses (1064 nm) are used for non-linear generation of UV light (266 nm). The UV pulses are directed into the ionization chamber straight underneath the sample gas inlet needle of the transfer line. Soft photoionization of the aromatics in the exhaust is induced in the TOFMS ion source by a two-photon absorption process, resonantly enhanced via an UV active electronic transition state (i.e. one photon resonance). The generated molecular ions are extracted into the flight tube of the reflectron TOFMS. Mass spectra are recorded via a transient recorder PC card (Acquires, Switzerland) and data processing is done with a custom-made LabView (National Instruments, USA) program.

Calibration and quantification is carried out by applying external gas standards (benzene, toluene, xylene). Other compounds were semi-quantified by taking into account the ratios of the known photoionization cross-section of the target compound and a calibration compound. The photoionization cross-section is a property that accounts for the compound's probability of being ionized under certain conditions and is constant for a fixed UV wavelength and photon density (Wilkerson et al., 1989). As a consequence, the ratio of two photoionization cross-sections is also constant. These ratios

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were determined beforehand under lab-conditions for a large number of compounds. In principle, 20 complete mass spectra per second can be recorded since a 20 Hz laser was used. In this work, on-line data was averaged to a time-resolution of 1 Hz.

### 2.3.6 High Resolution Fourier transform infrared spectrometer (HR-FTIR)

5 Small chain HC (saturated and unsaturated with less than 4 carbons), nitrogen species (NO, NO<sub>2</sub>, N<sub>2</sub>O, NH<sub>3</sub> and HCN), sulfur dioxide (SO<sub>2</sub>) as well as other oxygenated small compounds (formaldehyde, acetaldehyde, methanol) were monitored with a high resolution Fourier transform infrared spectrometer (HR-FTIR – MKS Multigas analyzer 2030, Wilmington, MA). The sampling point was placed directly at the tailpipe to mini-  
10 mize any compound wall-losses. Therefore, the HR-FTIR was connected to the same sampling system as the REMPI-TOFMS.

### 2.3.7 Regulated compound analyzers

Gas phase regulated compounds were measured in accordance with legislative methods for vehicle emissions using a non-dispersive infrared spectrometer (NDIR, CO and  
15 CO<sub>2</sub>), a chemiluminescence detector (CLD, NO<sub>x</sub>) and a heated flame ionization detector (HC, Hartmann & Braun in VELA1, HORIBA in VELA2 and AVL AMA 4000 advanced in VELA7).

## 2.4 Test protocols

Different driving cycles were conducted in accordance with the type of vehicles tested.  
20 Figure 2 shows the test cycles used during this work and the information about some parameters of the legislative cycles is reported in Table S3 (Barlow et al., 2009). All tests were performed in accordance with the related legislative regulation and following amendments (Directive 98/77/EC).

The tests with the HDDV(EIII) were carried out following the FIGE Cycle, the New  
25 European Driving Cycle (NEDC) and a steady state cycle. The FIGE cycle, from which

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the European Transient Cycle (ETC) has been derived, is based on road-type-specific driving patterns of HD and comprises three parts: the first part simulates the driving in urban areas, the second part on rural roads and the last one on motorways. The NEDC is used for emission type approval from passenger vehicles, but in this study it was also used to test the HDDV(EIII) and therefore, the maximum speed was limited to 90 km h<sup>-1</sup>. During the speed ramps with the HDDV(EIII) the speed increased from idle to 40, 60 and 90 km h<sup>-1</sup> and each speed was held constant for 5 min.

The tests with passenger vehicles were performed following the NEDC, steady state speed tests and speed ramps. Steady state tests and speed ramps were performed to characterize the vehicle emissions at different speeds. During the speed ramp tests, the speed was gradually increased from idle to 50, 90, 120 and 140 km h<sup>-1</sup>, then the same step-wise sequence was repeated backwards. Each steady-speed step lasted 2 min (acceleration or deceleration included). With the steady state tests, the speed increased from idle to 60, 90 and 120 km h<sup>-1</sup> and the first two speeds were held constant for 2.5 min, and the last two for 5 min.

The tests with the scooters were performed using the European legislative driving cycle for 2-stroke 50cc displacement engines (ECE47), a “short version” of the world-wide motorcycle test cycle (WMTC) and a steady state test. The aim of the WMTC is to harmonize the test protocols for motorcycles to establish a more realistic driving cycle. It consists of three different phases and in this study only the first part (phase 1) was taken into account, because phase 2 and phase 3 simulate extra-urban driving conditions for motorbikes and are not suitable for scooters. The speed in phase 1 was limited to 50 km h<sup>-1</sup> in order to align the test conditions with ECE47 and the scooters’ engine performances. In the WMTC a cold phase to warm up the engine is not considered, thus the WMTC was repeated twice in succession to compare the results with those from the ECE47 test. The first WMTC was considered as the “cold phase”, while the second WMTC was considered as the “hot phase”. The cold and hot phases in the ECE47 and in the WMTC were both investigated. In the WMTC there are more load changes than in the ECE47 test and the speed is less constant. The duration of the

modified WMTC is 1200 s, while the duration of ECE47 test is 896 s. The steady state test had a first part with no load, then the speed was gradually increased to 30 km h<sup>-1</sup> and to 50 km h<sup>-1</sup> and at the end the no-load condition was repeated. Each speed was held constant for 5 min.

## 2.5 Calculations

The data acquired by the various instruments were first corrected for the delay in time due to the different sampling points and flows. Signals from the instruments connected to the CVS (OA, BC and particle concentrations) were synchronized using the CO<sub>2</sub> concentration measured at both tailpipe and CVS (see Fig. 1) according to the subsequent methodology. The first step consisted in calculating the CO<sub>2</sub> concentration in the CVS based on the CO<sub>2</sub> concentration measured with the NDIR detector at the tailpipe:

$$[\text{CO}_2]_{\text{CVS},t} = \frac{([\text{CO}_2]_{\text{TP},t} \times F_{\text{exh},t}) + ([\text{CO}_2]_{\text{Back},t} \times F_{\text{dilution},t})}{F_{\text{CVS}}} \quad (1)$$

The instantaneous concentration of CO<sub>2</sub> at the tailpipe, in the dilution tunnel, and in the dilution air are [CO<sub>2</sub>]<sub>TP,t</sub>, [CO<sub>2</sub>]<sub>CVS,t</sub> and [CO<sub>2</sub>]<sub>Back,t</sub> respectively (homogeneous units). The background CO<sub>2</sub> concentrations in the dilution air were obtained by multiplying the measured concentrations after dilution with the dilution ratios calculated from CO<sub>2</sub> measurements at the tailpipe and after the dilution steps. For the calculation of the dilution ratios, background CO<sub>2</sub> was measured before the beginning of each experiment during 5 min in order to compute an averaged constant value for the whole test. The instantaneous flow rates of the exhaust, the dilution tunnel, and the dilution air are  $F_{\text{TP},t}$ ,  $F_{\text{CVS},t}$  and  $F_{\text{Back},t}$  respectively. The flow rates were estimated in the standard conditions for temperature and pressure ( $T$ : 273.15 K and  $P$ : 100 kPa).

The second step consisted in synchronizing the signals computed with Eq. (1), with the CO<sub>2</sub> concentration monitored with the NDIR analyzer connected after the ejector diluters (if used). The precise synchronization was done using the highest correlation coefficient of the linear regression between both signals. The phase delay estimated in



this way was applied to the signals of the other instruments connected at the CVS (OA, BC and particle concentrations). The slope of the linear regression was considered as the dilution factor DF (applied by the ejector diluters) between the CVS and the instruments. Once synchronized, the last step was the integration of the instrument signals over the cycle in order to estimate the emission factors:

$$EF_x = \frac{[\overline{x}] \times DF \times \overline{F_{CVS}} \times t}{D} \quad (2)$$

The emission factor of the compound “x” is  $EF_x$  in  $\text{mg km}^{-1}$ .  $[x]$  refers to the averaged concentration of the compound “x” in  $\text{mg m}^{-3}$  monitored by the instrument during the cycle or the sub-cycle. DF is the dilution ratio estimated previously. The flow rate of the dilution tunnel is  $F_{CVS}$  in  $\text{m}^3 \text{min}^{-1}$ , and the duration of the cycle or sub-cycle is  $t$  in min.  $D$  is the distance driven in km. The emission factor expressed in  $\text{mg m}^{-3}$  of exhaust results from the Eq. (2) by changing the distance in the denominator by the exhaust flow rate integrated over the cycle duration. Table S4 reports the emission factors for OA, BC and particle number. Data presented in this paper are not corrected for wall losses because they were negligible (< 5 % for 20 nm particles and < 1 % for 100 nm particles).

Only the average values are reported in the tables either when the relative standard deviation (RSD%) was below 15 % (for tests with three repetitions) or when the relative percent difference (RPD%) was below 15 % (for tests with two repetitions). Otherwise, values from all tests are reported together with the average values. In the Figures only the average values are reported.

### 3 Results

The results will be presented separately for the gaseous compounds and the particles.



### 3.1 Particle emissions

Black carbon (BC from MAAp), organic aerosol mass (OA from AMS), and particle number (PN from CPC) were measured from the CVS. Figure 3 shows the results for different speeds (PN, OA and BC), while Fig. S1 shows the results for all cycles (PN, OA, BC, OA/BC). Table S (OA, BC, PN, OA/BC) summarizes the results for all cycles.

#### 3.1.1 Organic aerosol mass emission

The organic aerosol mass emissions ranged between 5–40 mg km<sup>-1</sup> for the HDDV(EIII), 0.12–18 mg km<sup>-1</sup> for the diesel vehicles, < 0.02 mg km<sup>-1</sup> for the gasoline and 30–472 mg km<sup>-1</sup> for the scooters (Figs. 3, and S1, Table S4). It should be noted that OA emission factors do not only depend on the combustion concept, engine load and temperature, fuel and lubricant but also on many other parameters, like cold start, speed, accelerations, pre-history and dilution (Sharma et al., 2005; Lipsky and Robinson, 2006; Leskinen et al., 2007; Tang et al., 2007).

Extremely high emissions were observed for the two scooters, which use a mixture of gasoline fuel and lubricant oil. The huge OA emissions may be explained by unburned or incompletely combusted oil from the high scavenging losses of this type of vehicles. Scooter(E1), without an oxidative catalyst, showed higher emission of OA during the cold phases of both the ECE47 and the WMTC cycles, while Scooter(E2), equipped with an oxidative catalyst and a secondary air system showed the highest emission factors for OA (EF(OA)) during the hot phases of both ECE47 and WMTC. The different behavior of the emissions can be attributed mainly to the combustion strategy of the two scooters (Scooter(E1) was equipped with a carburetor while Scooter(E2) had a direct injection technology) and to the different exhaust temperature due to the secondary air injection system (Clairotte et al., 2012). The different exhaust gas temperatures, light-off temperatures of the catalysts (temperature at which the conversion of an exhaust gas component reaches 50 %) and efficiencies affected also the results.

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Similar conclusions were also drawn by other authors (e.g. Andersson et al., 2003; Ntziachristos et al., 2005).

In comparison with the scooters, the HDDV and the diesel vehicles had one order of magnitude lower OA emissions. It clearly demonstrates the efficiency of four stroke engines and the effect of the oxidation catalysts. Gasoline vehicles had 3 orders of magnitude lower emissions than the diesel vehicles. This has to do with the low concentration of particles (note that the OA refers to organic material on particles). The OA from the Euro 4 vehicle was 66 % (NEDC) and  $43 \pm 49$  % (speed ramp, average value  $\pm 1$  standard deviation) lower than from the Euro 3 vehicle (both with 10 ppm sulfur in the fuel). This result may be vehicle specific (engine calibration and oxidation catalyst) and cannot necessarily be extended to other vehicles.

With 10 % biodiesel blend (Diesel-P(E4)) and with 30 % biodiesel blend (Diesel-V(E3)) a reduction in the OA emissions was observed: reduction by 22 % and 21 % during the NEDC cycle for Diesel-P(E4) and the Diesel-V(E3), respectively, and by  $40 \pm 15$  % for the speed ramp with Diesel-V(E3). The reduction of the sulfur fuel content from 50 to 10 ppm did not affect the OA emissions, as expected.

In general, the highest emission factors were obtained at higher speeds for the diesel and gasoline vehicles ( $90 \text{ km h}^{-1}$  for the HDDV(EIII) and at  $140 \text{ km h}^{-1}$  for the diesel light duty vehicles), while for the legislative driving cycles the highest EF(OA) among the four-wheel vehicles were observed during the urban part of the cycles (UDC for the NEDC cycle and urban for the ETC cycle) characterized by low speeds. High OA emissions at low speeds can be explained by the lower conversion of the catalyst due to the lower exhaust gas temperatures. This is especially true for the cold start cycles and for the first seconds of the cycle where the catalyst hasn't reached its light-off temperature. The effect is more profound at accelerations where the combustion is incomplete. At high speeds desorption and/or pyrolysis of organic material deposited in the vehicle tailpipe and aftertreatment device or the transfer hose to the CVS could explain the high OA emissions (Maricq et al., 1999). The tailpipe and the aftertreatment

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devices have been found to store substantial amounts of particles which are emitted at accelerations or high speeds (Andrews et al., 2001).

For the HDDV(EIII) (no aftertreatment device) the first acceleration in the UDC part of the NEDC and in the urban part of the ETC yielded a peak in the OA concentration that was 440 and 320 times higher than the average concentration for the remaining UDC and Urban part of the cycles, respectively. 70 % (NEDC) and 17 % (ETC) of total organic emissions during the whole cycles were produced with this first acceleration. In the last part of the ETC cycle (Motorway) both the higher average speed ( $84.4 \text{ km h}^{-1}$ ) and the lower dilution ratio can be the reasons for the higher OA emission compared to the second part of the cycle (Rural,  $69.3 \text{ km h}^{-1}$ ) as both phases have a similar number of accelerations per km.

There are two possible reasons for the high OA at high speeds: either due to desorption from the vehicle and sampling system pipes or due to lower dilution ratios in the dilution tunnel. Concerning the first explanation, high OA can be found at high speeds is desorption and/or pyrolysis of organic material deposited in the vehicle tailpipe and aftertreatment device or the transfer hose to the CVS (Maricq et al., 1999).

Concerning the second explanation, it has been shown that the OA mass measurement can be affected by the dilution of the exhaust. For example,  $\text{PM}_{2.5}$  mass emitted by a diesel power generator with no aftertreatment devices can decrease by 50 % when the dilution ratio is increased from 20 : 1 to 350 : 1 (Lipsky and Robinson, 2006). This mass reduction has been associated with semi-volatile organic compounds (SVOCs) that shift to the gas phase with increasing dilution to maintain thermodynamic equilibrium (Lipsky and Robinson, 2006). In the case of the HDDV(EIII), during the high speed part of the cycles the dilution ratios in the dilution tunnel were lower than those associated to the low speed parts. For instance, the dilution ratio in the last part of the FIGE cycle (motorway) was 103 compared to the second part of the cycle (rural) where it was 158 (for the UDC and the EUDC parts of the NEDC the dilution ratios were 330 and 166, respectively). Moreover, for the steady state test with the HDDV(EIII) the av-

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average dilution ratio for the 40 and 60 km h<sup>-1</sup> speeds were 210, while for the 90 km h<sup>-1</sup> the dilution ratio was 98.

To evaluate the effect of the dilution on the OA concentration, two speed ramp tests with Diesel-V(E3) were performed with different dilution ratios using either only one or two ejector diluters. With one ejector diluter after the CVS, the range of the final dilution ratios was 34–115, while with two ejector diluters the range was 473–1600, which included also atmospherically relevant dilution ratios (> 1000). Constant engine conditions were observed within the two different speed ramps. A 14-fold difference in the dilution ratio between the two tests with the same vehicle did not affect the OA concentration measurements at the tailpipe probably because either the 14-fold difference in the dilution ratios was not enough to have an influence on the volatility of the SVOCs or more time was needed to reach thermodynamic equilibrium. For all speeds the ratio of the OA concentrations from the two experiments was ~ 1 with the exception of the 140 km h<sup>-1</sup> speed where the ratio was ~ 2 but with higher OA concentration for higher dilution, in contrast to the expectation. Two speed ramp tests with the Scooter(E2) were also performed with different dilution ratios (~ 250 ± 50 when one diluter was used, 4000 ± 500 with two) and also in this case the OA concentrations at the tailpipe were not affected by differences in the final dilution and the ratio was ~ 1 for both speeds. These results are in agreement with other researchers who found that for residence times in the order of 1 s, the primary dilution (in the CVS in our case) is the most important in the adsorption/condensation/nucleation of the volatile precursors (e.g. Khalek et al., 1999; Giechaskiel et al., 2009).

### 3.1.2 Black carbon mass emission

With the speed ramps and steady state tests the EF(BC) was in the range 59–208 mg km<sup>-1</sup> for the HDDV(EIII), 2.8–113 mg km<sup>-1</sup> for the diesel vehicles, 0.14–1.15 mg km<sup>-1</sup> for the scooters and 0.01–0.30 mg km<sup>-1</sup> for the gasoline vehicle (Figs. 3 and S1, Table S4). For the regulated test cycles (ETC, NEDC, and hot ECE-47

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for Heavy-duty vehicle, light-duty vehicle, and scooters, respectively) the EF(BC) was  $168 \text{ mg km}^{-1}$  for the HDDV(EIII),  $14\text{--}36 \text{ mg km}^{-1}$  for the diesel vehicles,  $0.23 \text{ mg km}^{-1}$  for the gasoline vehicle, and  $1.1\text{--}2.6 \text{ mg km}^{-1}$  for the scooters. Thus, the HDDV(EIII) was the main emitter of BC during the tests with both legislative and unregulated driving cycles.

One striking finding is that for diesel vehicles at  $140 \text{ km h}^{-1}$ , a speed higher than the maximum during the cycles, the BC emissions are often extremely high due to the very low air to fuel ratio and incomplete combustion. Similarly, for the HDDV(EIII) the emissions at  $90 \text{ km h}^{-1}$  (its maximum speed) were the highest. In general, the emissions at steady state were lower than during the cycles indicating that a high contribution to BC originates from the acceleration of the vehicles. For both scooters the BC emissions were higher ( $62 \pm 41 \%$ ) during the cold phases of the cycles (ECE47 and WMTC).

With 10 % biodiesel (Euro 4 vehicle) the EF(BC) was reduced by 20 % and with 30 % biodiesel (Euro 3 vehicle) the EF(BC) was reduced by 41 % (NEDC),  $26 \pm 15 \%$  (speed ramp) and  $45 \pm 6 \%$  (steady state). Similar reductions have been found by other researchers (e.g. Mayer et al., 2005).

### 3.1.3 OA to BC ratios

The OA/BC ratios of the diesel vehicles during the steady state and speed ramp tests were below 0.2 with only a few exceptions, but always remaining below 1. These ratios are well within the range of values found in the literature, typically determined from filter measurements (Geller et al., 2006; Ntziachristos et al., 2004). The OA/BC ratios from diesel vehicles were always higher in the UDC part of the NEDC cycle, and in the urban part of the ETC cycle. Values up to  $\sim 0.25$  were obtained in the UDC part, while ratios below 0.1 were found in the EUDC part. The lower ratios for the second part of the cycles are due to the higher decrease of the OA compared to the BC. For all experiments with the diesel vehicles and the HDDV, the OA emissions in the EUDC part of the cycle was on average  $69 \pm 15 \%$  lower than the UDC part, while for the BC emissions the reduction was non-significant ( $8 \pm 23 \%$ ). As explained previously the

cold start results in high OA emissions which significantly decrease as the catalyst reaches its light off temperature (Katare et al., 2007). OA/BC values below 0.09 were found for the gasoline vehicle. For the gasoline vehicle the OA/BC ratios during the first and the second part of the NEDC cycle were comparable. This is in agreement with other researchers who found similar fractions of OA and BC for gasoline vehicles (e.g. Kirchstetter et al., 1999; Grieshop et al., 2006).

For the scooters the OA/BC values were between 27 and 725 (idle not included, Fig. S1 and Table S4). For the ECE47 and WMTC tests the OA/BC values measured from the scooters were 115–142. For the Scooter(E1) the cold phases of the ECE47 and WMTC cycles had the highest OA/BC ratios, while for the Scooter(E2) the highest values were found during the hot phases. These ratios are within the range found by other researchers as well and confirm that the emitted aerosol contains a large amount of non-refractory material.

### 3.1.4 Particle number emissions

The particle number emissions of the HDDV(EIII) and diesel light duty vehicles (LDV) were in the order of  $10^{14} \text{ km}^{-1}$ . The emissions of the gasoline vehicles were in the order of  $10^{12} \text{ km}^{-1}$ , while those of the scooters were in the order of  $10^{13} \text{ km}^{-1}$  (Figs. 3 and S1, Table S4).

Typical size distributions from vehicle emissions are bimodal with a usually volatile nucleation mode (diameter < 30 nm) and an accumulation mode (median diameter between 50 and 100 nm) (Kittelson, 1998). The nucleation mode, similarly to OA, is sensitive to many parameters like engine, fuel, operation mode, sampling conditions, etc., while the accumulation mode generally depends mainly on the engine operating mode. Particle number emissions in this study were determined with a CPC connected to the CVS. Total (volatile and non-volatile) particles > 7 nm were measured and reported.

For the HDDV(EIII) the increase of the emissions with increasing speed was correlated with the increase of the accumulation mode, since no nucleation mode appeared with this vehicle. The PN emissions behavior was thus similar to the BC behavior (see

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Table S4). Diesel vehicles in addition showed high PN emissions at the beginning of the cycle and during the accelerations. A cold start is generally associated with a nucleation mode due to the low hydrocarbons oxidation efficiency of the catalyst. The accelerations also result in nucleation mode particles due to the low available surface for condensation of the volatile species. A speed dependence of EF(PN) was already found in other studies (e.g Kristensson et al., 2004; Imhof et al., 2005) for both HDV and LDV. More details about these topics can be found in Giechaskiel et al. (2007b, 2010).

At 50 and 90 km h<sup>-1</sup> speeds during the speed ramp test the particle emissions were higher when the speed sequence was repeated backwards from 140 km h<sup>-1</sup> to idle than for the sequence from idle to 140 km h<sup>-1</sup> for diesel vehicles while the opposite was observed for gasoline cars. The emissions of the diesel cars are connected with the exhaust temperature which enhances the oxidation of SO<sub>2</sub> to SO<sub>3</sub> in the DOC and the subsequent conversion to sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) during dilution and sampling. The sulfuric acid acts as condensation nuclei, enhancing number concentrations (Burtscher, 2005; Kozak and Jerzy, 2005; Scheer et al., 2005; Schneider et al., 2005, 2006; Giechaskiel et al., 2007b).

At speeds lower than 140 km h<sup>-1</sup>, more than 95 % of the total mass (sum of the non-refractory species measured by the HR-ToF-AMS and BC) from diesel passenger vehicles was made only of BC and OA, while at 140 km h<sup>-1</sup> (including the acceleration from 120 km h<sup>-1</sup> to 140 km h<sup>-1</sup>) a sharp increase in particle-associated sulfate was measured (in these cases, sulfate represented up to 70 % of the total PM). A tail in the sulfate concentration was then present when the speed was decreased until idle (Giechaskiel et al., 2010). The addition of either 10 % or 30 % biodiesel most of the times lowered the particle number emissions for diesel vehicles even if for some single speeds the particle number was higher (50 and 90 km h<sup>-1</sup> speeds with 30 % biodiesel). In general, many authors have reported an increase in particle number emission in the nucleation mode when biodiesel blends were used but the very low sulfur content of

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biodiesel fuels can also be an explanation for the decrease in nanoparticle concentrations (Lapuerta et al., 2008 and references therein).

For the Scooter(E2) with the SAS and oxidation catalyst, the particle emission factors were 3.4–5.0 times higher than for the Scooter(E1) with oxidation catalyst only (steady state and hot phases of ECE-47 and WMTC cycles). Both but especially Scooter(E1) had higher emissions during the cold phases of the ECE-47 and WMTC cycles in agreement with other studies (e.g. Andersson et al., 2003).

It should be mentioned that some particle number measurements were conducted according to the new UNECE Regulation 83 for light duty vehicles (i.e. only the non-volatile particle concentration was measured, using hot dilution and an evaporation tube at 300 °C) (EU, 2008). The results showed that the non-volatile particle number concentration was similar to the total concentration (i.e., no nucleation mode particles existed) at low speeds. However, at high speeds, due to the formation of a nucleation mode, the non-volatile particles were < 10 % of the total concentration. More details can be found in Giechaskiel et al. (2010).

## 3.2 Trace gas emissions

### 3.2.1 Emissions of regulated gaseous compounds and CO<sub>2</sub>

The HC emissions from the gasoline vehicle were above the limit of 0.1 g km<sup>-1</sup> (+15 %) defined by regulations for Euro 4 vehicles, and also the sum of HC plus NO<sub>x</sub> from the Diesel-P(E3) and the Diesel-P(E4) were above the limit of 0.56 g km<sup>-1</sup> (+36 %) and 0.3 g km<sup>-1</sup> (+70 %) defined for the Euro 3 and the Euro 4 diesel vehicles, respectively (Fig. 4 and Table S5). The gasoline vehicle complied with the Euro 4 regulation for NO<sub>x</sub>, while only the Diesel-V(E3) with reference diesel fuel and 30 % biodiesel blended complied with the Euro 3 emission standard for NO<sub>x</sub>. The NO<sub>x</sub> emissions from the Diesel-P(E3) and Diesel-P(E4) were above the limits (0.5 g km<sup>-1</sup> for Euro 3 and 0.25 g km<sup>-1</sup> for Euro 4). The NO<sub>x</sub> emissions of gasoline and diesel passenger vehicles were 6–10 times lower than the emissions from the HDDV(EIII) over the entire NEDC cycle. The



NO<sub>x</sub> emission was reduced by a factor of 1.7 from Diesel-P(E3) to Diesel-P(E4). With biodiesel the NO<sub>x</sub> emission increased only by 5 % compared to the standard diesel fuel.

In accordance with the European legislation, only the hot phase of the ECE47 was taken into account to define if the emissions of NO<sub>x</sub> plus HC from the scooters complied with the limits. The EF(NO<sub>x</sub>+HC) for Scooter(E1) were below the emission limit of 3 g km<sup>-1</sup>, while for Scooter(E2) the emission was 1.2–1.3 times higher than the limit (1.2 g km<sup>-1</sup>). Among the various vehicles, the scooters were those with the highest emissions of HC. Considering the cycles used for emission homologations of passenger vehicles and scooters (NEDC, hot phase from ECE47) and the NEDC also for the HDDV(EIII) (the NEDC was used for the HDDV(EIII) for comparison even though this is not used for the homologation of trucks), the EF(HC) for scooters were 11–36 times higher than for the other vehicles. The results from the Scooter(E2) are within the range of values found with other Euro 2 scooters (0.10–5.55 g km<sup>-1</sup>, Adam et al., 2010). With 30 % biodiesel the EF(HC) decreased by 15 % compared to the same vehicle powered with standard diesel. The lowest emission of HC from the HDDV(EIII) could be explained by the higher engine temperature, which resulted in a more complete fuel combustion.

The gasoline vehicle complied with the Euro 4 regulation for NO<sub>x</sub>, while only the Diesel-V(E3) with reference diesel fuel and 30 % biodiesel blended complied with the Euro 3 emission standard for NO<sub>x</sub>. The NO<sub>x</sub> emissions from the Diesel-P(E3) and the Diesel-P(E4) were above the limits (0.5 g km<sup>-1</sup> for Euro 3 (+31 %) and 0.25 (+57 %) for Euro 4). The NO<sub>x</sub> emissions of gasoline and diesel passenger vehicles were 6–10 times lower than the emissions from the HDDV(EIII) over the entire NEDC cycle. With biodiesel the NO<sub>x</sub> emission increased only by 5 % compared to the standard diesel fuel. The EF(NO<sub>x</sub>) of the Scooter(E2) was 14 and 18 fold higher than of the Scooter(E1) for the entire ECE47 and WMTC cycles, respectively. The EF(NO<sub>x</sub>) for the Scooter(E2) from the cold (0.35 g km<sup>-1</sup>) and hot (0.39 g km<sup>-1</sup>) phase of the ECE47 were higher than the values (< 0.20 g km<sup>-1</sup>) measured from other Euro 2 scooters (Adam et al., 2010).

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With 30 % biodiesel the EF(HC) decreased by 15 % compared to the same vehicle powered with standard diesel. The lowest emission of HC from the HDDV(EIII) could be explained by the higher engine temperature, which provided a more complete fuel combustion.

The emissions of CO were below the limits for the Diesel-P(E3) and Diesel-P(E4), and above for the Diesel-V(E3) (+108 %) and Gasoline-P(E4) (+36 %). Using biodiesel the EF(CO) decreased by 15 % but the value was still above the limit. A decrease in CO emissions when biodiesel was added to the diesel has been considered a general trend, partially explained by the enhancement in the complete combustion due to the additional oxygen content in the fuel (Lapuerta et al., 2008 and references therein). The EF(CO) of the HDDV(EIII) from the NEDC and the ETC cycles were higher than the emissions from the other passenger vehicles but the Scooter(E1) featured the highest EF(CO). Most of the CO emissions appeared during the start up of the engines when the low temperature of the engines did not allow for a more complete combustion and oxidation in the catalysts. Reductions in EF(CO) up to 99 % were measured between the urban part and the extra-urban part of the NEDC cycle. Only for the Scooter(E1) the EF(CO) increased from the cold phases to the hot phases of the ECE47 and WMTC cycles. The EF(CO) for the Scooter(E2) are in good agreement with the values measured from other Euro 2 scooters (Adam et al., 2010). In general, the emissions of HC and CO were higher during the coldest phases of the cycles (UDC in the NEDC, cold phase in ECE47, etc) and this behavior reflects the well-known occurrence of incomplete combustion while the engine and catalytic converter have not warmed up yet. The different results from the two scooters, with higher emissions of HC and CO for Scooter(E1) and higher emissions of NO<sub>x</sub> for Scooter(E2), could be related to the older oxidative catalyst of the Scooter(E1) and the SAS of the Scooter(E2). The presence of SAS together with an efficient catalyst could contribute to the reduction of the HC and CO and to the increase of NO<sub>x</sub> for Scooter(E2).

The HDDV(EIII) showed the highest emissions of CO<sub>2</sub>, followed by passenger vehicles and scooters. The emission from the HDDV(EIII) was on average (total NEDC and

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ETC cycles) 2.7 times higher than the emissions from passenger vehicles and 11 times higher than the emissions from scooters. The effect of biodiesel the EF(CO<sub>2</sub>) over the entire NEDC cycle was not noticeable.

### 3.2.2 Unregulated trace gas emissions

5 The emissions of a selection of unregulated gaseous compounds, such as nitrogen-containing compounds (NO, NO<sub>2</sub>, N<sub>2</sub>O, NH<sub>3</sub>, HCN), small oxygenated organic compounds (formaldehyde, acetaldehyde), SO<sub>2</sub> and methane for the various tests are shown in Fig. 5 and reported in Table S6. The nitrogen compounds had in general higher emission factors than the other compounds with the only exception of  
10 Scooter(E1) where the CH<sub>4</sub> emission factor was highest. Within the nitrogen compounds, the NO emissions were the most important for all vehicles (up to 96 % of the total nitrogen-containing compounds). The HDDV(EIII) had the highest EF(NO), being 5–233 higher than the emissions of the other vehicles. The contribution of NO to NO<sub>x</sub> was 85 % for the HDDV(EIII) (average value from ETC and NEDC), 59 % for the Diesel-V(E3)\_10 ppm, 55 % for the Diesel-V(E3)\_30 %Bio, more than 99 % for the Gasoline-P(E4), and more than 98 % for the scooters. In Alvarez et al. (2008), NO was  
15 75 % of the NO<sub>x</sub> emitted from diesel vehicles without particle filter, while for Euro 4 gasoline vehicles the NO<sub>x</sub> emissions almost entirely consisted of NO. The formation of NO<sub>2</sub> in diesel vehicles is due to the presence of an oxidation catalyst, and the relative contribution to NO<sub>x</sub> increases at higher temperature when the light-off of the DOC is reached (Katare et al., 2007). NO<sub>2</sub> emissions are a greater concern than NO emissions because NO<sub>2</sub> is toxic and is a direct precursor for ozone formation. NO<sub>2</sub> concentrations remain high and still surpass the legal thresholds in various areas in Europe in spite of substantial NO<sub>x</sub> reductions, due to the shift from NO to NO<sub>2</sub> emissions (Zielinska,  
20 2005; Alvarez et al., 2008; Grice et al., 2009; H.E.I., 2010). Gasoline-P(E4) with regular fuel and Scooter(E1) had the highest emission factors of NH<sub>3</sub> (4.2–6.5 mg km<sup>-1</sup>; 19–31 % of the total nitrogen-containing compounds) while for the other vehicles the relative contribution was below 0.015 %. The gasoline vehicle featured high EF(NH<sub>3</sub>)  
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because in the gasoline vehicles  $\text{NH}_3$  is produced in the TWC under reducing conditions when the light-off temperature is reached. The formation mechanism involves NO and  $\text{H}_2$ . NO is generated by the oxidation of  $\text{N}_2$  during combustion whereas  $\text{H}_2$  is mainly produced in the catalyst during the water gas shift reaction of CO (Bradow et al., 1977; Barbier et al., 1994). The emissions of  $\text{NH}_3$  can also dominate over those of NO during the cold start in particular at low ambient temperature (Heeb et al., 2008; Clairotte et al., 2012a). The lambda value showed a rich combustion in Scooter(E1) and with these conditions  $\text{NH}_3$  production was favored (Whittington et al., 1995; Czerwinski et al., 2010).

The Scooter(E1) and the HDDV(EIII) had the highest emissions of HCN ( $1.0\text{--}1.2\text{ mg km}^{-1}$ ), comprising  $5.2\text{--}6.5\%$  of the total nitrogen-containing compounds for the Scooter(E1) and only  $0.04\text{--}0.06\%$  for the HDDV(EIII). HCN is a toxic compound that is produced from  $\text{NO}_x$  by reduction reactions (Liu et al., 1999; Baum et al., 2007). The Diesel-V(E3), with regular fuel and with biodiesel, had the highest emission factors of  $\text{N}_2\text{O}$  ( $13\text{--}53\text{ mg km}^{-1}$ ;  $4.2\text{--}5.6\%$  of the total nitrogen compounds). For the other vehicles the values were lower than  $2.5\text{ mg km}^{-1}$ .

The emission of the sum of formaldehyde and acetaldehyde was  $4.28\text{--}159\text{ mg km}^{-1}$  for the Diesel-V(E3),  $65\text{ mg km}^{-1}$  for the Scooter(E2) (average between the two cycles),  $50\text{ mg km}^{-1}$  for the HDDV(EIII) (average between the two cycles),  $41\text{ mg km}^{-1}$  for the Scooter(E1) (average between the two cycles),  $38\text{ mg km}^{-1}$  for the Diesel-V(E3)\_30 % Bio, and  $1.3\text{ mg km}^{-1}$  for the Gasoline-P(E4). The carbonyl emission rates of diesel vehicles were found to be higher than those of gasoline vehicles. In 2006, diesel/gasoline emission ratios of 7.9 and 6.3 for formaldehyde and acetaldehyde, respectively were measured in the Caldecott tunnel (USA) (Ban-Weiss et al., 2008). Considering only the NEDC tests with the conventional diesel and gasoline fuels, the average diesel/gasoline emission ratios from this work were 35–136 and 26–90 for HCHO and  $\text{CH}_3\text{COH}$ , which confirms the importance of diesel vehicles in the emissions of carbonyl compounds. The HDDV(EIII) was the vehicle with the highest

EF(SO<sub>2</sub>) (63 mg km<sup>-1</sup>), while the Scooter(E1) featured the highest emission of CH<sub>4</sub> (71 mg km<sup>-1</sup>).

### 3.2.3 Monocyclic and polycyclic aromatic hydrocarbon emissions

The measurements of the gaseous monocyclic and polycyclic aromatic hydrocarbons comprised 13 substituted and non-substituted compounds (Fig. 6 and Table S7). The scooters featured the highest emissions of aromatic compounds (99–211 mg km<sup>-1</sup>), followed by the gasoline vehicle (47 mg km<sup>-1</sup>) and the diesel vehicle with the HDDV(EIII) (5.3–10 mg km<sup>-1</sup>).

More than 99 % of the total hydrocarbons from the scooters and the gasoline vehicle were made of benzene plus substituted benzenes, 87 % for the Diesel-V(E3) and 56 % from the HDDV(EIII). Around 7.1–13 % and 29–43 % of the total emissions were due to naphthalene and substituted naphthalene for the Diesel-V(E3) and the HDDV(EIII), respectively. The contribution of PAHs with 3 and 4 rings to the total emissions was less than 1.9 % for all vehicles. The emissions of mono-aromatic compounds (MAHs) from the Gasoline-P(E4) was 8.3–12 and 5.0–6.9 times higher than the emissions from the HDDV(EIII) and Diesel-V(E3) vehicle, respectively, while the emissions of PAHs from the HDDV(EIII) and Diesel-V(E3) were 4.0–8.0 and 1.8–2.6 times higher than the gasoline vehicle. Previous chassis dynamometer tests with 13 gasoline and 17 diesel vehicles have shown that on average the emissions of MAHs from gasoline vehicles are 6 times higher than the emissions from diesel vehicles (Caplain et al., 2006). The HDDV(EIII) had the highest emission of PAHs (1.6–3.2 mg km<sup>-1</sup>, NEDC and ETC cycles), followed by the scooters (0.93–1.5 mg km<sup>-1</sup>, Scooter(E1) and Scooter(E2) for ECE47 and WMTC cycles), and for the other vehicles the emission was below 1.0 mg km<sup>-1</sup>.

The benzene/toluene ratio is sometimes used as photochemical clock for urban plumes traveling away from traffic sources because toluene is five times as reactive as benzene with OH radicals; therefore, a change in the ratio is observed dur-



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ing the aging of the plume (Gelencser et al., 1997; Jordan et al., 2009). The average benzene/toluene values measured for the primary emissions were 3.3–3.9 for the HDDV(EIII), 2.3–2.6 for Diesel-V(E3) vehicle (3.8 for Diesel-V(E3) with biodiesel), 0.45 for the gasoline vehicle and 0.24–0.90 for the scooters. Thus, this ratio can not only vary with plume age but also with the vehicle types.

With biodiesel the total aromatic emissions from the Diesel-V(E3) decreased by 37–51 %. The emissions of MAHs and PAHs decreased by 34–52 % and 37–56 %, respectively. Experiments conducted in a six-cylinder heavy-duty diesel engine fuelled with pure diesel and biodiesel blends (2 %, B2; 5 %, B5 and 20 %, B20) have also shown a reduction in the emissions of MAHs (4.2 %, B2; 8.2 %, B5; 21.1 %, B20) and of PAHs (2.7 %, B2; 6.3 %, B5; 17.2 %, B20) (Corrêa and Arbilla, 2006). The main sources of aromatic compounds from vehicles are pyrosynthesis processes from small unsaturated carbonaceous molecules and unburned or partially decomposed aromatics from fuels (Lima et al., 2005). In particular, the emissions of aromatic compounds are directly correlated to their initial concentration in the fuel (Lima et al., 2005). Using biodiesel the emissions of aromatics were thus reduced because of the lower aromatic content in the biodiesel blend. Also the excess of air might have produced a more efficient combustion of aromatics (Lima et al., 2005).

The combustion temperature of the engines affects the amount of alkylated aromatics in exhaust (Lima et al., 2005). As the temperature increases, the alkyl-substituted-to-parent compound ratio decreases. The reason for this is the higher thermodynamic stability of the aromatic carbon skeletons (parent compounds) in comparison to the substituted derivative. The ratios of the emission factors of substituted aromatics over the emissions of the parent compounds are reported in Table 3. The two scooters were the vehicles with the highest emissions of substituted-benzene.

## 4 Conclusions

The emission factors of gas phase and particle-associated regulated and unregulated species from seven different vehicles circulating in Europe were presented. The aim of this work was to improve the knowledge about the emission factors from the various vehicles tested with legislative European driving cycles, steady state cycles and speed ramp sequences using standard gasoline and diesel fuels but also rapeseed methyl ester biodiesel blend.

Diesel vehicles, without particle filters, featured the highest emissions of particle number, followed by scooters and then gasoline vehicles. The particles from diesel vehicles were mainly made of BC with a low fraction of OA, while the particles from the scooters were mainly OA. Scooters were characterized by high emissions factors for OA, which were orders of magnitude higher than for the other vehicles.

Higher emissions of particle number and OA were observed at higher speeds. However, cold start emissions and accelerations were the main contributors to the high emissions of particle number, BC and OA.

The heavy duty diesel vehicle featured the highest NO<sub>x</sub> emissions, while the gasoline vehicle had the highest emissions of NH<sub>3</sub> due to the reducing conditions in the three-way catalyst. The NO emissions were the most important for all vehicles within the nitrogen compounds analyzed.

The scooters featured the highest emissions for HC and aromatic compounds due to the unburned and partially burned gasoline and lubricant oil mixture. Scooters, and in general two-stroke engines, are important for urban transport in many cities in Europe and even more in Asian megacities congested by traffic. Thus, the findings of this paper confirm that powered two-wheelers are a potentially important source of enhanced pollution in urban areas (PM, PAHs) due to the delay in more stringent emission regulations.

The measured gaseous monocyclic and polycyclic aromatic hydrocarbons from all vehicles were dominated by aromatic mono- and bicyclic compounds. The gasoline

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vehicle had higher emissions of mono-aromatic compounds than diesel vehicles, while the diesel vehicles featured higher emission of polycyclic aromatic hydrocarbons than the gasoline vehicle.

With biodiesel the emission factors of OA, HC, BC and total aromatics were lower than those from the regular fuel, confirming biodiesel as a valid alternative fuel to reduce diesel engine exhaust emissions.

The results presented in this paper can be used to compare or check emissions and emission ratios in emission inventories for non-regulated compounds used in chemical transport models. Also ambient concentration ratios can be compared with the presented results. Since the number of tested vehicles and the number of repetition of each test for each vehicle were rather low, more measurements of unregulated compounds including vehicles of the latest generation are needed to provide a more reliable basis for emission estimates for current and future vehicle fleets in Europe.

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**Table 1.** Technical characteristics of the vehicles and fuels tested with each vehicle.

Vehicle type	Heavy duty truck	Light duty vehicle	Passenger transport	Light duty vehicle	Light duty vehicle	Motorcycle	Motorcycle
Vehicle code (for Figures)	HDDV(EIII) (HDDV(EIII))	Diesel-P(E3) (D-P(E3))	Diesel-V(E3) (D-V(E3))	Diesel-P(E4) (D-P(E4))	Gasoline-P(E4) (G-P(E4))	Scooter(E1) (S(E1))	Scooter(E2) (S(E2))
Data production	15/03/2002	12/02/2002	19/10/2006	25/09/2006	10/06/2008	26/10/2007	22/04/2004
Km start program	140 000	48 923	15 132	68 141	29 707	7716	5574
Vehicle mass – [kg]	8000	1305	1975	1105	1182	90	110
Combustion type	Compression Ignition	Compression Ignition	Compression Ignition	Compression Ignition	Spark Ignition	2-stroke	2-stroke
Engine Supply	T-DI	T-DI	DI-common rail	DI-common rail	Gasoline	Carburetor Gasoline + Oil	Electronic DI Gasoline + Oil
Engine capacity cm <sup>3</sup>	5880	1995	2179	1248	1596	50	50
Max Power @ rpm	176 kW – 3500 rpm	74 kW – 3250 rpm	74 kW – 4000 rpm	55 kW – 3000 rpm	85 kW – 4500 rpm	2.8 kW – 4875 rpm	(2.8 kW)
Aftertreatment	None	DOC	DOC	DOC	TWC	Oxi-cat	Oxi-cat + SAS
EU Emission Stand	1999/96/CE EuroIII	Swiss emission standard [FTP75] Euro3 equivalent	2001/1/CE Euro3	2003/76/CE B Euro4	2003/76/CE B Euro4	97/24/CE Euro 1	97/27/5/CE Euro2
Fuels used (sulfur)	D 10 ppm	D 10 or 50 ppm	D 10 or 10+30 % Bio	D 10 or 10+10 % Bio	G	G+2 % lube	G+2 % lube

T-DI = Turbo Direct Injection; DI = Direct Injection; DOC = Diesel Oxidation Catalyst; TWC = Three Way Catalyst; SAS = Secondary Air System, D = Diesel fuel, G = Gasoline fuel; Bio = Biodiesel

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**Table 2.** List of the investigated compounds.

Gas phase		Particulate phase
<b>FT-IR</b>	<b>REMPI-TOFMS</b>	<b>HR-ToF-AMS</b>
NO	Benzene	Organic aerosol
NO <sub>2</sub>	Toluene	Sulfate
N <sub>2</sub> O	C2-Benzene	<b>MAAP</b>
NH <sub>3</sub>	C3-Benzene	Black carbon
HCN	Napthalene	<b>CPC</b>
HCHO	Methyl-Naphthalene	Particle number
CH <sub>3</sub> CHO	C2-Naphthalene	
SO <sub>2</sub>	C3-Naphthalene	
CH <sub>4</sub>	Phenanthrene	
<b>NDIR</b>	Methyl-Phenanthrene	
CO	C2-Phenanthrene	
CO <sub>2</sub>	C3-Phenanthrene	
<b>FID</b>	Pyrene	
THC		
<b>CLA</b>		
NO <sub>x</sub>		

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**Table 3.** Emission factors of substituted aromatics over the emission factors of the parent compounds.

Vehicles	Cycles	Sub-BEN/BEN	Sub-NAP/NAP	Sub-PHE/PHE
HDDV(EIII)	NEDC and ETC	1.1–1.4	3.4–3.9	1.6–2.1
Diesel-(E3)_10 ppm	NEDC	0.84–2.3	0.75–1.1	1.3–3.5
Diesel-V(E3)_30 %Bio	NEDC	0.52	1.2	1.7
Gasoline-P(E4)	NEDC	6.3	0.96	0.28
Scooter(E1)	ECE47 and WMTC	8.5–8.6	2.2–2.4	4.0
Scooter(E2)	ECE47 and WMTC	4.0–15	0.13–0.24	0.99–2.3

Sub = substituted; BEN = benzene; NAP = naphthalene; PHE = phenanthrene

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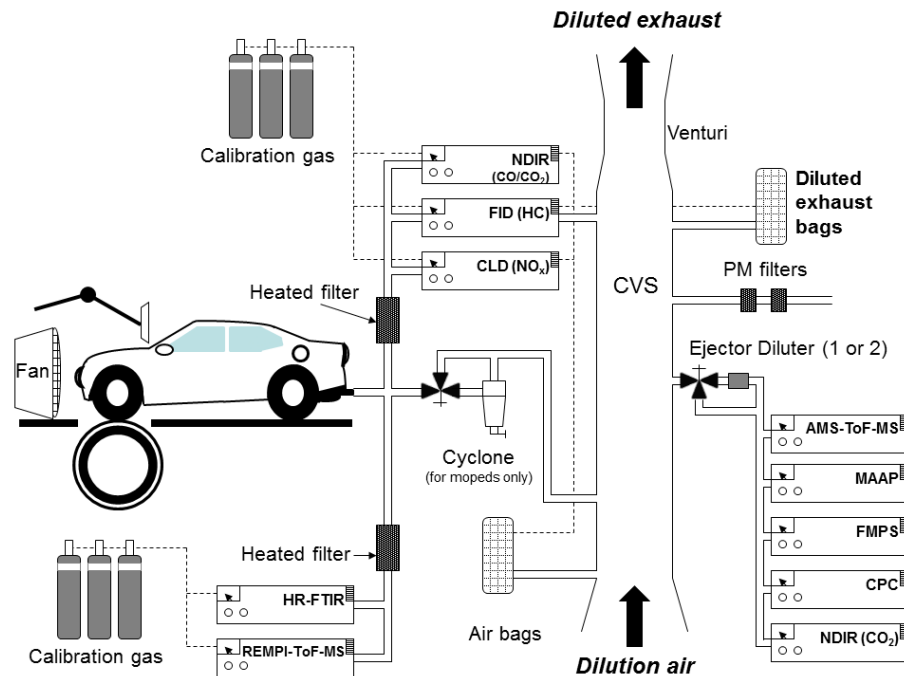
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**Figure 1.** General schematic diagram of the experimental setup (Courtesy of M. Clairotte, JRC).

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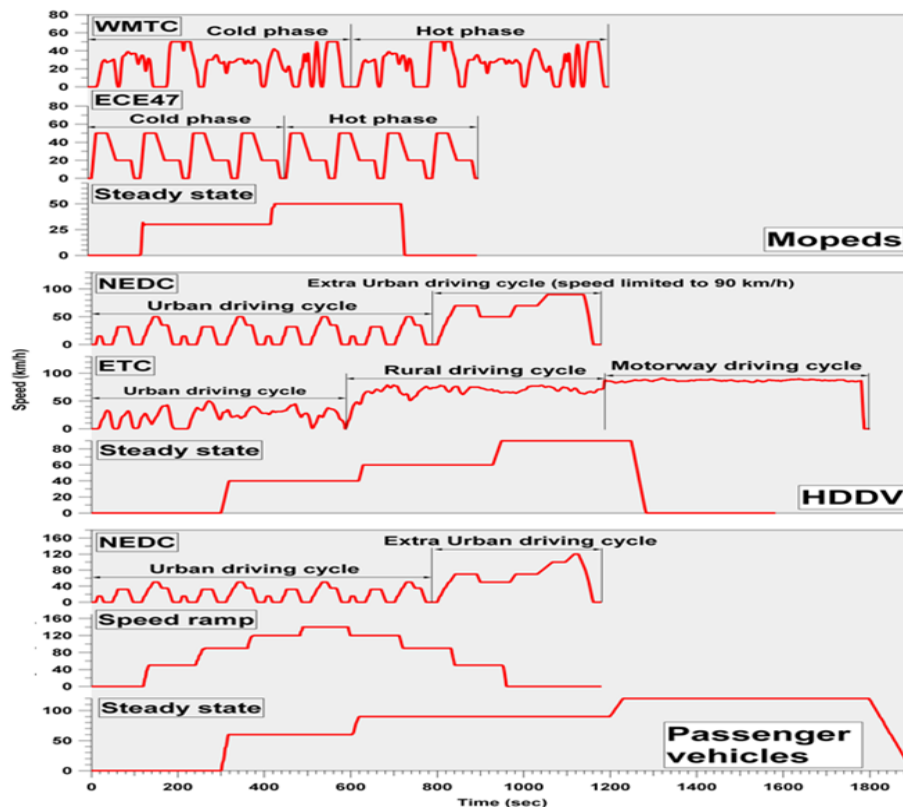
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**Figure 2.** Speed profiles of regulated (NEDC, ETC, WMTC, ECE47) and unregulated (speed ramp, steady state) test cycles.

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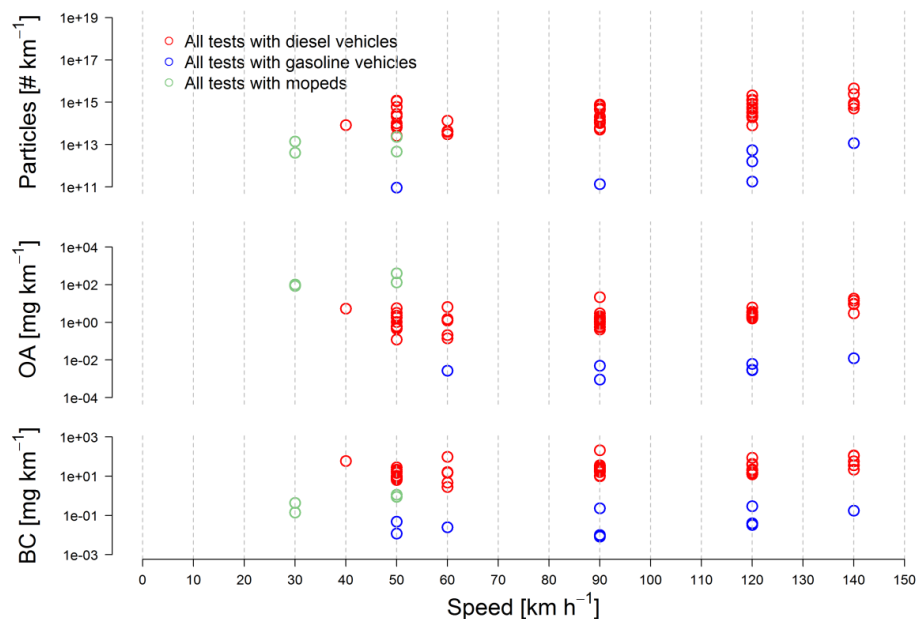
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**Figure 3.** Overview of emission factors of particles, organic aerosol and black carbon from all types of vehicles at different speeds.

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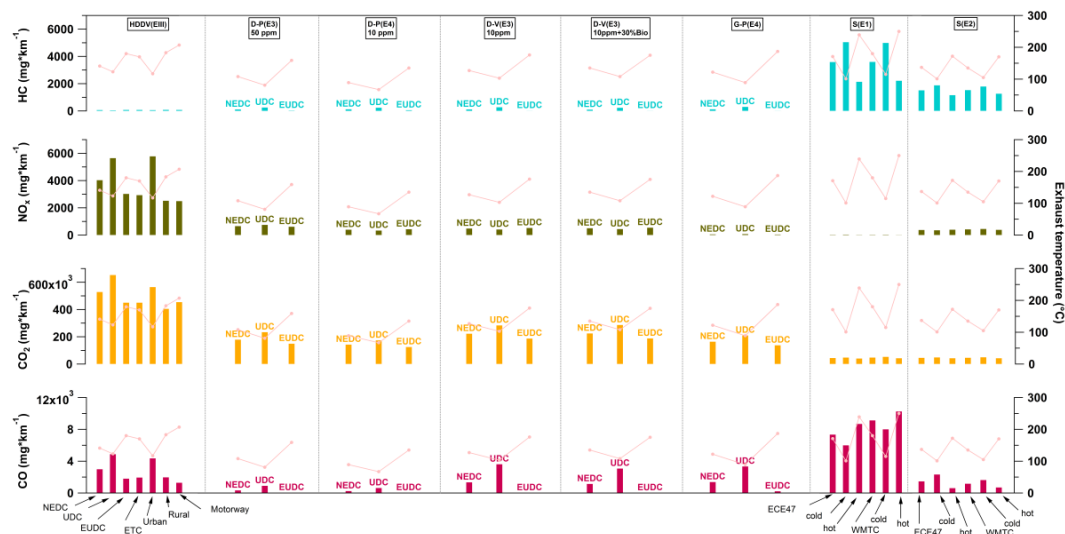
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**Figure 4.** Emission factors of regulated compounds and CO<sub>2</sub>.

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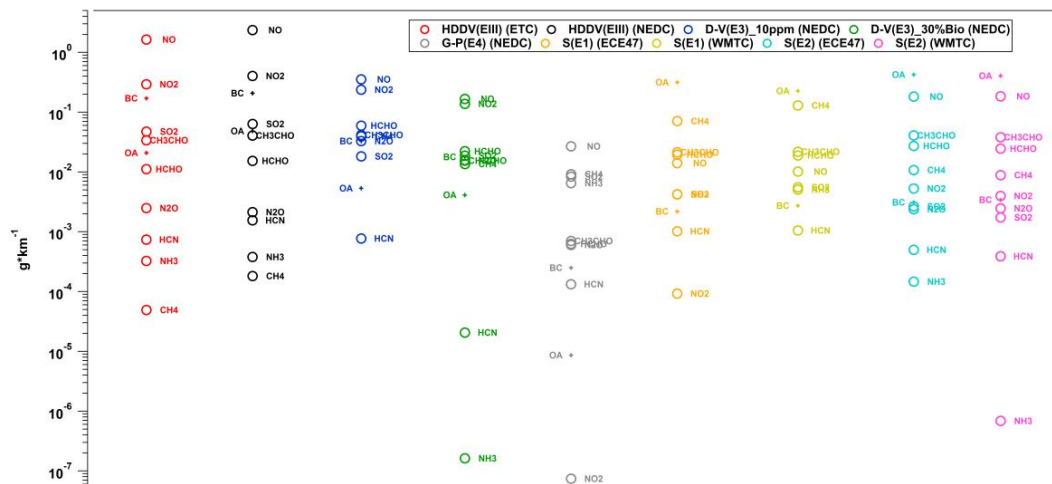
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**Figure 5.** Emission factors of gas phase unregulated compounds, OA and BC from regulated test cycles.

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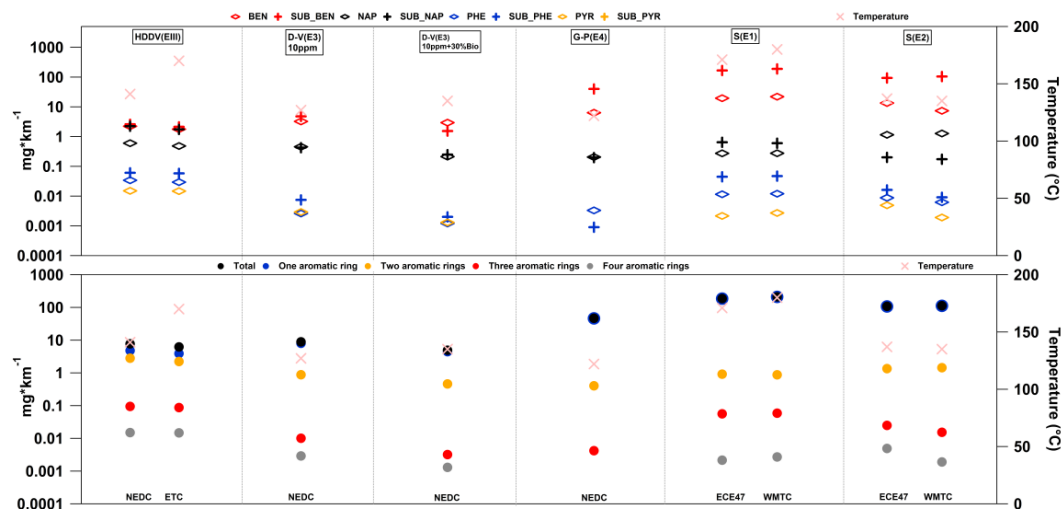
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**Figure 6.** Emission factors of aromatic compounds from regulated test cycles.

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