Emission Factors and Detailed Chemical Characterization of PM and VOCs from 5 in-use Petrol and Diesel Passenger cars

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1. Introduction

Today, diesel exhaust particles represent a very hot topic. The link between long-term residential exposures to high level of particle matter (PM) derived from traffic and several adverse health outcomes is now well established (Araujo et al, 2009, Iannuzzi et al 2010). Improving air quality for reducing morbidity and premature death has become an urgent need. In addition to health outcomes, multiple impacts of vehicle exhausts on environment were highlighted, including particularly their impact on global warming, acid rain and urban ecosystem (Bell et al, 2011). Volatile organic compounds (VOCs) are also an important part of the mobile source combustion emissions. They are part of the primary pollutants from road traffic, and are also the precursors of photo-oxidants which are formed under the influence of sunlight in ambient conditions (Seildfeld and Pandis, 1998). Many carbonyls are classified as toxic air pollutants by the World Health Organization (WHO). Several studies about the characterization of particulate emissions from passenger cars have been performed in the USA (Schauer et al 2002, Zielinska et al, 2012) and in Asia (Oanh et al 2010), for heavy-duty diesel vehicles (Biswas et al 2008, Biswas et al 2009, Yanowitz et al, 1999). In Europe, few studies have characterized PM or VOCs emissions from the exhaust of passenger cars (Kerminen et al, 1997, Geller et al 2005, Ntziachristos et al, 2004b, Weilenmann et al, 2009). The detailed chemical characterization of exhausts from typical diesel and petrol passenger vehicles currently in use in Europe is needed. Previous European works dedicated to the determination of VOCs in exhaust emissions were performed some time ago, from 1991 to 1995 (Fontaine, 2000), 1989-1999 (Flandrin, 2000), 1993-2001 (Caplain, 2006). The vehicles that were tested are now old or no longer in use, and no more representative of the current traffic.

This paper presents results about the detailed characterization of particulate organic and inorganic compounds and VOC's from recent passenger cars, i.e. 3 diesel and 2 petrol in-use and representative cars, tested over real-world driving cycles from the Artemis project (André, 2004).

2. Experimental

2.1 Selected vehicles and driving conditions

In 2011, France supports a large fleet of diesel vehicles with 68.5 % of diesel vehicles and 31.5% of petrol vehicles. The major part of the fleet complies with emission standards from Euro 2 to Euro 5.

The vehicles were selected to represent the French fleet according to the European emission regulation (EURO classes), the motorization (diesel or petrol), the engine capacity (defined as below 1.4 L, 1.4 to 2 L, above 2 L), and the possible after-treatment system. Current models and vehicle manufacturers were preferred whenever possible. Selected vehicles are the following:

- A 2003 Euro 3 diesel vehicle (Citroën Picasso 1.9dCi), with a total mileage of 140000 km and a 25 000 km-aged catalyst (Euro 3D)
- A 2005 Euro 4 diesel vehicle (Renault Kangoo 1.5dCi), with 146 000 km (Euro 4D),
- A 2009 Euro 4 diesel vehicle (Audi) , equipped with a diesel particle filter (DPF), 73 800 km (Euro 4D DPF),
- A 1999 Euro 2 petrol vehicle (Ford KA 1.3dCi), with 72 000 km (Euro 2P),
- A 2006 Euro 4 petrol vehicle (Renault Clio 1.4dCi), with 82 000 km (Euro 4P).

Selected vehicles were driven on a chassis dynamometer under two real-world Artemis driving cycles, developed within the framework of the Artemis project. The ARTEMIS Road (ArtRoad)

and ARTEMIS Urban (ArtUrb) cycles are representative of real driving behaviour in rural and urban areas, respectively (André, 2004; André et al. 2006). Each vehicle was driven with both urban driving cycles with cold- (ArtUrb-C) and hot- start (ArtUrb-H). The regulated NEDC driving cycle (New European Driving Cycle) was also performed, but for the measurements of regulated gases only (CO, CO_2, NO, NO_2, total hydrocarbons, particle mass) in order to check whether the vehicle was still complying with its Euro emission class. ArtRoad and ArtUrb-C cycles were repeated twice and ArtUrb-H only once per vehicle. The Euro 4D DPF vehicle was however tested with only one ArtRoad and two ArtUrb-C and ArtUrb-H cycles.

2.2 Sampling

Tests were conducted on the IFSTTAR Chassis dynamometer (Lyon, France). Vehicle exhausts were primarily diluted with filtered ambient air through a constant volume sampling system (CVS). Measurements and samplings were conducted from the dilution tunnel. The sampling system included 2 lines dedicated to the sampling of particulate and three inlets dedicated to the sampling of VOCs. Quartz fibre filters (47mm) have been used for the sampling of particles. Quartz filters were pre-baked at 500℃ for 8h and s tored in baked aluminum foil-lined containers prior to their use. Sampled flows for particle collection were adapted according to emission levels of the tested vehicles (from 5 to 50L/min). The diluted exhaust gas was pulled through a DNPH coated silica cartridge for collection of carbonyls and ketones compounds (flow rate of 1l/min) and through TENAX/carbosieve III cartridges for the collection of hydrocarbons (C6-C15) (flow rate of 150 ml/min. Laboratory blanks, processing blanks and dynamic blanks (sampling of dilution air from dilution tunnel in the same conditions as the exhaust samples without emissions) were recorded. Samples were stored at 4-6℃ before analyses. The dynamic blanks were determined several times a day, and have been used for the correction of the final results. One sampling for gases and PM was performed during the whole duration of each tested configuration, and Emission Factors (EF) were subsequently calculated knowing the concentrations and mileage for each cycle.

2.3 Analysis

The elemental and organic carbon (EC and OC) content of deposited PM was analysed with the thermo-optical method EUSAAR2 (Cavalli et al, 2010). Filters were extracted by a solvent mixture acetone/DCM 50-50 v/v with an Accelerate Solvent Extractor (ASE 200, Dionex). PAHs (Phenanthrene, Anthracene, Fluoranthene, Pyrene, Triphenylene, Retene, Benz(a)anthracene, Chrysene, Benzo(e)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Benzo(ghi)perylene, Dibenzo(a)anthracene, Indenopyrene, Coronene) were analysed by HPLC-UV. Apolar (Alkanes (C11-C40, phytane, pristane, hopanes) and polar compounds (Levoglucosan) after derivatization were analysed by GCMS (Piot, 2012). Inorganic compounds including metals and trace elements were analysed by ICP-MS and ions by Ion Chromatography. The measurement of regulated pollutants was performed with a series of analysers (HORIBA). Carbonyl compounds collected on DNPH cartridge were eluted with 3mL of HPLC grade acetonitrile (ACN) and analysed by HPLC-mass (LCQ Fleet MS) with a solvent gradient water/ACN. Metals composition was not analysed for the Euro 4 petrol.

3. Results

1. Particle phase: Comparison between the 5 passenger cars tested

The average chemical composition of the PM for the ArtRoad cycle is given figure1. This chemical speciation includes EC/OC, NH_4^+, NO_3^-, SO_4^{2-}, others ions like Cl^-, NO_2^-, Br^-, oxalate, Na^+, K^+, Mg^{2+}, Na^+, and metals (33 compounds). The Organic Matter fraction (OM) was calculated according to an OM-to-OC conversion factor of 1.2 (El Haddad et al, 2011).

Each vehicle was tested only once or twice for a specific cycle. However, the variation coefficients of the EF (ratio between the standard deviation and the average of emission factors (EFs) for each cycle) have been calculated with the Euro 3D which was tested several times for the same cycle. The range of coefficient of variation for ArtRoad cycle is 40-60% depending on the species analysed. It is 11-30% for the ArtUrb-C and 3-40% for the ArtUrb-H. In our case, the variability for the same test and the same vehicle could be due to the emission part (reproducibility of the cycle, operating conditions) or the sampling and analysis parts (collection efficiency, sampling representatively).

The EFs of the 5 passenger cars show strong variations (Table 1). The EC/TC ratios ranged from 0.65 to 0.78 for diesel cars and from 0.14 to 0.38 for petrol cars. This is in agreement with the ratios values of 0.7 and 0.4 for diesel and petrol cars respectively found by Zielinska et al (2004) and Geller et al (2006).The Euro 3D produced significantly higher PM concentrations (sum of the total components analysed) than the Euro 4D and Euro 4D DPF. Emission factors of total components analysed were 42.2 mg/km, 29.7 mg/km and 297 µg/km for the Euro 3D, the Euro 4D, and the Euro 4D DPF, respectively. The use of a DPF on a diesel passenger car induces a large decrease of the particulate emissions (Ntziachristos et al, 2005). The strong variation of the EC proportions in the total components analysed can be highlighted, with fractions of 70%, 63% and 9% for Euro 3D, Euro 4D and Euro 4D DPF, respectively. This is in agreement with previous works (e.g. Oahn et al, 2010). The DPF-diesel vehicle demonstrates the lowest EC-OC carbon mass emissions due to the effective removal of solid particles by the catalysed DPF (Geller et al, 2006). Similarly to observations by Geller et al. (2006), OC EFs were higher than EC EFs for the Euro 4D DPF. However, the Euro 4P shows a higher EC EF for the ArtRoad cycle than the Euro 4D DPF, but this result is reversed for the ArtUrb-C and ArtUrb-H cycles. The Euro 2P shows an EF of EC higher than the Euro 4P only for the ArtUrb-C (259 µg/km and 114 µg/km, respectively). In conclusion, diesel cars were the highest emitters of EC for the cycles, except for ArtRoad. The same trend is noticeable for OM, but the emissions of Euro 2P are always higher than the Euro 4D DPF ones.

The chemical composition of petrol exhaust differed strongly from the diesel exhaust one. First, the former showed lower EFs of major ions like NH_4^+ and SO_4^{2-} and much higher proportions of OM and trace metals elements (representing only 73% and 24% of the total mass analysed, respectively). Second, the sum of the PM measured for the Euro 2P composition was about 300 µg/km for the ArtRoad cycle, i.e. lower than for the Euro 3 and Euro 4 D but same as the Euro 4 D DPF. Moreover, very low concentrations of particulate alkanes and PAHs were measured for the Euro 4P (about 2.2×10^{-2} µg/km) driven with the 3 cycles. However, the Euro 2P and Euro 4D DPF were the highest emitters of PAHs (on average 34.8 and 6.3 µg/km, respectively), particularly with ArtUrb-C (73.5 and 108 µg/km, respectively), but the Euro 4D had the lowest EFs for the same species. The Euro 3 and Euro 4D were the highest emitters of alkanes (on average 97 and 21 µg/km, respectively). The same trends were observed for the ArtUrb-C. To conclude, diesel cars were the highest emitters of alkanes for the 3 cycles, but petrol cars were the highest emitters of PAHs for the cycles, except for the ArtUrb-C where the Euro 4D DPF emitted more than others (108 µg/km).

The relative proportions of trace metals were quite the same for these 3 diesel cars, but EFs were different: the Euro 4D DPF emissions released on average about 99% lower emissions of metals per kilometer driven, as already indicated by Geller and al (2006) (about 70-95% of reduction of metals elements with a DPF). The difference between ArtUrb-C and ArtUrb-H cycles was even larger, with about 15 mg/km for the Euro 3D and 2×10^{-2} mg/km for the Euro 4D DPF. Results for the Euro 4D were close to the Euro 3D ones. The major trace elements for diesel and petrol vehicles were Al, Ca, Fe, K, Mg, Mo and Na. The largest differences between the Euro 4D and the Euro 4D DPF were observed for Ba et Cd, whose emission rates were almost 600 times higher for the Euro 4D. Euro 2 petrol emissions were only about 13 times larger than the ones of the Euro 4D DPF. The largest differences between the Euro 2P and the Euro 4D were observed for Zn (55 times higher for the Euro 4D), and for Sr, Mo and La (almost 45 times higher for the Euro 4D). Emissions of the lubricant oil additives (Ca, Zn) were decreased by >99% for the DPF-equipped vehicles compared to the Euro 4D, as indicated by Hu et al (2009). It has been shown that Ca and Zn were the major compounds of ash metals collected onto the surface of the DPF (McGeehan et al, 2005). In our study, major compounds were Al, Ca, K, Mo, and Fe. Zn and Ca concentrations were below the detection limit of the method for the two cycles for the Euro 4D DPF. The 2 diesel cars without DPF were the highest emitters of these metals elements, followed by the Euro 2P then the Euro 4D DPF.

Table 1: Emissions factors (µg/km) for the 5 passenger cars for the particle phase during the ArtRoad cycle.

	Sum	EC	OM	others ions	SO_4^{2-}	NO_3^-	NH_4^+	Metals	Alkanes	PAHs
Euro 3D	42442	29486	8123	0	0	0	0	4731	97	4
Euro 4D	29730	18615	6273	53	9	56	2	4700	21	0.01
Euro 4D DPF	300	24	167	7	0.32	35	10	37	14	6
Euro 2P	298	0	185	3	1	0	3	60	10	35
Euro 4P	167	55	112	0.03	0	0	0	unid.	0.02	0.02

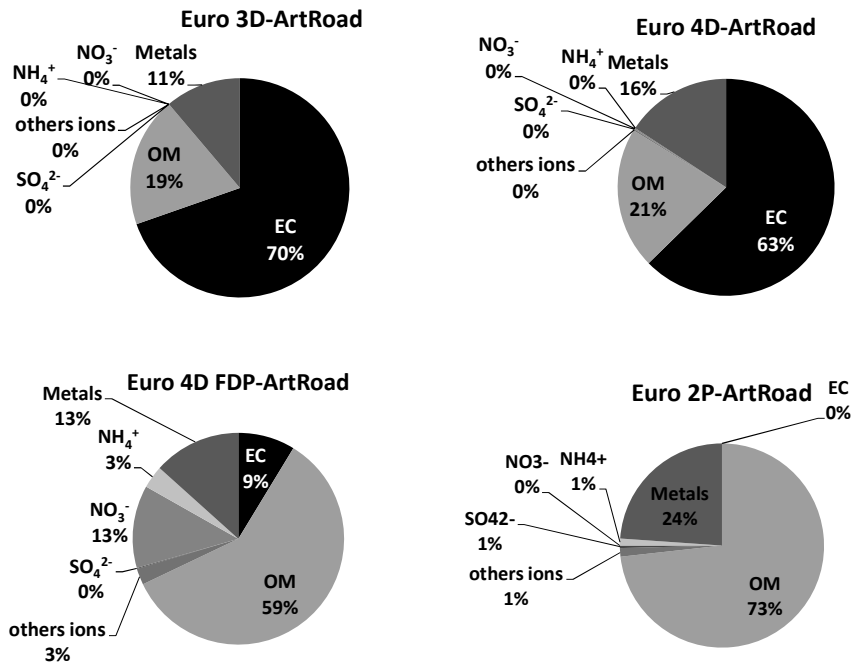

Figure 1: Chemical composition for components analysed of diesel and petrol particulate emissions for 4 vehicles driven with ArtRoad cycle

2. Gas Phase

Figure 2 displays the relative proportions of aldehydes, alkanes and aromatics in the exhaust of the 5 passenger cars tested with the ArtRoad cycle. The sum of the analysed VOCs (CH_4 not included) explains 7-16% of the total hydrocarbons (HCT), with 15 carbonyls (C1-C9), 13 aromatics (C6-C10 and isomers) and 13 alkanes (C6-C16) compounds measured.

The highest proportions of aldehydes, alkanes and aromatics were produced by the Euro 3D and the lowest proportion of aldehydes by the Euro 2P. However, the Euro 2P had the highest EF of THC (on average 68 mg/km) and the Euro 3D had the second highest EF (on average 36.3 mg/km, see table 2). Compared to the Euro 4D, the Euro 4D DPF THC EFs for the ArtUrb-C and the ArtUrb-H cycles were 3 times higher (between 31 and 42 mg/km for the Euro 4D DPF and between 14 and 11 mg/km for the Euro 4D). Moreover, the Euro 4D DPF driven with urban cycles released three times higher concentrations of aldehydes and 10 times higher concentrations of alkanes and aromatics than the other vehicles. After comparison with results from a previous study PROPCARB (Pillot and al, 2009), we can conclude that the Euro 4D DPF has on average a higher EF of THC than the average of other Euro 4D DPF tested within the PropCarb project for the ArtUrb cycle. Overall, the diesel vehicles tested have lower VOC EF than the petrol ones, as already pointed out by Caplain et al (2006).

The Euro 4D THC emissions were 7 times lower than the ones of the Euro 3D but the former ones included 46% of CH_4. Its total aldehyde EF was 14 times lower than the Euro 3D one but was close to the ones of the Euro 4D DPF. Alkanes and aromatics compounds in the exhaust of the Euro 4D DPF were below the detection limit. As opposed to the results from the ArtRoad cycle, the Euro 4 DPF EFs for aldehydes, alkanes and THC were 2-4 times higher than the ones of the Euro 4P during the ArtUrb-C and ArtUrb-H. However, its EFs of aromatics were lower than the Euro 4P ones. The highest fraction of the measured hydrocarbons was observed for aldehydes in the Euro 4P exhausts, but the amount was 5 times lower than for the Euro 2P. The Euro 4D THC emissions were lower than the Euro 4P ones when vehicles were ran with the ArtUrb-C cycle, in agreement with Weilenmann (2009). Moreover, the transition from Euro 2P to Euro 4P shows a twenty-fold decrease for cold-start emissions and a twelve-fold decrease for the ArtRoad cycle. Other important unidentified compounds may possibly be produced by these vehicles.

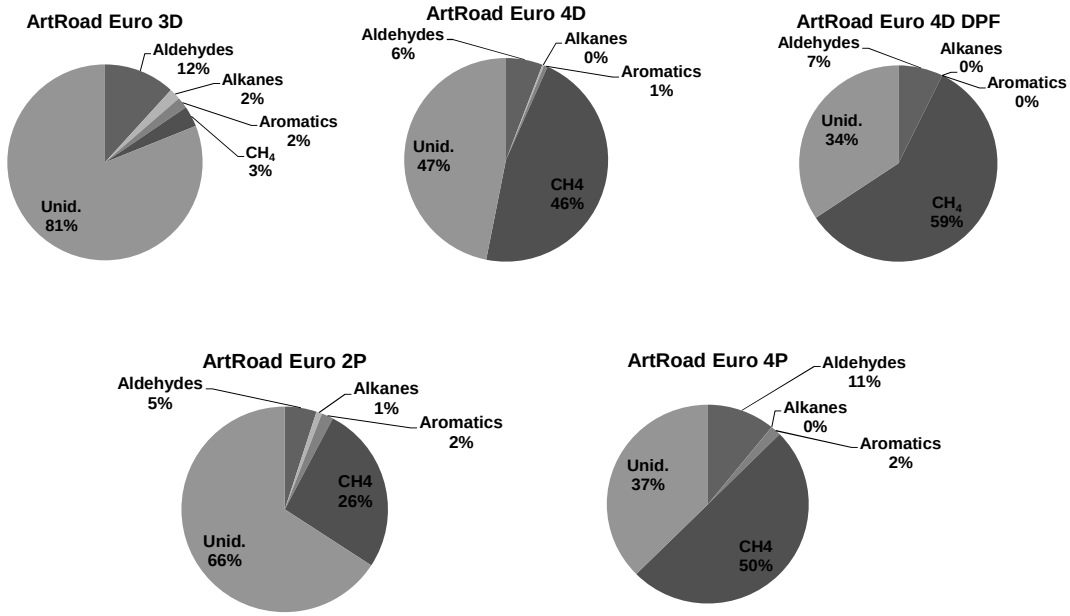

Figure 2: Relative proportions of VOC emissions in the exhaust of 5 passenger cars

Table 2: Gas phase emission factors for 5 passenger cars (mg/km) for the ArtRoad cycle. The Limit of Detection (DL) is 226 ± 36 ng/support depending of compounds (alkanes and aromatics).

	Euro 3D	Euro 4D	Euro 4D DPF	Euro 2P	Euro 4P
Aldehydes	4.28	0.31	0.46	3.37	0.61
Alkanes	0.68	0.01	<DL	0.62	<DL
Aromatics	0.67	0.03	<DL	1.25	0.10
Total sum	5.63	0.35	0.46	5.24	0.71
CH4	1.24	2.43	3.69	17.97	2.80
HCT	36.26	5.24	6.32	67.87	5.61

4. Conclusions

This study reports detailed chemical composition for the particulate and the gas phases for diesel and petrol passenger cars typically in use in Europe. Results show several differences between diesel and petrol exhausts, various engine configurations and diesel vehicles with or without DPF. The mass of the chemically determined PM shows a two-fold decrease between the Euro 2P and the Euro 4P, and a 1.4 times decrease between the Euro 3D and the Euro 4D. Moreover, the Euro 4D emissions of identified PM are much larger than for the Euro 4P. The identified total sum of PM emission factors of the Euro 4D DPF is 100 times lower than the Euro 4D ones. The results for the gas phase are quite different. THC emissions show a twelve-fold decrease between the Euro 3D and the Euro 4D and between the Euro 2P and the Euro 4P. As opposed to the particulate phase, the Euro 4D DPF does not show any significant decrease for HCT EF in comparison with the Euro 4D. Furthermore, the largest differences between the Euro 4D and the Euro 4D DPF were observed for urban cycles. The latter vehicle emitted aldehydes, alkanes, PAHs and THC EFs between 3 and 10 times higher than the first one. Its emissions of aldehydes, alkanes and THC were 2-4 times higher than the Euro 4P ones during the ArtUrb cycles. Since the number of tested vehicles is relatively low, the results obtained should be considered with caution.

Acknowledgments

This project is funded by the French environmental agency (ADEME CORTEA programme, n°1162C0002). One of us (L.P.) acknowledges support from a Rhône Alpes Region PhD grant.

The authors thank Patrick Tassel and Pascal Perret for technical operations during the chassis dynamometer experiments and staff from LGGE for chemical analysis.

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