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Emissions from Light-Duty Diesel and Gasoline In-Use Vehicles Measured on Chassis Dynamometer Test Cycles

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ABSTRACT

The reduction in vehicle exhaust emissions achieved in the last two decades is offset by the growth in traffic, as well as by changes in the composition of emitted pollutants. The present investigation illustrates the emissions of eight in-use gasoline and diesel passenger cars using the official European driving cycle and the ARTEMIS real-world driving cycles. Measurements comprised gaseous regulated pollutants (CO, CO_2, NO_x and hydrocarbons), particulate matter and its carbonaceous content (organic and elemental carbon, OC and EC), as well as about 20 different volatile organic compounds (VOCs) in the C_6–C_{11} range. It was observed that some of the vehicles do not comply with the corresponding regulations. Significant differences in emissions were registered between driving cycles. Not all regulated pollutants showed a tendency to decrease from Euro 3 to Euro 5. The particulate carbon emission factors were significantly lower under the ARTEMIS Road compared with the ARTEMIS Urban driving cycle with cold start. In general, cold start-up driving conditions produced the highest emission factors. A tendency to the decline of carbonaceous emissions from Euro 3 to Euro 5 diesel vehicles was observed, whilst this trend was not registered for petrol-powered cars. The fraction of total carbon composed of EC was much lower in particles emitted by petrol vehicles (< 10%) than by diesel engines (50–95%). However, the EC content in emissions from more modern vehicles equipped with diesel particulate filter (DPF) is almost negligible. Among VOCs, benzene, toluene and xylenes were generally the dominant species. A significant decrease in emissions from Euro 4 to Euro 5 petrol-powered vehicles was observed. The trend in VOC emissions is unclear when diesel engines are considered. During DPF regeneration cycles, pollutant emissions are several times larger than those during normal engine operation.

Keywords: Chassis dynamometer; Emission factors; Regulated pollutants; OC/EC; VOCs.

INTRODUCTION

Emission testing in the laboratory constitutes an essential part of the European type approval process for light-duty vehicles, yielding reproducible and comparable data and providing clear design criteria for vehicles that have to meet the terms of applicable emission limits. Although emission limits have become increasingly strict in the past years, road transport remains the most significant source of urban air pollution in Europe with respect to particulate matter (PM), hydrocarbons (HC), NO_x and CO (Carlslaw and Rhys-Tyler, 2013; Pant and Harrison, 2013). In particular, airborne PM is one of the main environmental problems in most cities and the target of scientific interest due to its role in climate change and detrimental effects on human health (Calvo *et al*., 2013, and references therein). Improved information about the chemical characteristics of PM emissions is essential to model source contributions and to implement either source-oriented mitigation measures or health protection programmes. Diverse approaches have been used to quantify vehicle emissions, including chassis dynamometer tests (Zielinska *et al*.; 2004; Lim *et al*., 2006) and tunnel studies (Gillies *et al*., 2001; Phuleria *et al*., 2006; Lawrence *et al*., 2013; Pio *et al*., 2013), but most of the traffic emission profiles have been obtained in USA (Lough *et al*., 2005, 2007; Ning *et al*., 2008). However, the European fleet is quite different, with lower engine power and higher % of diesel vehicles. Some work have been performed to determine the driving cycles for light-duty vehicles as part of enhancing traffic management systems, determining fuel consumption patterns and reducing transport impacts on health (Lee *et al*., 2005; Tzirkasi *et al*., 2006; Hung *et al*., 2007; Saleh *et al*., 2010). However, comprehensive studies reporting emissions of light-duty diesel and gasoline vehicles representative of the Southern European fleet under typical driving cycles

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are, as far as we know, still inexistent. This work aimed at assessing the composition and emission characteristics of the in-use vehicle fleet in Portugal.

METHODOLOGIES

Description of the Chassis Dynamometer

The exhaust emission tests were carried out using a chassis dynamometer belonging to the French Institute of Science and Technology for Transport, Spatial Planning, Development and Networks (IFSTTAR). The chassis dynamometer platform consists of a large roller placed underneath the vehicle's tyres. When a chassis dynamometer test is run, the vehicle to be tested is driven onto the dynamometer platform according to a defined driving cycle. The dynamometer platform simulates road resistance. During a test, the chassis dynamometer gives an accurate reading of the engine's power, speed, torque, exhaust temperature, etc. The exhausts of tested vehicles are diluted with filtered ambient air through a Constant Volume Sampler (CVS) composed of two dilution tunnels, one dedicated to diesel vehicles and the other one to petrol vehicles. Measurements and samplings are made from the dilution tunnel. The sampling units and the chassis dynamometer are servo-controlled in order to relate the measurements to the activity of the vehicle so that the emission factors may be computed. A schematic representation of the dynamometer facility is given in Fig. 1.

Sampling of vehicle exhausts was performed using two real-world driving cycles determined within the European ARTEMIS project. The ARTEMIS Road (ArtRoad) and ARTEMIS Urban (ArtUrb) cycles are representative of real driving behaviour on roads and in an urban environment, respectively (André *et al*., 2004, 2006). In addition, the regulated MVEG driving cycle (Motor Vehicle Emissions Group, also called NEDC - New European Driving Cycle) was only performed for the measurements of regulated gases (CO, CO_2, NO, NO_2, and total hydrocarbons) in order to relate the vehicle to a Euro emission class, and to possibly exclude high emission vehicles. Although NEDC is used as reference cycle for homologating vehicles in Europe and some other countries, the test has been criticised as it doesn't represent real life driving conditions. Indeed, accelerations are very soft; there are a lot of constant speed cruises and a lot of idle events (Fig. 2). ARTEMIS cycles are not used for certification of pollutants. However, manufacturers use this kind of cycle to better understand real driving conditions and to assess real performances of their vehicles. The ARTEMIS cycles incorporate more transient operating modes derived from real-world driving and are widely used as the basis of emission factors for modelling of emissions. Before starting the ARTEMIS driving cycles, the homologation test NEDC was applied once to all vehicles. Each one of the ARTEMIS driving cycles was repeated, at least, three times for each vehicle.

Sampling and Measurements

Collection of PM exhaust emissions was performed using two sampling lines operating at flow rates up to 50 L/min onto pre-combusted (500°C, 6 h) 47 mm quartz fibre filters. Samples were refrigerated immediately after the chassis dynamometer experiments. It should be noted that the gravimetric determination of the PM mass was not possible for all the replicate tests because, as a result of over-tightening of the filter-holders, some quartz fibres were lost on the o'rings. In these cases, the PM mass was indirectly estimated from OC or EC to PM ratios reported in the literature for the same category of vehicles (Geller *et al*., 2006; Chow *et al*., 2011; Caserini *et al*., 2013). The comparison of these rough estimates with gravimetric determinations, when available, gave quite comparable results. PM emissions factors will be presented as a range of values rather than averages.

Conditions of sampling, including dilutions and the repetition of driving cycles, were defined for each vehicle, depending on its emission levels, which were checked using the NEDC cycle. Each driving cycle was repeated 3 to 5 times. A minimum of one blank per day was performed. Blanks correspond to the sampling of dilution air in the same conditions as the exhaust samples (including sampling time, transfer in the CVS, etc.). The following driving cycles were tested:

- urban driving cycle with cold start,
- urban driving cycle with hot start,
- road driving cycle (always hot start).

In the absence of available data, it was considered that the proportion of vehicles with cold start in urban areas may be as high as vehicles with hot start.

The measurement of regulated pollutants was simultaneously done by means of a series of common analysers (nondispersive infrared for CO and CO_2, chemiluminescence for NO_x and flame ionisation detection for total hydrocarbons). Based on national statistics, 8 representative vehicles of the Portuguese fleet, according to motorisation, European emission class and engine capacity, were selected for the chassis dynamometer tests (Table 1). In Portugal, light-duty passenger cars represent 78% of the total fleet. Around 55% of these vehicles belong to the Euro 3 and Euro 4 classes. In 2013, Renault, Volkswagen, Peugeot, Opel, Citroen and Toyota accounted for 10.1, 10.0, 8.8, 6.7, 6.3 and 5.1%, respectively, of the light-duty passenger cars on the roads. The most common engine displacements are 1251–1500 cm^3 (28%) and 1001–1250 cm^3 (22%), followed by 1751–2000 cm^3 (21%) and 1501–1750 cm^3 (18%). As in other European countries, a significant shift from petrol to diesel cars has been recently observed in Portugal. The country holds one of the largest share in the sales of new diesel passenger cars in the EU – more than 70% (Oliveira, 2012, and references therein).

Steel tubes filled with solid adsorbents (200 mg of 60–80 mesh Carbopack B and 200 mg of 60–80 mesh Carbopack C from Supelco) were used, after particle filtration, to sample volatile organic compounds (VOCs) from the CVS tunnel at a flow of 150 mL/min. Considering that VOC measurements were not envisaged by the research project, in which the dynamometer experiments were included, and due to budget limitations, VOC sampling was only carried out for four vehicles (two petrol- and two diesel-powered), belonging to the Euro 4 and 5 classes. Based on the consistency between repeated measurements of total

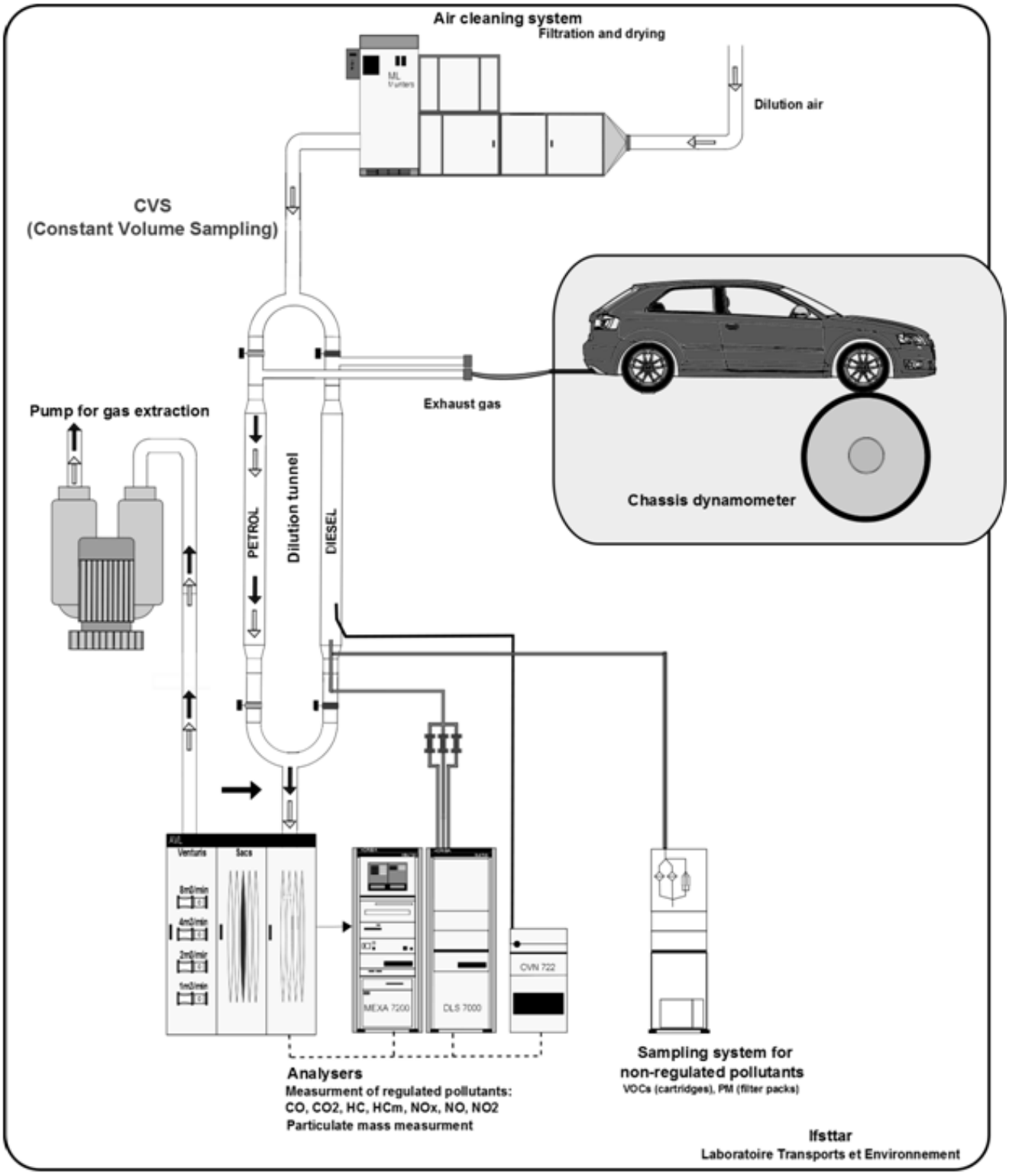

Fig. 1. Schematic representation of the chassis dynamometer emission test facility.

hydrocarbons, for some driving cycles, from the three replicates, only one sample was taken for VOC analysis.

Analysis of VOCs

VOCs were desorbed and analysed by a thermal desorption/cryogenic concentration method on a Trace Ultra (Thermo Scientific) gas chromatograph (GC) equipped with a thermal desorption injector Master TD (DANI) and a flame ionisation detector (FID). VOCs in the adsorbent tubes were thermally desorbed at 250°C with pure helium at 8 psi for 15 min and cryofocused in a cold trap of the thermal desorber at –30°C. The trap was connected to the

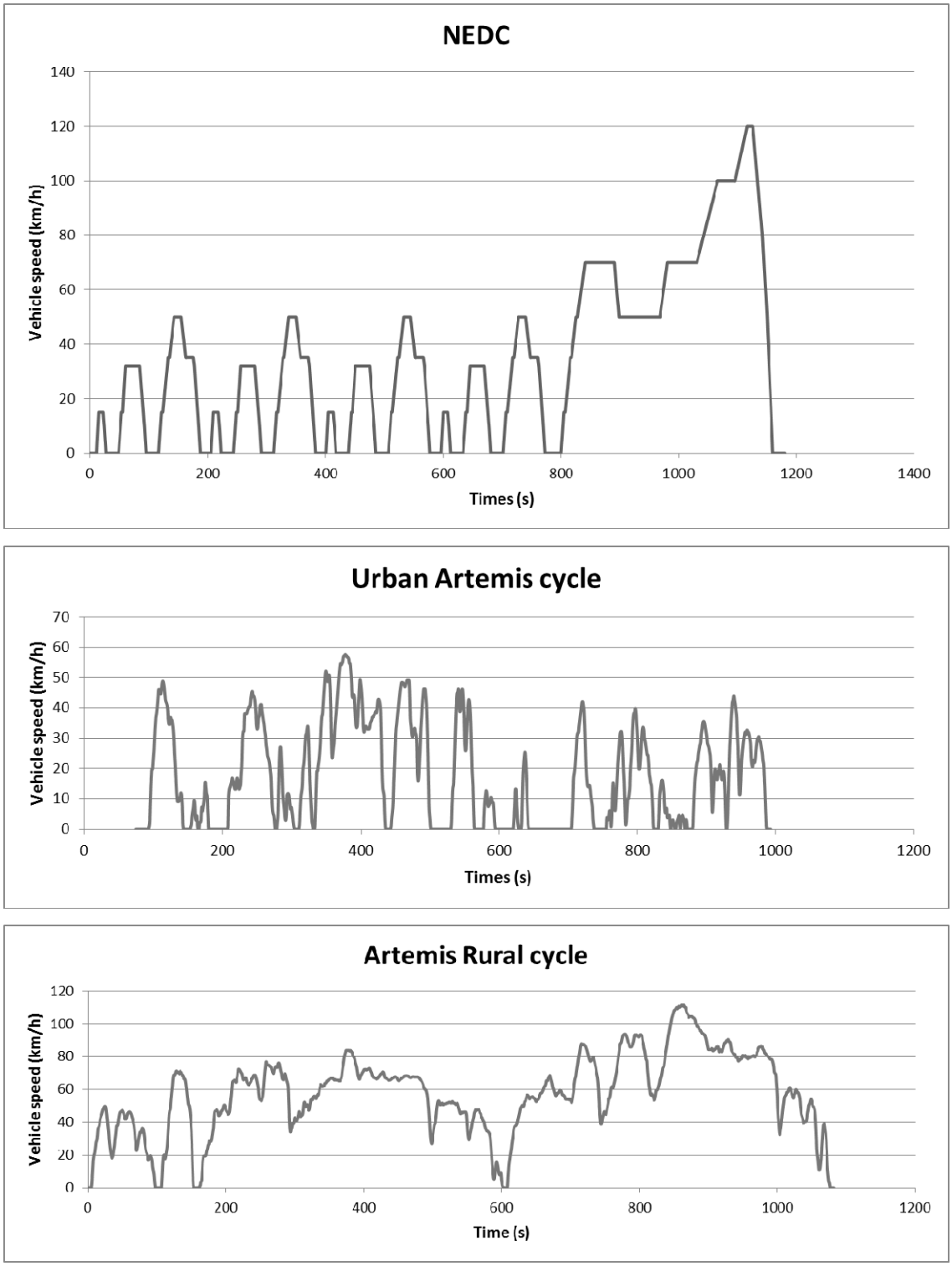

Fig. 2. European driving cycles followed in this study.

GC split/splitless injector by a transfer line heated to 250°C. Compounds were injected into a column (split ratio 25) by fast heating of the trap to 250°C using helium as carrier gas (8 psi). A TRB-1MS capillary column (50 m × 0.20 mm i.d., 0.50 µm) was used for separation of VOCs. The oven temperature programme was as follows: 40°C – 3 min, from 40 to 160 °C at 4 °C/min, from 160 to 250°C at 10 °C/min, and 250 °C – 4 min. For calibration, pure liquid hydrocarbons and the EPA VOC analytical standards Mix-1 and Mix-2 from Supelco were dissolved in methanol (20 to 100 ng/µL). Three to five µL of standard solutions were injected into clean adsorbent tubes, through which pure nitrogen was then passed at a flow rate of about 40 mL/min for 3 min to remove the solvent.

Table 1. Vehicles selected for the tests.

N°	Vehicle class	Model (year)	Engine (L)	Mileage (km)	DPF
1	Euro 3 Petrol (< 1.4 L)	Peugeot 206 (2004)	1.1	69,413	No
2	Euro 3 Diesel (1.4–2 L)	Renault Megane Scénic (2003)	1.5	127,700	No
3	Euro 4 Diesel (1.4–2L)	Citroën Xsara Picasso (2006)	1.6	57,764	No
4	Euro 4 Petrol (< 1.4 L)	Toyota Aygo (2006)	1.0	31,238	No
5	Euro 5 Diesel (1.4–2 L)	Opel Astra (2011)	1.7	39,600	Yes
6	Euro 5 Petrol (< 1.4 L)	Opel Agila (2012)	1.2	9,900	No
7	Euro 4 Diesel (1.4–2 L)	Volkswagen Passat (2009)	2.0	75,110	Yes
8	Euro 4 Diesel (< 1.4 L)	Opel Tigra Twin Top (2008)	1.3	69,463	No

Carbonaceous Content of Exhaust Particles

Two 9 mm punches of each filter were used to determine the carbonaceous content (OC and EC) by a thermal-optical technique developed by the University of Aveiro. Controlled heating in anoxic conditions was performed to separate OC into two fractions of increasing volatility. The first fraction corresponds to the volatilisation at T < 200°C of lower molecular weight organics (OC1). The second fraction is related to decomposition and oxidation of higher molecular weight species at temperatures ranging from 200 to 600°C (OC2). The last fraction of OC is identified by transmittance and corresponds to pyrolysed organic carbon (PC) produced in the previous heating steps. Separation between OC and EC was achieved by initially heating the filter punches under an inert atmosphere to evaporate first the OC fraction. The remaining fraction is sequentially evaporated/burnt under a gas flow containing O_2. This last carbon fraction contains initial EC plus OC that has pyrolysed during heating under an inert atmosphere. The interference between PC and EC can be controlled by continuous evaluation of the blackening of filter using a laser beam and a photodetector measuring the filter light transmittance. The OC and EC are volatilised to CO_2, which is quantified continuously by a non-dispersive infrared analyser.

The methodology used in this study was tested with the NIST (National Institute of Standards and Technology) 8785 filter standard and in an intercomparison experiment with real aerosol samples (Schmid *et al*., 2001). The procedure was also compared with the EUSAAR (European Supersites for Atmospheric Aerosol Research) II protocol through the analysis of samples of different types and origins and the results proved to be similar.

RESULTS AND DISCUSSION

Gaseous Regulated Pollutants

Emissions tested over the MVEG (NEDC) chassis dynamometer procedure allowed to evaluate whether the vehicles fulfil the EU emission standards or not. This step is necessary to identify vehicles that emit abnormal levels compared to vehicles of the same category. Comparisons with EU emission standards showed that vehicles 1 (Euro 3, petrol, 1.1 L), 3 (Euro 4, diesel, 1.6 L), 4 (Euro 4, petrol, 1.0 L), 5 (Euro 5, diesel, 1.7 L) and 6 (Euro 5, petrol, 1.2 L) fulfil the EU emission standards (Fig. 3). Vehicles 2 (Euro 3, diesel, 1.5 L) and 7 (Euro 4, diesel, 2.0 L) presented slightly higher CO emissions than the Euro 3 and Euro 4 standards for diesel powered models, probably due to catalyst ageing. However, the difference is weak and it can be considered that the diesel cars are representative of aged vehicles of their categories. HC emissions from vehicle 7 are higher than those from other light-duty passenger cars, including other Euro 4 diesel vehicles. Besides the possibility of aging of the catalyst, the larger engine displacement of this vehicle can justify this observation. It has been described that vehicles with high engine capacity emit more hydrocarbons because they burn more fuel than vehicles with smaller engine when travelling similar distances (Abu-Allaban *et al*., 2007). Vehicle 8 (Euro 4, diesel, 1.3 L) no longer fulfils the EU emission criterion because of NO_x emissions that are higher than the standard for diesel cars of that category.

In general, the effect of cold start driving conditions on exhaust emissions was rather significant, especially in diesel vehicles (Figs. 4 and 5). Cold start emissions are of particular interest because these generally occur in urban areas and might substantially exceed average on-road emission levels. The temporary ineffectiveness of motor vehicle emission controls at start-up causes emission rates to be much higher for a short period after starting than during fully warmed, or stabilised, vehicle operation. Strict stoichiometric control of the air-fuel ratio results in lower levels of CO and HC production relative to fuel-rich operation, and lower levels of NO_x production relative to fuel-lean combustion. Stoichiometric air fuel mixtures are also required for the treatment of exhaust gases by three-way catalytic converters, which simultaneously oxidise HC and CO to carbon dioxide (CO_2) and reduce NO to N_2. New vehicles, equipped with these and other emission controls, typically emit less than 5% of the pollutants emitted by pre-control vehicles (Singer *et al*., 1999). One drawback of contemporary vehicle emission control systems is that they are ineffective for a short period after a vehicle is started. At start-up, the fuel-air mixture is purposely enriched to help ignition and improve cold engine operation. This enrichment leads to enhanced formation of pollutants during combustion, and limits the oxidation of these exhaust constituents in the catalytic converter. Cold-start emissions of individual vehicles span over a relative large value range. More detailed insights into cold-start emission patterns require a more careful analysis and additional testing.

NO_2 emissions of gasoline vehicles are negligible in comparison to the emissions of diesel vehicles, while the share of NO_2 in the total NO_x emissions is substantially higher for diesel than for gasoline vehicles (data not shown). Contrary to what has been reported for on-road emissions

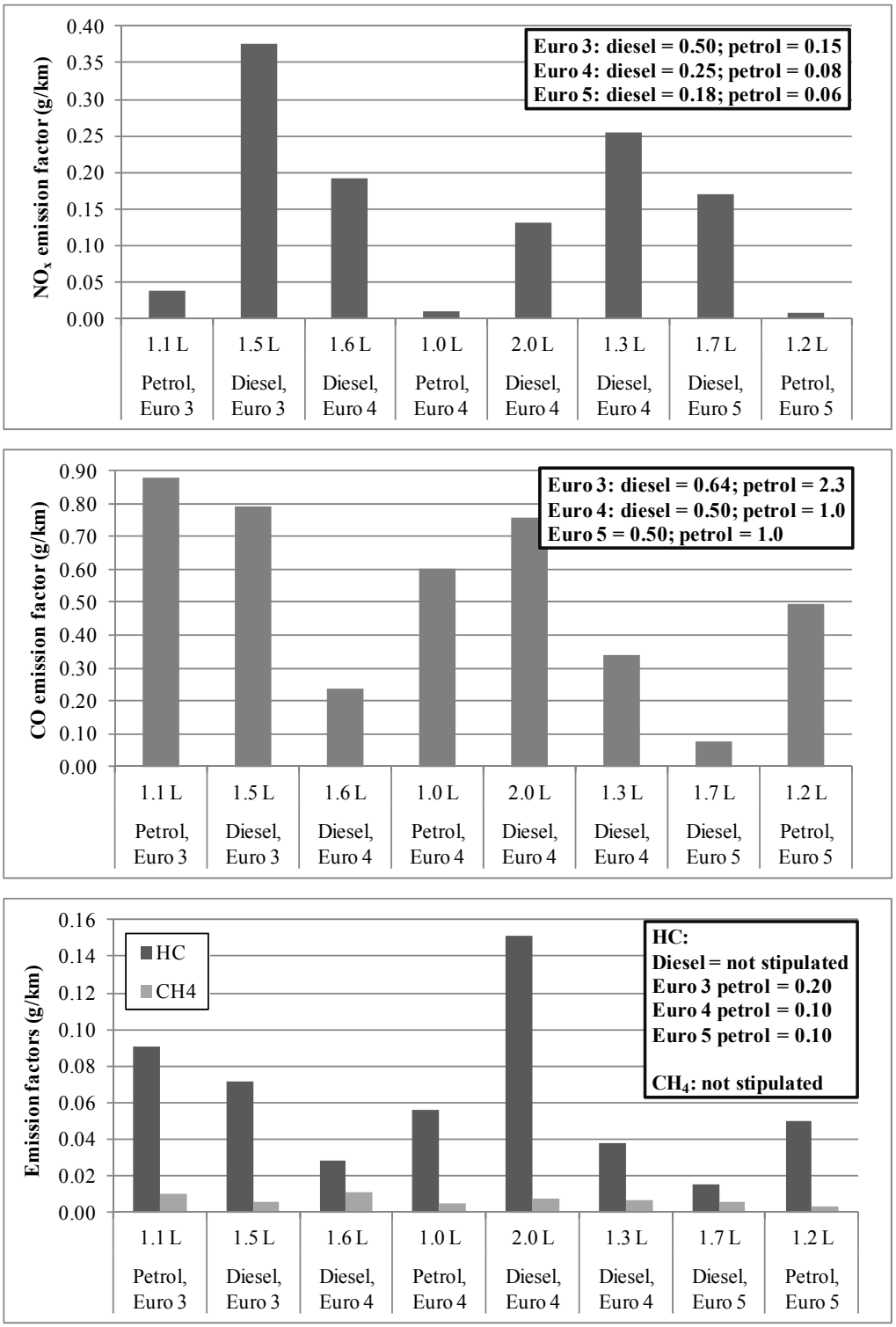

Fig. 3. Average emission factors obtained with the New European Driving Cycle and comparison with the European emission standards for passenger cars (inserted text boxes).

of light-duty vehicles with portable emission measurement systems (Weiss *et al*., 2011), in the present study total HC emissions do not show a general increase from Euro 3 to Euro 4 gasoline vehicles both in absolute terms and as percentage of Euro 3–4 emission limits. An overall downward in CO emissions from gasoline vehicles was registered: Euro 3–1.001 g/km, Euro 4–0.426 g/km and Euro 5–0.051 g/km. Unlike other pollutants, results suggest that there is not any clear tendency to the decline in the on-road NO_x emissions of Euro 3 towards Euro 5 gasoline vehicles (Fig. 4). NO_x emissions of diesel and gasoline vehicles are generally higher during NEDC testing than they are on the real-world driving

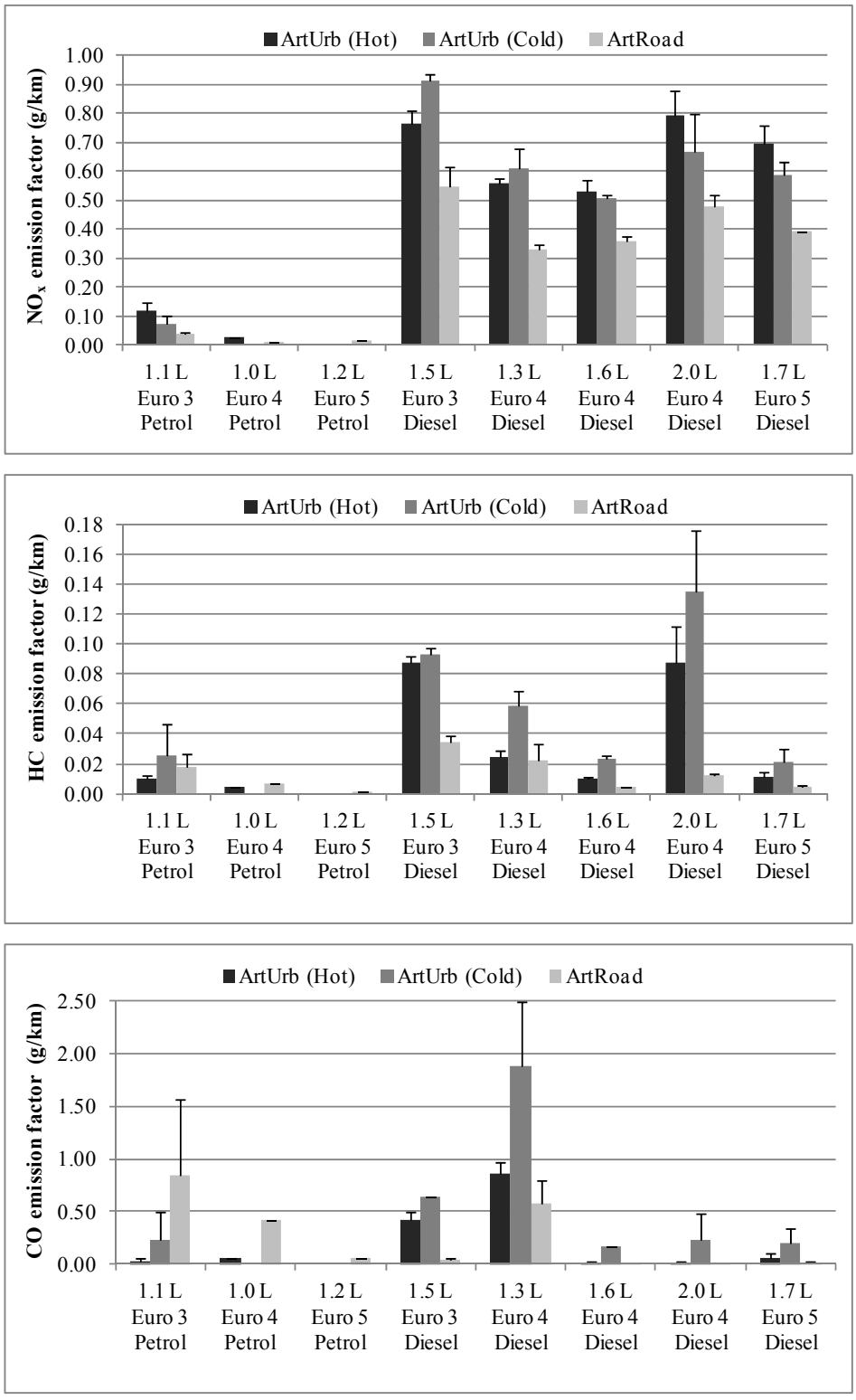

Fig. 4. Average NO_x, hydrocarbon and CO emission factors on the ARTEMIS Urban and Road driving cycles.

cycle ARTEMIS. Also, the NEDC tests have generally higher HC and CO emissions than the ArtUrb (hot start) and ArtRoad cycles. This can be explained by the NEDC cold start effects. The results do not allow identifying a trend towards lower CO emissions from Euro 3 to Euro 5 diesel vehicles, while it seems there is a decrease for gasoline cars.

Next to regulated pollutants, on-road CO_2 emissions are of particular interest to policy makers. To reduce greenhouse gas emissions from transport, the European Commission sets a target of 130 g CO_2/km for new passenger cars of a reference mass of 1372 kg (EC, 2009). For reasons of simplicity, we uniformly use here 130 g CO_2/km as benchmark for all test

vehicles, thereby disregarding the specific mass of vehicles. The CO_2 emissions of all vehicles tested under the ArtUrb cycles exceeded the EC target value. Excepting the Euro 5 diesel car, the limit was met when the engines were operated under the ArtRoad driving cycle (Fig. 5). The average CO_2 emissions of all vehicles tested on NEDC amount to 134 ± 13 g/km. Under this cycle, diesel vehicles emit on average 138 ± 10 g CO_2/km, whereas gasoline vehicles emit 126 ± 17 g CO_2/km. These deviations might increase if vehicles are driven at extremely high speeds, e.g., as it frequently occurs on the German Autobahn (Weiss *et al*., 2011). Blumberg *et al*. (2003) reported that conventional diesels typically use only 70% of the fuel of a comparable gasoline engine, significantly reducing per-km CO_2 emissions. This reduction was not observed in the present study.

In general, the emission factors (EFs) of all regulated pollutants are lower than those proposed in the EMEP/CORINAIR guidebook. In most cases, the EFs obtained in the present work for gasoline vehicles are also lower than those reported in other dynamometer studies (e.g. Bergvall *et al*., 2009; Fontaras *et al*., 2011), on-board measurements (Ropkins *et al*., 2007; Achour *et al*., 2011; Huo *et al*., 2012) and tunnel experiments (Pierson *et al*., 1996; Kristensson *et al*., 2004; McGaughey *et al*., 2004; Martins *et al*., 2006). In the case of diesel vehicles, the EFs are lower than those obtained from on-board and tunnel measurements, but higher when compared with the results of other dynamometer tests.

With respect to diesel cars, especially those belonging to the lower Euro emission category, the concentrations of all the gaseous pollutants increase with the stop frequency and duration. NO_x and CO_2 are sensitive to the frequency and intensity of accelerations, whilst CO emissions are more sensitive to high speeds. The effect of the strongest accelerations/decelerations on CO emissions seems more evident for ArtRoad than for ArtUrb cycles. Concerning the petrol cars, within urban driving, all the pollutants are sensitive to acceleration parameters (frequency of accelerations and strong accelerations, average acceleration, time spent at high acceleration), CO_2 and HC increase with the stops, and CO_2 decreases when the speed increases. As for urban driving, on rural roads, the pollutants are strongly sensitive to acceleration and CO_2, HC and NO_x increase with the stops. Quite contrasted performances between diesel (rather sensitive to speed and stop parameters) and petrol cars (rather sensitive to accelerations) were observed. For both categories of vehicles, instantaneous peak concentrations are in general concomitant with high speeds/accelerations (Fig. 6). In accordance with previous studies, with deceleration, emission rates were low and insensitive to speed, reflecting an unloaded and essentially idling engine (Bokare and Maurya, 2013; Zhang *et al*., 2013). Deceleration modes contribute relatively little to total emissions for any of the pollutants compared to cruise, acceleration, and cold start emissions. It has been observed in other studies that high accelerations and speeds (e.g., aggressive driving behaviour) and rapid speed fluctuations (e.g., quick deceleration) can produce large increases in emissions of CO and HC. It has also been reported that both the increased load on the engine from climbing a hill and the decreased load that accompanies engine deceleration significantly increase vehicle emissions (GAO/RCED, 1997). In fact, motor vehicle emissions are highly dependent on the modal activity of a given trip. Power enrichment (acceleration) and motoring (deceleration) events are discrete vehicle operating modes that are each capable of producing significant emissions. High vehicle emissions during rapid vehicle acceleration result from enrichment of the engine's fuel-air mixture, which achieves maximum engine power but creates high levels of unburned HC and CO. Laboratory tests have shown that high acceleration rates are significant contributors to instantaneous emission rates, and that in some cases one sharp acceleration can cause as much pollution as the entire remaining trip. Similarly, the poor combustion caused by rapid throttle closing (i.e., sharp deceleration) can also result in high emissions of unburned HC and CO. The fuel injection systems in most newer vehicles stop the addition of fuel during vehicle decelerations, but the resulting rapid throttle closing still causes a "spike" of unburned HC and CO (EPA, 1998).

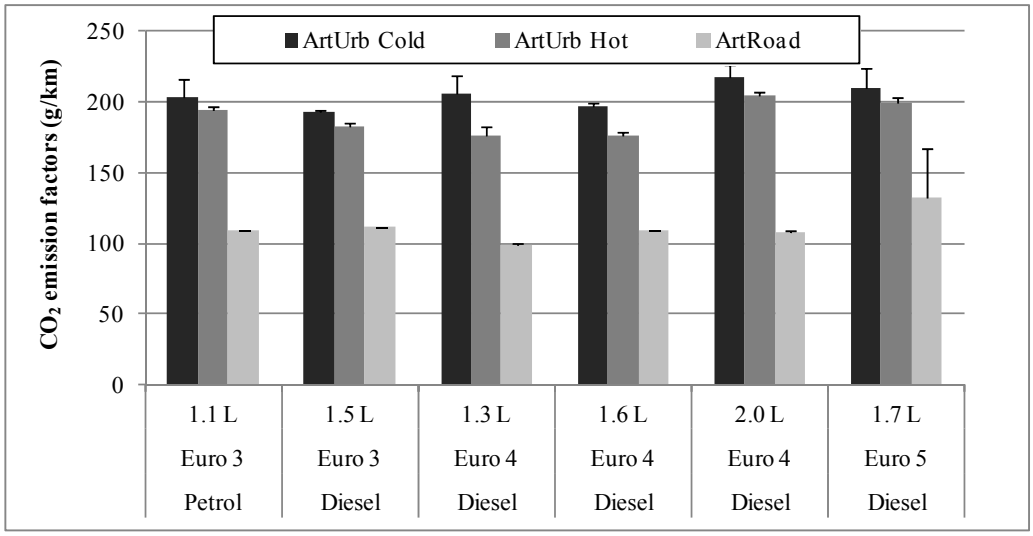

Fig. 5. Average CO_2 emissions for some vehicles under different ARTEMIS driving cycles.

During an ArtRoad driving cycle with the Euro 5 diesel vehicle (1.7 L), the regeneration of the DPF took place. In the course of this stage, the amount of fuel consumed by the vehicle increased by 35%. Comparatively to the "normal" ArtRoad cycles, the emissions of hydrocarbons, NO_x, CO, CO_2 and carbonaceous particles increased by 95, 15, 95, 35 and 99%, respectively.

Particulate Matter and Carbonaceous Content

Contrary to expectations, the filter samples from the exhaust of the Euro 3 petrol-powered vehicle had a very light colour and their weights were of the same order of magnitude of the blanks. Due to the very low loads, the laser of the thermo-optical system was unable to accurately separate OC and EC. Hence, caution should be exercised in

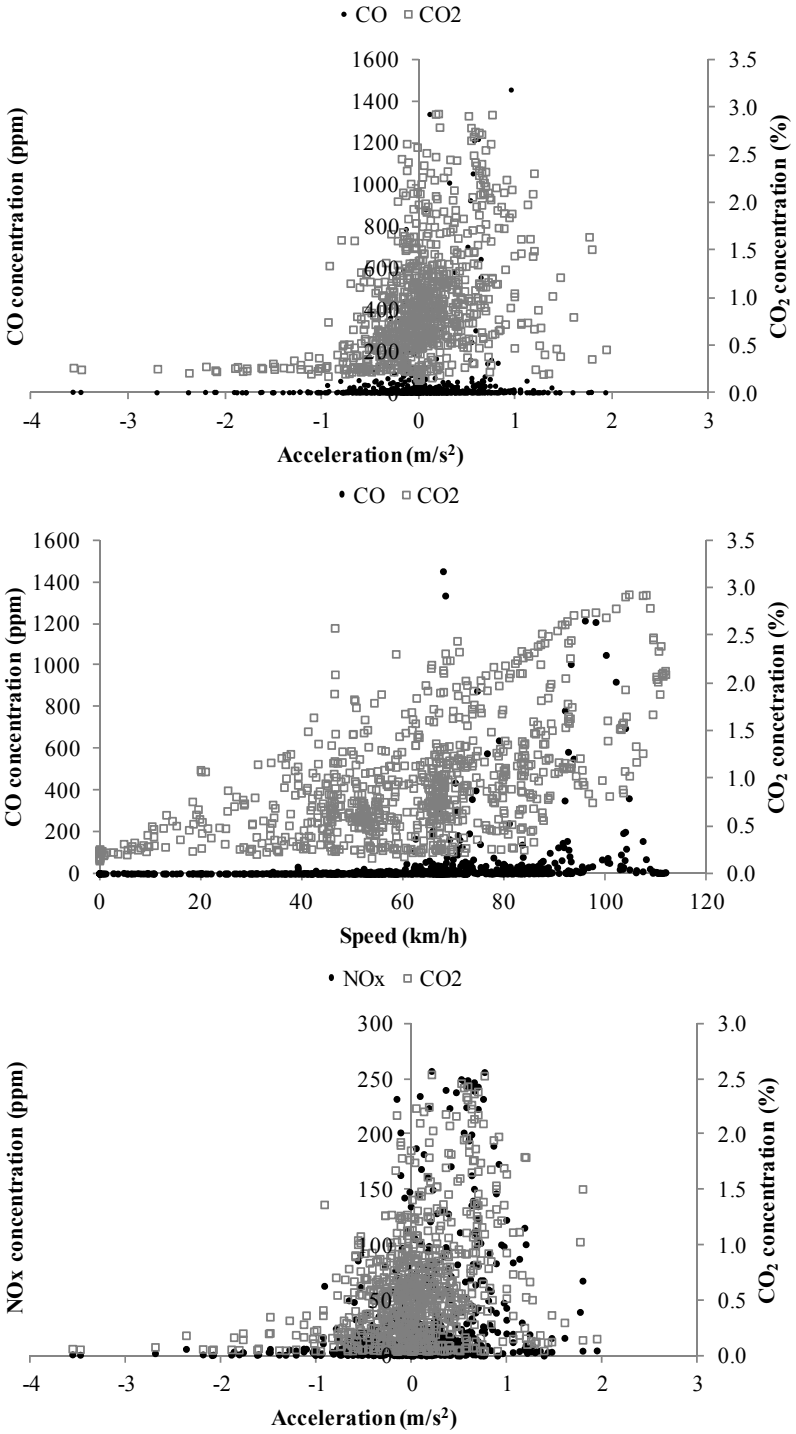

Fig. 6. First two panels – Concentrations of CO and CO_2 as a function of acceleration and speed for a petrol-powered vehicle; Last two panels – Concentrations of NO_X and CO_2 as a function of acceleration and speed for a diesel-powered vehicle.

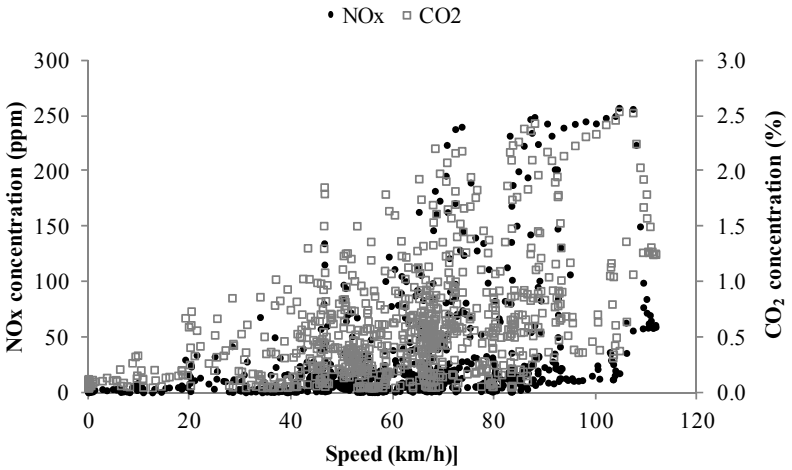

Fig. 6. *(continued).*

making broader inferences based on these measurements. Particulate matter is formed from gasoline-fuelled engines from incomplete fuel and oil combustion. The amount of oil consumed in combustion and its contribution to emissions varies greatly from vehicle to vehicle. Also, there is a wide assortment of technologies in vehicles that can affect particle formation. The deterioration of emission control systems and wear of engine components may also influence emissions (Nam *et al*., 2008). Inappropriate maintenance, repair or use and accelerated catalyst aging may be pointed out as possible factors justifying the high particle emissions of the diesel-fuelled Euro 4 vehicle (1.3 L) compared to the other models (Table 2).

The increased PM emissions for the diesel vehicles in the ArtUrb tests could possibly be due to the rapid acceleration segments in that driving cycles. This observation is consistent with the results of previous measurements by other groups (Bergvall and Westerholm, 2009). The modern diesel engines have extremely low particle emissions, almost at the level of the measurement error of the existing gravimetric method. Since coarse particles are eliminated by new engine technologies, fine particles, with very negative effects on human health, dominate in the emission of Euro 5 vehicles. Therefore, it is necessary not only to measure mass of emitted particles but also to investigate other important particle characteristics, such as size distribution, number and composition (Petrovic *et al*., 2011).

The PM emission factors obtained in this study are within the wide range of values reported in the literature. Bergvall and Westerholm (2009) tested two gasoline- (Euro 2 and 3) and two diesel-fuelled (Euro 4) light-duty vehicles driven on a chassis dynamometer. Particle emissions factors of 1.6–1.9 and 28–69 mg/km were, respectively, obtained for the gasoline and diesel automobiles in the ArtUrb tests, whereas the corresponding values in ArtRoad were 3.0–3.3 and 12–43 mg/km. Pelkans and Debal (2006) applied tests on chassis dynamometers, focused mainly on NEDC. The particle emissions of a 1.9 L diesel vehicle belonging to the Euro 3 class were 60–80 mg/km. Li *et al.* (2014) tested 6 vehicles (model years: 2009 and 2012), including 3 gasoline direct injected (GDI) vehicles, 2 port fuel injected (PFI) vehicles, and one diesel vehicle, over the U.S. Federal Test Procedure (FTP) driving cycle on a light-duty the chassis dynamometer. Particle mass emissions were determined by gravimetry and the IPSD method, which combines particle size distributions with size dependent particle effective density. The results showed a systematic bias between methods, with the IPSD underestimating particle mass relatively to gravimetry. The diesel car with DPF presented PM emission factors always below 0.3 mg/km, whilst wider ranges were obtained for the GDI (0.12–3.9 mg/km) and PFI (< 0.06–1.8 mg/km) vehicles. Emission samples were collected by Zielinska *et al.* (2004) from a variety of gasoline- and diesel-fueled in-use vehicles operated on the Unified Driving Cycle on a chassis dynamometer. Gasoline vehicles included normal particle emitters, "black" and "white" smokers, and a new-technology vehicle. Diesel vehicles included current-technology vehicles and a high particulate matter emitter. Total PM emission rates ranged from below 2 mg/km up to more than 435 mg/km for the white smoker gasoline vehicle. Particulate matter emissions from four non-smoking gasoline powered motor vehicles were measured by Schauer *et al.* (2008) using three different driving conditions: a cold-cold start Unified Driving Cycle (UDC), a hot UDC, and a steady state cruise driving cycle. Mass emissions rates for the test vehicles using both the hot UDC and steady state driving cycles ranged from < 0.1 to 1.3 mg/km, while the average cold-cold UDC cycle emissions ranged from 1.0 to 7.1 mg/km for the four vehicles. The cold-cold start UDC emissions averaged 5–30 times higher than the hot start UDC emissions.

The particulate carbon emission factors were significantly lower under the ArtRoad compared to the ArtUrb driving cycle with cold start. In general, hot start-up driving conditions produced the lowest emission factors (Fig. 7). A tendency to the decline of carbonaceous emissions from Euro 3 to Euro 5 diesel vehicles is observed, whereas this trend is not registered for petrol-powered cars. The fraction of total carbon composed of EC is much lower in particles emitted by petrol vehicles (< 10%) than by diesel engines

Table 2. Particle emission factors and European standards (mg/km).

Vehicle	ArtUrb (Hot)	ArtUrb (Cold)	ArtRoad	Emission Standards
1.1 L, Euro 3, Petrol	BDL	BDL	BDL	-
1.0 L, Euro 4, Petrol	0.043–0.27	0.019–0.121	0.11–0.68	-
1.2 L, Euro 5, Petrol	0.10–0.65	0.044–0.275	0.02–0.13	5.00
1.5 L, Euro 3, Diesel	50–64	51.2–66.1	25–32	50.0
1.3 L, Euro 4, Diesel	383–495	545–704	285–367	25.0
1.6 L, Euro 4, Diesel	38–49	39.8–51.4	24–31	25.0
2.0 L, Euro 4, Diesel	0.023–0.030	0.059–0.091	BDL	25.0
1.7 L, Euro 5, Diesel	0.031–0.040	0.042–0.054	BDL	5.00

BDL – below detection limit.

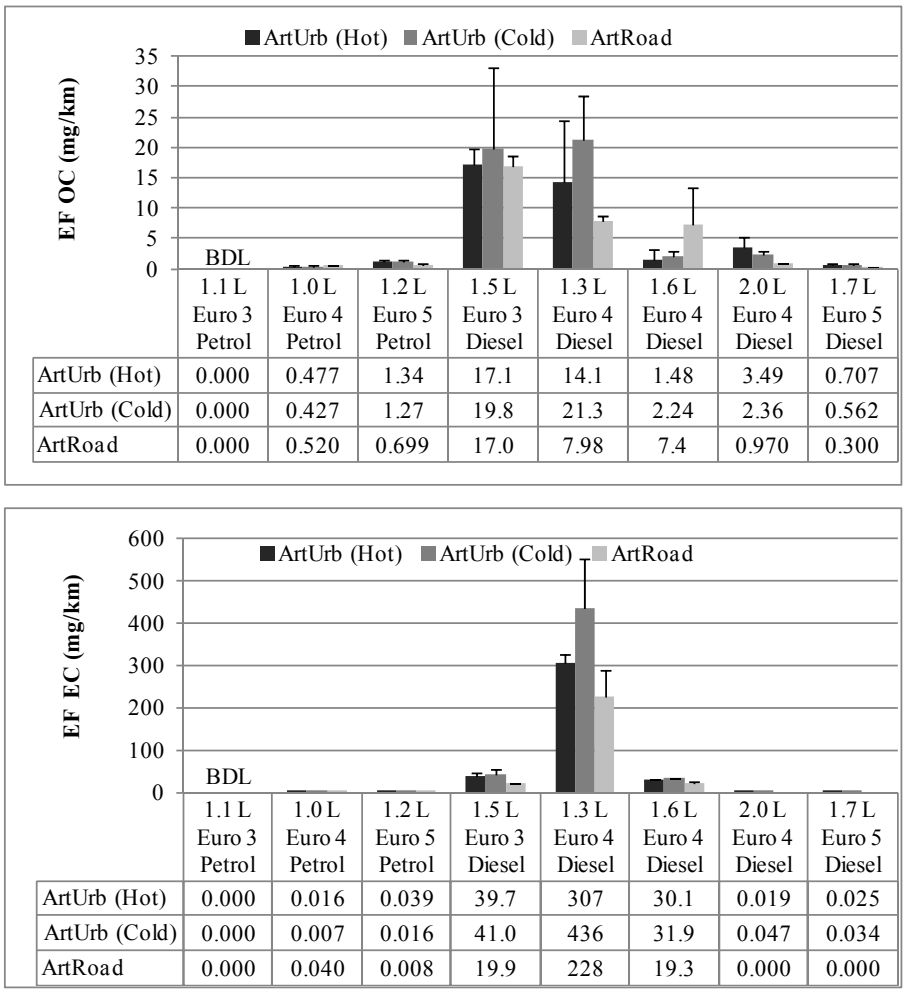

Fig. 7. Emission factors of organic and elemental carbon.

(50–95%). However, the EC content in emissions from more modern vehicles equipped with DPF (diesel particulate filter) is almost negligible. In fact, EC emitted by pre-Euro 4 and Euro 4 vehicles without DPF was higher than OC, but an inversion in the proportion between the two carbonaceous components occurred after the introduction of this clean-diesel technology. DPFs are effective in controlling the solid fraction of diesel particulates, including EC (soot) and the related black smoke emission. However, filters may have limited effectiveness, or be totally ineffective, in controlling non-solid fractions of PM emissions and organic vapours, which condense and form OC particles.

The fraction of organic carbon evolved at temperatures < 200°C (OC1) represented 25–48%, 18–51% and 11–58% of the total OC for the ArtUrb with hot start, ArtUrb with cold start and ArtRoad cycles, respectively. Organic compounds that volatilise at temperatures above 200°C (OC2) accounted for 11–63%, 22–63% and 14–51% of the total OC emissions under the same three driving cycles. The emission factors of both OC fractions were higher for the ArtUrb cycles, especially under hot start-up conditions, than for the ArtRoad driving tests. The highest OC1 and OC2 emission

factors (5.43 mg/km and 8.29 mg/km, respectively) were obtained for the diesel-powered Euro 3 vehicle. Concerning the diesel engines, 78–87% and 56–84% reductions in OC1 emissions were observed between Euro 3 and Euro 4 and between Euro 4 and Euro 5 vehicles, respectively. The correspondent declines in OC2 emissions were 66–84%, from Euro 3 to Euro 4, and 88–97% when moving from Euro 4 to Euro 5. An opposite trend was evidenced for petrol-powered cars. The significant reduction in tailpipe particulate matter achieved in vehicles with DPF lowers the aerosol surface area available for the condensation of semi-volatile organic vapours. Thus, the particulate OC concentrations in the exhaust are also reduced. Further, the DPF may also participate in the oxidation of OC vapours, which may represent a second mechanism to reduce OC particulate concentrations in the exhaust (Moore *et al.*, 2011). It has been recently demonstrated that gasoline exhaust readily forms secondary organic aerosol (SOA). It was also found that the SOA formation potential is significantly higher for gasoline exhaust than for diesel exhaust and increases from Euro 3 to Euro 5 vehicles (Nordin *et al*., 2013; Platt *et al*., 2013). Part of the ageing processes leading to SOA formation takes place in the CVS tunnel, which simulates the conditions at which particulates are released from vehicles into the atmosphere.

The carbonaceous content of particles emitted by diesel vehicles belonging to European standards before Euro 5, without DPF, present OC/EC ratios < 1. Modern diesel passenger cars exhibit high OC/EC ratios (Table 3). Although the emission control systems will not have difficulties complying with the regulations of PM, which raises problems regarding the precise quantification of the material emitted, it seems that the trend observed here towards a substantial increase of the OC/EC values will collide with the widespread source apportionment technique based on the utilisation of a minimum ratio (Pio *et al*., 2011). This technique enables to distinguish between primary and secondary organic carbon and have been assuming OC/EC minimum ratios < 1 to represent the primary carbon emitted by vehicle exhausts. Despite the fleet of European countries still has a large representation of vehicles < Euro 4, in the future, the adoption of OC/EC minimum ratios for source apportionment purposes must be rethought.

From dynamometer experiments with Euro 3 and Euro 4 vehicles, Geller *et al*. (2006) concluded that diesel cars emit the highest amounts of EC per km, with the transient and steady-state cycles ranked first and second in emission rates. In contrast to the EC data, the OC emissions during steady-state operation of the diesel vehicle were quite analogous, but still the highest of all vehicles tested. The average emission factors were in the ranges 13–12911 and 230–4967 ng/km for EC and OC, respectively. An effective removal of carbonaceous material was observed by the catalysed DPF of the diesel vehicle. However, a much more efficient reduction of the EC in relation to the OC content was noticed, sustaining the argument that OC is not reduced as efficiently as EC, probably because an important fraction of OC in the form of vapours condense downstream of the DPF (Zielinska *et al*., 2004; Geller *et al*., 2006).

The OC/EC ratio varied substantially with vehicle type. Geller *et al.* (2006) obtained values lower than 1 for an Euro 3 diesel car, but the ratio increased to around 3.5 and 3.1 for DPF-diesel and Euro 3 gasoline vehicles, respectively. As observed in the present study, Chen *et al.* (2002) also observed OC/EC ratios greater than 1 for carbonaceous aerosols generated by gasoline powered vehicles. Chiang *et al*. (2012) measured the carbonaceous content of PM emitted by light-duty diesel vehicles in a dynamometer study following the driving pattern of the federal test procedure of Taiwan. The EC and OC emission factors were 72 and 37 mg/km. It should be noted that all vehicles were without pollution control equipment and their displacement volume ranged from 2184 to 2835 cc, including inline-four cylinder engines. Oanh *et al*. (2010) characterised the $PM_{2.5}$ from in-use diesel vehicles in Bangkok reporting a maximum EC emission factor of 0.13 g/km for the van group of model years before 1995, whilst other light-duty vehicles presented lower EC (0.01–0.07 g/km). In the same chassis dynamometer tests, OC emission factors ranging from 0.012 g/km (pickup 1999–2004) to 0.067 g/km (van 1995–1996) were obtained.

Volatile Organic Compounds

The measurement of unregulated pollutants comprised about 20 different VOCs in the C_5–C_{11} range. Among these, benzene, toluene and xylenes (BTX) were generally the dominant species. A significant decrease in emissions from Euro 4 to Euro 5 petrol-powered vehicles was observed (Table 4). The trend in VOC emissions is unclear when diesel engines are considered. In general, higher proportions of VOCs in cold-start samples were observed, indicating a larger fraction of unburned fuel in start-up profiles. Higher temperature is prone for the decomposition of VOCs;

Table 3. Average organic carbon-to-elemental carbon ratios.

Vehicle	ArtUrb (Hot)	ArtUrb (Cold)	ArtRoad
Euro 3 Petrol, 1.1 L	BDL	BDL	BDL
Euro 4 Petrol, 1.0 L	30.1	59.6	13.0
Euro 5 Petrol, 1.2 L	34.9	78.1	92.0
Euro 3 Diesel, 1.5 L	0.431	0.482	0.854
Euro 4 Diesel , 1.3 L	0.046	0.049	0.035
Euro 4 Diesel, 1.6 L	0.049	0.070	0.381
Euro 4 Diesel, 2.0 L	186	49.9	BDL
Euro 5 Diesel, 1.7 L	28.7	16.7	BDL

BDL – below detection limit.

Table 4. Emission factors for volatile organic compounds.

Compound	EF (mg/km)		
	ArtRoad	ArtUrb (Cold)	ArtUrb (Hot)
Euro 4, Petrol, Toyota Aygo (2006), 1.0 L			
2,2-dimethylbutane	29.6 ± 5.10	31.8 ± 0.64	33.3 ± 3.72
i-Hexane	144 ± 29	104 ± 6.0	85.2 ± 10.2
n-Hexane	32.5 ± 3.2	23.2 ± 1.4	18.0 ± 2.2
Benzene	139 ± 22	70.8 ± 6.8	51.0 ± 17.7
n-Heptene	10.1 ± 1.2	7.21 ± 0.23	4.76 ± 0.17
n-Heptane	37.6 ± 3.5	35.5 ± 2.4	19.8 ± 1.1
i-Octane	229 ± 88	218 ± 23	249 ± 119
Toluene	191 ± 5.0	250 ± 19	66.4 ± 0.50
Hexanal	4.34 ± 0.46	3.48 ± 0.57	2.44 ± 0.26
n-Octane	39.7 ± 2.5	56.2 ± 4.50	21.8 ± 1.7
Ethylbenzene	51.9 ± 2.6	106 ± 11	20.4 ± 0.20
m,p-Xylene	195 ± 2.0	465 ± 45	75.9 ± 1.7
Styrene	17.9 ± 1.8	36.3 ± 4.4	6.61 ± 0.02
o-Xylene	66.4 ± 0.90	174 ± 21	25.4 ± 1.5
n-Nonane	10.3 ± 0.50	25.3 ± 2.3	6.04 ± 0.01
i-Propylbenzene	4.18 ± 0.13	11.48 ± 0.90	4.51 ± 0.14
Bromobenzene	3.12 ± 0.15	6.02 ± 1.49	ND
1,3,5-Trimethylbenzene	25.6 ± 0.38	138 ± 24	10.9 ± 0.80
1,2,4-Trimethylbenzene + *tert*-buthylbenzene	69.0 ± 7.7	456 ± 84	20.1 ± 27.1
n-Decane	2.88 ± 1.1	10.3± 0.9	1.51 ± 1.94
n-Butylbenzene	8.49 ± 0.52	46.7 ± 1.8	1.26 ± 0.11
3-Methylbenzaldehyde	7.37 ± 0.35	41.9 ± 4.6	3.23 ± 0.23
n-Undecane	0.42	3.03 ± 0.03	0.42
Naphtalene	4.02 ± 2.68	66.9 ± 8.76	BDL
1,2,3-Trichlorobenzene	BDL	3.76 ± 1.95	1.11 ± 0.24
Euro 5, Petrol, Opel Agila (2012), 1.2 L			
2,2-dimethylbutane	BDL	7.37	1.30 ± 0.15
i-Hexane	2.68 ± 0.77	48.0	11.6 ± 3.07
n-Hexane	10.7 ± 2.4	12.1	6.04 ± 1.10
Benzene	5.1 ± 4.60	36.6	12.2 ± 9.2
n-Heptane	BDL	BDL	BDL
n-Heptane	6.37 ± 0.40	9.59	3.07 ± 0.05
Toluene	39.2 ± 3.02	81.9	16.6 ± 0.95
n-Octane	11.5± 0.05	19.9	4.46 ± 0.47
Ethylbenzene	11.9 ± 0.6	25.8	4.44 ± 1.20
m,p-Xylene	44.0 ± 1.2	107	23.3 ± 2.60
Styrene	3.80 ± 0.22	8.93	1.28 ± 0.69
o-Xylene	14.8 ± 0.38	37.8	7.76+1.01
n-Nonane	3.24 ± 0.13	7.58	1.81 ± 0.29
n-Propylbenzene	2.20 ± 0.03	6.59	1.31 ± 0.16
i-Propylbenzene	1.18 ± 0.01	1.31	BDL
1,3,5-Trimethylbenzene	6.49 ± 0.28	22.6	4.71 ± 0.15
n-Decane	BDL	7.83	0.93 ± 0.06
n-Butylbenzene	0.48	BDL	BDL
3-Methylbenzaldehyde	2.18 ± 0.03	6.35	2.44 ± 0.96
n-Undecane	0.55 ± 0.09	1.07	1.38
Naphtalene	0.23 ± 0.03	1.31	1.09
1,2,3-Trichlorobenzene	0.16	2.45	2.82
Euro 4, Diesel, Citroen Xsara Picasso (2006), 1.6 L			
Benzene	33.1 ± 14.0	275	50.0
n-Heptane	6.47 ± 0.97	39.5	22.3
Toluene	14.4 ± 0.75	61.1	10.6
n-Octane	38.2 ± 4.50	128	19.4
Ethylbenzene	4.17± 0.98	6.95	4.37

Table 4. *(continued).*

Compound	EF (mg/km)		
	ArtRoad	ArtUrb (Cold)	ArtUrb (Hot)
m,p-Xylene	10.6 ± 0.50	28.6	12.9
Styrene	2.53 ± 0.20	11.1	3.26
o-Xylene	6.81 ± 0.38	20.6	20.0
n-Nonane	16.1 ± 2.61	102	28.7
n-Propylbenzene	4.00 ± 1.25	5.33	3.06
1,3,5-Trimethylbenzene	4.43 ± 1.06	28.0	7.12
n-Decane	7.86 ±1.03	52.5	21.2
n-Butylbenzene	4.45 ± 2.60	BDL	BDL
3-Methylbenzaldehyde	9.06 ± 1.61	18.3	11.9
n-Undecane	15.3 ± 0.78	47.0	12.5
Naphtalene	4.08 ± 0.51	12.1	8.12
1,2,3-Trichlorobenzene	7.67 ± 0.09	18.3	3.31
Euro 5, Diesel DPF, Opel Astra (2011), 1.7 L			
Benzene	42.3	521	37.8
n-Heptane	26.7	110	BDL
Toluene	9.33	63.3	BDL
n-Octane	77.1	153	19.9
Ethylbenzene	3.25	4.11	BDL
m,p-Xylene	29.6	64.6	0.23
Styrene	2.14	BDL	BDL
o-Xylene	12.4	23.7	BDL
n-Nonane	51.0	112	18.9
n-Propylbenzene	1.04	1.68	2.56
1,3,5-Trimethylbenzene	4.51	10.7	4.39
n-Decane	12.1	53.0	BDL
n-Butylbenzene	BDL	BDL	BDL
3-Methylbenzaldehyde	9.05	17.6	BDL
n-Undecane	2.20	13.5	BDL
Naphtalene	1.12	BDL	BDL
1,2,3-Trichlorobenzene	BDL	0.66	BDL

BDL – below detection limit; ND – not detected.

particularly, benzene, toluene and xylene isomers have been reported to be decreased significantly at higher temperature (Cheung *et al*., 2008; Di *et al*., 2009). Caplian *et al.* (2006) also observed significantly higher VOC emissions during cold-start driving for Euro 1 to Euro 3 diesel and petrol vehicles tested on a chassis dynamometer. In accordance with a previous study by Sheng *et al*. (2006), it was found that gasoline emissions contained, in general, higher abundances of the lower-boiling aromatic hydrocarbons, such as benzene, toluene, ethylbenzene, xylenes, and trimethylbenzene, than diesel. An exception was observed for benzene emissions by diesel-powered vehicles under the ArtUrb driving cycle with cold start. The emission rates of large *n*-alkanes, such as *n*-nonane, *n*-decane, and *n*-undecane were higher in diesel exhaust compared to gasoline. Bromobenzene was only detected in the exhaust emission of the Euro 4 petrol-powered vehicle. The EF of 1,2,3-trichlorobenzene was significantly higher for the Euro 4 diesel car. Compositional differences in emissions may result not only from distinct vehicle technologies and categories, but also from different fuel formulations, fuel additives, efficiencies of catalytic converters, etc.

The emission factors of the present study fall in the range of values reported in the literature. Schauer *et al*. (2002) measured some VOCs in the tailpipe emissions from an in-use fleet of catalyst-equipped gasoline powered automobiles. The vehicles were driven through the cold-start FTP urban driving cycle on a transient dynamometer. The following EFs (mg/km) were reported: benzene - 11.9, toluene - 21.3, ethylbenzene - 4.18, *o*-xylene - 5.41, *m,p*-xylene - 14.3, and 1,3,5-trimethylbenzene - 1.98. Ho *et al*. (2009) determined vehicle emissions of VOCs at the Shing Mun Tunnel, Hong Kong, in 2003. The five most abundant species observed in the tunnel were, in decreasing order, ethene, toluene, *n*-butane, propane and *i*-pentane. The high propane and *n*-butane emissions were found to be associated with liquefied petroleum gas (LPG)-fuelled taxis. In relation to the dynamometer results of the present study, the mean BTEX emissions factors (mg/veh/km) derived from the tunnel experiment in Hong Kong were substantially higher: 4.5 ± 0.9 benzene, 1.3 ± 0.4 ethylbenzene, 12 ± 3.9 toluene, 1.6 ± 0.6 *o*-xylene, 2.6 ± 0.9 *m*-xylene and 1.1 ± 0.4 *p*-xylene. Shah *et al.* (2012) observed a substantial abatement in VOC emissions for a compressed natural gas fuelled vehicle as compared to a gasoline vehicle. An overall decrease of about 86% was reported for BTEX. The 1.3 L gasoline passenger vehicle tested on a chassis

dynamometer was an Euro 3, emitting 6.01, 11.9, 5.02 and 5.24 mg/km of benzene, toluene, *m,p*-xylene and *o*-xylene, respectively. Araizaga *et al.* (2013) performed a tunnel study in Monterrey (Mexico) in 2009, where 97% of vehicles were gasoline-powered. The average EFs (mg/veh/km) of the main emitted species were: *i*-pentane 47.5 ± 9.5, toluene 42.9 ± 3.9, ethane 32.4 ± 1.5, *n*-pentane 25.8 ± 3.4, acetylene 19.5 ± 0.5, propane 17.5 ± 1.8, benzene 15.9 ± 2.0, *m,p*-xylene 14.5 ± 3.5, 2,2,4-trimethylpentane 13.4 ± 5.0, and *i*-butane 10.3 ± 5.4. Differences in BTEX emission among studies may be related to the fact that vehicle exhaust gases typically contain aromatic compounds; however, toluene and xylenes are also found in solvent emissions while benzene is not. Thus, EFs obtained from tunnel measurements, where evaporative emissions are also captured, will be higher than those derived from exhaust sampling at dynamometer facilities. In addition, characteristic VOC emissions may directly reflect the vehicle technology and age, the local driving conditions and the specific formula of gasoline or diesel fuel used. All these aspects also demonstrate the need to establish local emission profiles.

CONCLUSIONS

The analyses have revealed quite contrasting emission behaviours for diesel (rather sensitive to speed and stop parameters) and petrol-powered engines (rather sensitive to accelerations). The temporary ineffectiveness of motor vehicle emission controls at start-up causes emission rates to be much higher, suggesting that the importance of cold-start emissions may be underestimated in current emission inventories. The technological development of the automobile industry appears to have had a positive impact on the CO and particle emissions, but an unclear impact on the NO_x and HC emissions, and a negative impact on the CO_2 emissions. Periodic performance checks, proper maintenance and repairs for those vehicles that fail emission tests are strongly encouraged, whilst tampering with emission control devices is unadvisable. Taking into account the evolution of new diesel vehicles equipped with after treatment systems, the current gravimetric methods for the legal determination of emissions will have difficulties accurately quantifying PM mass emissions. For this reason, it will be necessary to establish other monitoring programmes based on particle characteristics, such as size distributions and chemical composition. High OC/EC were obtained for gasoline-fuelled and modern diesel vehicles with PM emission control technologies. Thus, although the European fleet still have a great representation of vehicles < Euro 4, in the near future, the adoption of OC/EC minimum ratios less than 1 to represent primary vehicular emissions in source apportionment studies must be re-evaluated. Considering the small number of vehicles per category, these results should be faced as indicative and complementary tests are recommended.

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