Euro 6 unregulated pollutant characterization and statistical analysis of aftertreatment device and driving condition impact on recent passenger car emissions

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Abstract

12   This study aims to measure and analyze unregulated compound emissions for two Euro 6 diesel and

13   gasoline vehicles. The vehicles were tested on a chassis dynamometer under various driving cycles:

14   Artemis driving cycles (urban, road and motorway), the New European Driving Cycle (NEDC) and the

15   World Harmonized Light-Duty Test Cycle (WLTC) for Europe, and world approval cycles. The

16   emissions of unregulated compounds — such as total particle number (PN) (over 5.6 nm), black

17   carbon (BC), NO_2, BTEX (benzene, toluene, ethylbenzene and xylene), carbonyl compounds and

18   polycyclic aromatic hydrocarbons (PAHs) — were measured with several on-line devices and

19   different samples were collected using cartridges and quartz filters. Furthermore, a preliminary

20   statistical analysis was performed on eight Euro 4-6 diesel and gasoline vehicles to study the impacts

21   of driving conditions and aftertreatment and engine technologies on emissions of regulated and

22   unregulated pollutants. The results indicate that urban conditions with cold start induce high

23   emissions of BTEX and carbonyl compounds. Motorway conditions are characterized by high

24   emissions of particle numbers and CO, which mainly induced by gasoline vehicles. Compared with

25   gasoline vehicles, diesel vehicles equipped with catalyzed or additive DPF emit fewer particles but

26   more NOx and carbonyl compounds.

27

Keywords

29   Regulated and unregulated pollutants; Emission factors; Euro 6 vehicles; Chassis dynamometer;

30   Driving conditions; Aftertreatment systems

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33   **Abbreviation list**

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35	DPF	Diesel Particulate Filter
36	DI	Direct Injection
37	NEDC	New European Driving Cycle
38	WLTC	World harmonize Light-duty Test Cycle
39	PN	Particle Number
40	BC	Black Carbon
41	BTEX	Benzene, Toluene, Ethylbenzene, Xylene
42	PAH	Polycyclic Aromatic Hydrocarbon
43	DOC	Diesel Oxidation Catalyst
44	SCR	Selective Catalytic Reduction
45	TWC	Three-Way Catalyst
46	PCA	Principal Component Analysis
47	DCI	Direct Common rail Injection
48	CVS	Constant Volume Sampler
49	CPC	Condensation Particle Counter
50	PMP	Particle Measurement Program
51	ELPI	Electrical Low Pressure Impact
52	FMPS	Fast Mobility Particle Sizer
53	AE	Aethalometer
54	ArtUrb C	Artemis Urban with Cold start
55	ArtUrb H	Artemis Urban with Hot start
56	ArtROAD	Artemis Rural
57	ArtMW	Artemis Motorway
58	Add DPF	Additive DPF
59	Cat DPF	Catalyzed DPF

60

Introduction

Road transportation (more particularly, light-duty vehicles) is one of the main causes of air pollution. In urban areas, road traffic represents the main source of emissions of regulated pollutants as well as unregulated pollutants, such as BTEX, PAHs, and carbonyl compounds (*1*). Several of these pollutants have an important role in climate change while others could lead to serious negative impacts on human health (*2-4*).

To reduce road traffic emissions, the European Union is imposing increasingly stringent emission limits for regulated compounds. Various aftertreatment devices — such as the diesel oxidation catalyst (DOC), the diesel particulate filter (DPF), the selective catalytic reduction (SCR) or NO_X trap and the three-way catalyst (TWC) — are being used to bring the pollutant emissions below regulatory levels (*5-7*). Although these technologies make it possible to significantly reduce regulated compound emissions, they affect some emissions of pollutants. Catalyzed or additive DPF reduce particle mass emission, with efficiency near 100%, but they might induce an increase of fine and ultrafine particle emissions, and affect NO_2, volatile organic compound, PAH, BTEX, and black carbon (BC) emissions (*8-15*). The actual impacts of these aftertreatment technologies on unregulated pollutant emissions are not fully known (*13, 16-20*). The recent study by Louis et al. (*14*) showed that catalysed DPF vehicles emitted about 3 to 10 times more carbonyl compounds and particles than additive DPF vehicles, respectively, during urban driving cycles, while additive DPF vehicles emitted 2 and 5 times more BTEX and carbonyl compounds during motorway driving cycles.

Vehicle emissions are also affected by driving conditions. In the case of diesel vehicles, urban driving conditions or high engine RPM (revolutions per minute) involves high emissions of CO, NO_X and HC compared to a steady speed profile or low engine speed (*21-23*). For gasoline vehicles, cold start and high-speed conditions induce high emissions of the same compounds (*21-25*). For urban driving conditions, diesel vehicles emit more NO_X during hot start compared to cold start (*13, 14*). Various studies also show that cold start results in significant emissions of BC, PAHs, BTEX and aldehyde (*9, 12, 14, 21, 24-28*) compared to urban hot start. A vehicle running low speed produces high PAH and carbonyl compound emissions while a vehicle running at high speed produces high particulate emissions (*12, 26-28*). Emission factors of unregulated compounds reported in the aforementioned papers have been measured with Euro 1 to Euro 5 diesel and gasoline vehicles with a relatively small number of vehicle samples: six Euro 4–5 vehicles by Louis et al. (*15*), four Euro 2–4 vehicles by Rehn (*25*), and 25 Euro 1–3 vehicles by Caplain et al. (*26*). Emissions of unregulated compounds by Euro 6 vehicles have not been yet measured. Moreover, unregulated compound emission factors were often measured under Artemis driving conditions. Impacts of the WLTC (World Harmonize Light-Duty Test Cycle, future world approved driving cycle) on such emissions have not been studied to date.

In this paper, two recent in-use Euro 6 vehicles – diesel with catalyzed DPF and NO_X trap and gasoline direct injection (DI) with propulsion engine – were tested under Artemis urban, road and motorway, WLTC, and NEDC (New European Driving Cycle) driving cycles. Unregulated compound emissions were measured to improve knowledge on their emissions under different driving conditions and supplement the emission factor database used by diverse emission models. Furthermore, Clairotte et al. used the Principal Component Analysis (PCA) statistical analysis method for two mopeds (*31*) and two light duty flexible-fuel vehicles (*19*) to investigate the impact of driving conditions on vehicle emissions. This method makes it possible to analyze the effects of low temperature on cold start gaseous emissions and deeply characterize online emission patterns. Our

105 research thus used preliminary PCA to study the impacts of technologies and driving conditions on
106 regulated and unregulated emissions of pollutants from eight Euro 4–6 diesel and gasoline vehicles
107 tested in this research and previous studies (*15*).

108 **1. Materials and Methods**

109   **1.1. Characteristics of the vehicles**

110   One Euro 6 gasoline vehicle with a direct injection system, TWC, and propulsion engine (Vehicle
111 1) and one Euro 6 diesel vehicle with DOC, catalyzed DPF, and NO_X trap (Vehicle 2) were tested. The
112 propulsion engine was located at the rear of the rear-wheel drive vehicle. The technical
113 characteristics of the two Euro 6 vehicles are given in Table 1.

114 **Table 1. Technical characteristics of tested Euro 6 diesel and gasoline vehicles**

Vehicle	No. 1	No 2
Size class	0.9 DI	1.5 DCI
Technology	Gasoline	Diesel
Standard	Euro 6b	Euro 6b
Engine capacity (cm^3)	999	1461
Empty weight (kg)	864	1087
Mileage (km)	2164	4700
Gearbox type	Manual (5)	Manual (5)
Aftertreatment systems	TWC	DOC + Catalyzed DPF + NO_X trap
Registration date	12/11/2015	12/31/2015
Test date	03/31/2016	04/14/2016

115   **1.2. Experimental set-up**

116   Vehicle emissions were measured on the chassis dynamometer at the Transport and
117 Environment Laboratory (LTE) of the French Institute of Science and Technology for Transport,
118 Development and Networks (IFSTTAR). Exhaust gas was collected at the outlet of the tailpipe, and
119 sent through the constant volume sampler (CVS) to be diluted with filtered air. Pollutant emissions
120 were measured at the outlet of the CVS by various on-line gas and particulate analyzers and were
121 sampled on various filters and cartridges for off-line analysis.
122   Measurements were performed for five different driving cycles — NEDC, European approval
123 cycle, WLTC, world approval cycle, and Artemis urban, road and motorway driving — cycles that are
124 more representative of real-word driving conditions (*29, 30*). The characteristics of the driving cycles
125 are given in Table 2. Each cycle was repeated two to six times under the same experimental
126 conditions in order to check the emission level and exclude high emission vehicles. The only
127 exception was NEDC, for which only one measurement was conducted for each vehicle. All the
128 experiments (this research and previous studies) were performed using commercial fuel (less than 10
129 ppm sulfur content) from the same filling station to minimize the impact of fuel composition on
130 emissions. All the diesel and gasoline vehicles were filled with fuel meeting the requirements of EN

590 and EN 228, respectively. The detailed fuel properties are given in the Table S1 in the Supporting Information.

Table 2. Characteristics of the driving cycles

Cycles	Start	Mileage (km)	Duration (s)	Average speed (km/h)	CVS flow (m^3/min)
NEDC	Cold	11.2	1180	34	9
WLTC	Cold	23.25	1800	47	13
Artemis Urban	Cold/Hot	4.47	921	17	9
Artemis Road	Hot	14.7	862	61	9
Artemis Motorway	Hot	23.7	736	116	13

1.3. Analytical methods

Concentrations of regulated compounds used in PCA analysis (Section 3.4 herein) were measured using a HORIBA analytical emissions system. The analyzer using infrared absorption principle was used to measure carbon monoxide (CO), carbon dioxide (CO_2), flame ionization detection to total hydrocarbon (THC) and methane (CH_4) and chemiluminescence for nitrogen oxides (NO_X) and nitrogen oxide (NO). The concentration of nitrogen dioxide (NO_2) is determined by subtracting NO from NO_X. The concentration of CO_2 was also measured with a MIR-2M (Multi-gas InfraRed; Environment SA), which also uses infrared absorption. Both CO_2 analyzers show good correlation between measurements, with a relative gap of about 2%.

The total particle number was measured with condensation particle counter (CPC, 3775 TSI). The CPC has a butanol condensation chamber enabling the detection of particles between 4 nm and 2 µm. The instrument was operated once a second at 1.5 L/min, with a concentration range of 0 to 10^7 particle/cm^3. The Particle Measurement Program (PMP) has been proposed by the direction of Joint Research Center (JRC), a Directorate-General of the European Commission, as regulatory method for measuring particle numbers for Euro 5 and Euro 6 vehicles. PMP makes it possible to remove volatile particles with a 50% cut-point size of 23 nm. One of the main reasons for cutting volatile particles is that the measurement of non-volatile particles is more repeatable. However, studies by Louis et al. (*15*) showed that most particles emitted by tested Euro 4–5 vehicles were ultrafine particles with diameters of less than 23 nm. In order to obtain the fullest amount of data on total particle number emissions, the PMP was not used in this study. Furthermore, taking into account this volatile part, standard variations of particle number quantification with six repeated driving cycles ranged between 7 and 20%, which was quite low.

The particle size number distribution was measured with two different devices. The first was the Electrical Low Pressure Impactor (ELPI; DEKATI), which has 12 filter stages and determines particle number distributions from 7 nm to 10 µm. The ELPI was operated once a second at a flow rate of 10 L/min. The minimal detection limit ranged from 250 to 0.1 particles/cm^3 depending on the impactor stage. The second devices what the Fast Mobility Particle Sizer (FMPS; TSI), which measures the total particle number and distribution ranging from 5.6 to 560 nm, with a concentration range from 0 to 10^7 particle/cm^3 and with a flow rate of 8 L/min. The particle numbers obtained by these three devices were fairly well correlated, with a relative gap of about 20%. This gap might be explained by the fact that measurements of the size range of particles are not the same for all three devices.

The black carbon concentration was measured using an aethalometer (AE 33-7, Magee Scientific). The experimental data were collected once a second with the instrument operating at a flow rate of 5 L/min. The detection limit for 1 hour was 5 ng/m^3 with a concentration range of 10 to 10^5 ng/m^3. Light attenuation was measured at seven wavelengths, from UV to IR (370, 470, 525, 590, 660, 880 and 940 nm). The 880 nm wavelength corresponding to the maximum amount of black carbon was used for black carbon quantification in this study.

Unregulated compounds, such as BTEX, carbonyl compounds and PAHs, were sampled on various cartridges or quartz filters. Emissions of three repeated Artemis cycles or two repeated WLTC cycles were sampled on one cartridge to collect enough pollutants for chemical analysis. Before each exhaust sample, one blank sample (dilution air in CVS) was collected under the same experimental conditions. Gas phase PAHs were collected with ORBO 43 cartridges. The sampling flow rate was 0.5 L/min. Particulate phase PAHs were collected on quartz filters at a flow rate of 50 L/min. BTEX were collected on Tenax cartridges at a flow rate of 0.5 L/min. Carbonyl compounds were collected on DNPH cartridges at a flow rate of 2 L/min. The cartridges and filters were analyzed by TERA-Environment, a private laboratory with standardized analytical methods (for detailed of the analytical methods see ISO-16000-6, ISO 16000-3, NIOSH 2549, NIOSH 5506 and NF X43-025) (See Table S2 in the Supporting Information). The complete list of compounds analysed using the cartridges and filters, which includes six BTEX, 11 carbonyl compounds and 16 PAHs, is given below.

- BTEX: benzene, toluene, ethylbenzene, m-xylene, p-xylene, o-xylene

- Carbonyl compounds: formaldehyde, acetaldehyde, acetone, acrolein, propionaldehyde, crotonaldehyde, methacrolein, butanal, benzaldehyde, pantanal, hexanal

- PAHs (gas and particulate phases): naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b,j)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene

1.4. Statistical analysis

The impacts of driving conditions and technologies on emissions produced by two Euro 6 vehicles (tested in this study) and six Euro 4–5 vehicles (tested in previous studies by Louis et al. (*15*)) were investigated using a statistical analysis method, i.e., the Principal Component Analysis (PCA). The basic objective of PCA is to reduce the data set and find the best space to project the variables. This dimension reduction process creates a limited number of eigenvectors called "principal components", which are linear combinations and explain most of the total variance of the data set. This method was used by Clairotte et al. (*31*) to separately analyze two motorcycles with around 20 measured pollutants. In this case, the variables corresponded to emission factors measured for 32 pollutants, cited above, and the individuals were the tested vehicles and driving cycles (Artemis urban with cold and hot start, road and motorway, NEDC). The SPAD8 software was used to create geometric interpretations between the variables and individuals from principal components. These representations allow make it possible to visually restore the relationships between the vehicles, or the driving cycles, and the emission factors (*33*).

205   Geometric representations are produced in 2D graphic form. Each dimension corresponds to one
206   principal component representing the maximum percentage of the total variance for the variable set.
207   Both dimensions are represented by two factorial axes. The projection of the variables according to
208   the two dimensions produces a graphic representation called "correlation circle". In this circle, each
209   arrow represents a variable (an emission factor in the present case). An arrow close to the circle
210   means that the circle can be interpreted. Any arrows that are clustered together are correlated and
211   represent similar emission behavior. For projection of the individuals, the individuals in our case are
212   vehicles or driving cycles, the PCA provides a factorial plan according to the same two factorial axes.
213   In this plan, any individuals that are clustered together have closed variable values indicating that
214   they have similar effects on emissions. This method makes it possible to study the impacts of vehicle
215   technologies and driving conditions on emission factors.

2. Results and Discussion

2.1. Euro 6 gasoline and diesel emission factors

218   Particles, BC, NO_2, BTEX and carbonyl compound emission factors for Euro 6, gasoline and diesel,
219   vehicles with the six driving conditions (Artemis urban cold start (ArtUrb C), Artemis urban hot start
220   (ArtUrb H), Artemis road (ArtROAD), Artemis motorway (ArtMW), WLTC) are presented in the Figure
221   1.
222   The article number emission factors for the gasoline vehicle varied between $2.3{\times}10^{12}$ to $2.9{\times}10^{14}$
223   #/km. The highest factors were obtained for the motorway cycle and the lowest were obtained for
224   the urban cycle with similar emissions between hot start and cold start. Compared to the diesel
225   vehicle equipped with DPF to emit few particles, the gasoline vehicle emitted 4 to 4500 times more
226   particles. The gasoline vehicle emitted 10 to 30 times more BC than the diesel vehicle under Artemis
227   urban and road driving conditions. Under the Artemis motorway and WLTC with high-speed
228   conditions, the gasoline vehicle emitted 200 to 250 times more BC than the diesel vehicle. NO_2
229   emissions from the gasoline vehicle were low, i.e., between 0.04 and 0.3 mg/km, and were 200 to
230   5000 less than for the diesel vehicle (45 to 229 mg/km) depending on the driving conditions. For the
231   unregulated compounds, the BTEX emission factors ranged from 0.03 and 4.9 mg/km for the gasoline
232   vehicle and 0.11 and 4.2 mg/km for the diesel vehicle. For the exhaust samples, only formaldehyde,
233   acetaldehyde and acetone were above the quantification limit that could be quantified. The diesel
234   vehicle emitted on average 11 times more carbonyl compounds than the gasoline vehicle for all the
235   cycles. The only exception was the motorway cycle, for which the gasoline vehicle emitted seven
236   times more carbonyl compounds than the diesel vehicle. The concentrations of the sixteen PAHs in
237   the particulate phase were below the detection limit for both vehicles (See Table S3 in the
238   Supporting Information).
239   Generally, Artemis urban cold start induces more emissions than hot start for all the pollutants
240   measured for both the diesel and gasoline vehicles. The diesel vehicle emitted 100 times more PN
241   under urban cold start condition than hot start. Cold start also induced 9–16, 2.5 and 10 times more
242   BTEX, carbonyl compound and BC emissions, respectively, than with hot start for the diesel and
243   gasoline vehicles. However, the diesel vehicle emitted three times more NO_2 under urban hot start
244   than under cold start. This same emission characteristic has been observed in other studies as well
245   (*13, 14*). The high NO_2 emissions in urban driving conditions and the increase in the number of Euro 6
246   diesel vehicles in the fleet raise serious concerns about urban air quality.
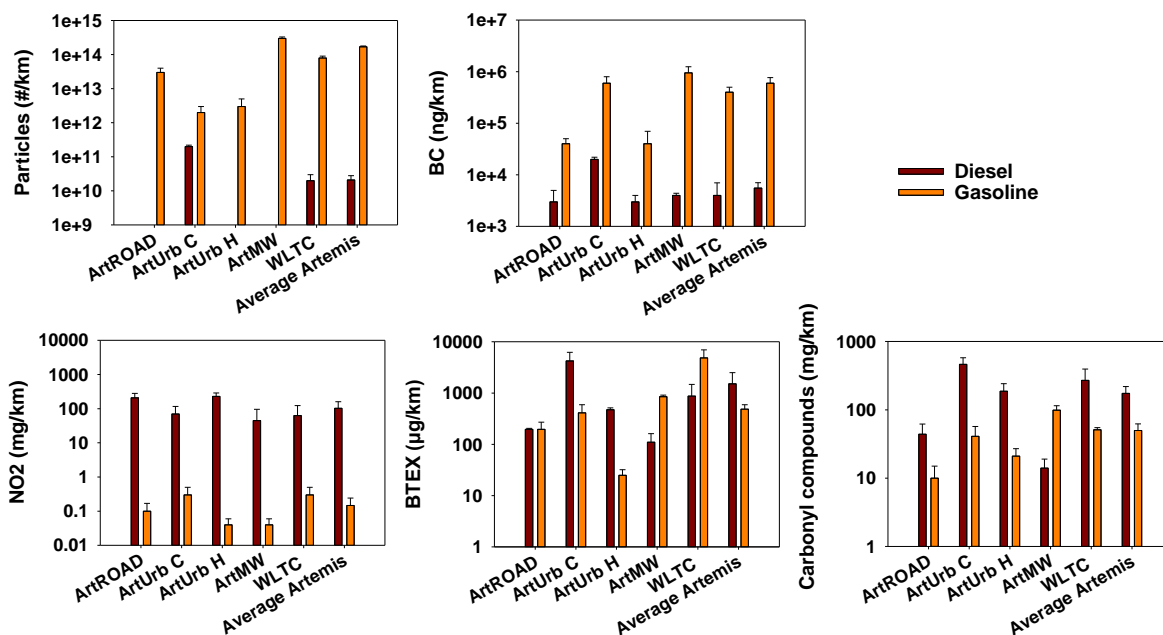
247
248 **Figure 1.** Particles, BC, NO_2, BTEX and carbonyl compounds emission factors for Euro 6 diesel and
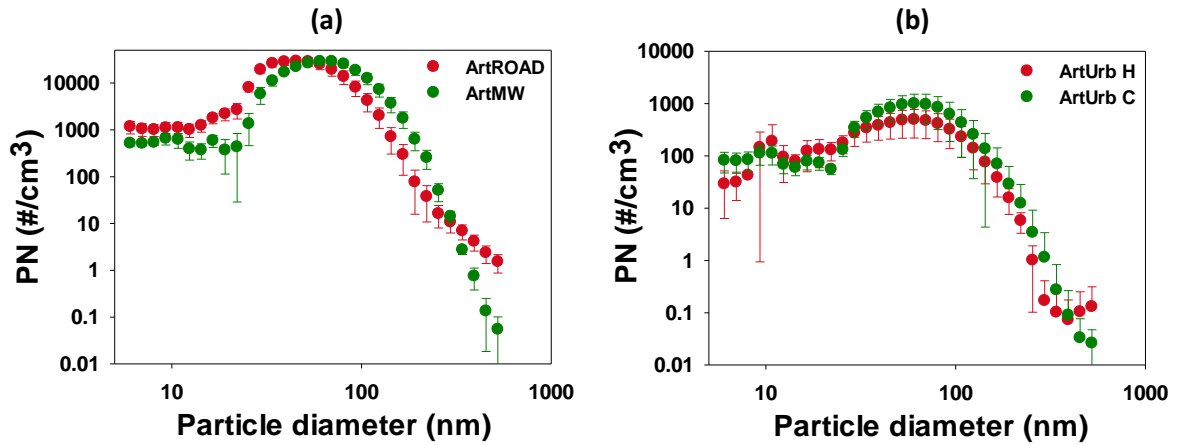249 gasoline vehicles.

250   Compared to the WLTC approval cycle, diesel emission levels of PN, BC, NO_2, BTEX and carbonyl
251 compounds are similar under the Artemis average cycles (urban cold start + road + motorway). For
252 the gasoline vehicle, all the pollutant emissions are similar between the average Artemis and WLTC
253 cycles. The only exception is BTEX: the WLTC cycle induced 4 to 13 times more emissions than
254 average Artemis cycle. However, only two vehicles in this study were tested using the WLTC cycle.
255 Further testing will have to be conducted to confirm the impact of the WLTC on emissions of
256 unregulated pollutants.

257   **2.2. Size distribution of the particle number**

258   The particle size distributions were measured with the FMPS for all the Artemis driving cycles.
259 Figure 2 (a) and (b) shows the particle size distributions for the gasoline vehicle under motorway and
260 road conditions (Figure 2a) and urban conditions with hot and cold start (Figure 2b). The particle size
261 ranged from 22 ± 1.4 to 220 ± 15.6 nm for all the Artemis driving cycles. The peak number
262 concentrations were around 45 ± 3.6 nm, 70 ± 4.7 nm and 60 ± 4.7 nm for the road, motorway and
263 urban driving conditions, respectively.
264   The particle emissions for the diesel vehicle were near the background level (i.e., undetectable)
265 for Artemis road, motorway and urban with hot start (See Table S3 in the Supporting Information).
266 Only Artemis urban cold and hot start is presented in Figure 2c. For urban cycle with cold start, the
267 particle sizes varied between 22 ± 1.4 to 220 ± 15.6 nm, with two modes around 10 ± 0.8 and 40 ± 2.5
268 nm. The results also show that the particles emitted by the diesel vehicle were smaller than those
269 emitted by the gasoline vehicle.

(a)

(b)

(c)
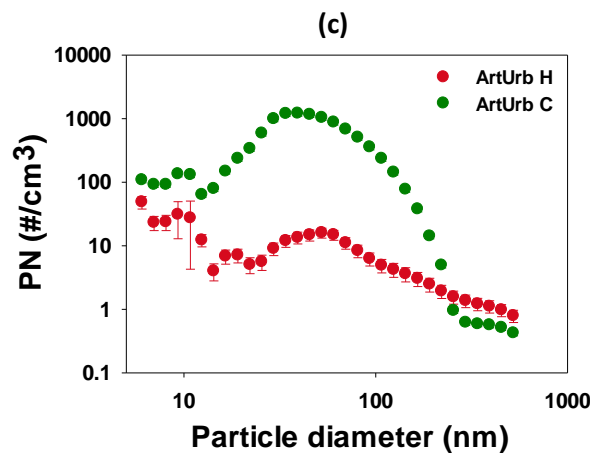
274 **Figure 2.** Particle size number distribution for the Euro 6 gasoline DI (a) and (b) and Euro 6 diesel
275 vehicles (c). (a) The Artemis road (ArtROAD) and Artemis motorway (ArtMW) driving cycles; (b) and
276 (c) the Artemis urban, hot and cold start (ArtUrb H/C) driving cycles.
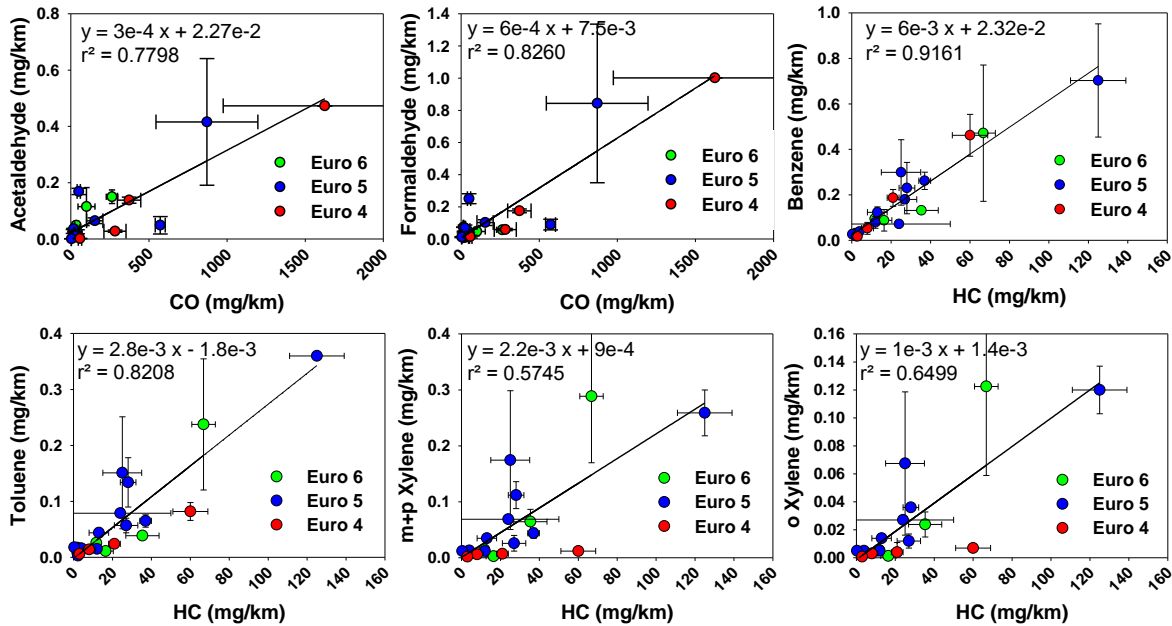
2.3. Pollutant correlations

278   The correlations between the pollutant emissions for the two Euro 6 vehicles tested in this study
279 and the six Euro 4–5 vehicles tested in the previous research (*15*) were studied. However, only the
280 emission factors of the diesel vehicles were used because the three gasoline vehicles did not show
281 good correlations between their pollutant emissions. This is particularly true for the Euro 6 gasoline
282 DI vehicle tested in this study and which showed very different emission behaviors. These differences
283 in behavior may be explained by the different vehicle technologies. The Euro 6 gasoline vehicle has a
284 propulsion engine that leads to a high exhaust temperature at the outlet of the tailpipe (up to 600 °C
285 during the motorway phases). The Euro 4 and Euro 5 gasoline vehicles tested by Louis et al. (*15*) were
286 fitted with a traction engine that led to a lower exhaust temperature (around 200 °C at the tailpipe).
287 Ghazikhani et al. (*34*) showed that the increase in exhaust temperature leads to an increase in
288 emissions of pollutant such as CO and HC.

289
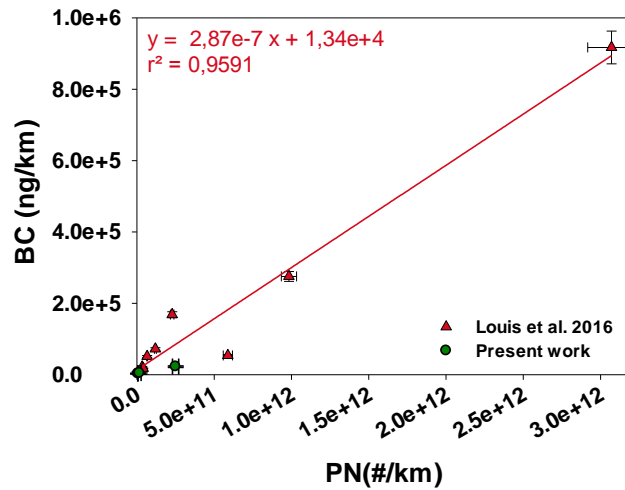
Figure 3. BC/PN correlation for the Euro 6 diesel vehicle (green dots, present study) and the Euro 4
and 5 diesel vehicles (red dots) (*15*) for emissions measured under the Artemis urban cold start,
WLTC and NEDC driving cycles.

At first, the correlations between PN and BC emissions for the diesel vehicles were studied.
Figure 3 shows the PN/BC correlation obtained from the Euro 6 diesel vehicle measured in this study
(green dots) and the correlation obtained by Louis et al. (15) for the Euro 4 (red dots) and 5 diesel
vehicles (green dots). The PN/BC correlation of the Euro 6 diesel vehicle tested in this study follows a
similar tendency, compared to the Euro 4 and 5 vehicles for the Artemis urban cold start, WLTC, and
NEDC driving cycles. However, the PN and BC emissions for the Euro 6 diesel vehicle were low,
making it difficult to arrive at a clear conclusion with uncertainties.

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Figure 4. Correlations between the various pollutants measured for the Euro 4 (red dots), Euro 5
(blue dots) and Euro 6 (green dots) diesel vehicles with all Artemis, WLTC and NEDC driving cycles.

The correlations between HC and CO (regulated compounds) and unregulated pollutant emissions measured for the Euro 6 diesel vehicle (present study) and Euro 4–5 diesel vehicles (*15*) were also studied under the Artemis urban, cold and hot start, Artemis road, Artemis motorway, WLTC, and NEDC driving cycles. Figure 4 shows the correlations between unregulated pollutants (benzene, toluene, xylene, formaldehyde and acetaldehyde), and regulated pollutants (HC and CO). The correlations are a positive linear correlation with r^2 varying from 0.57 to 0.91.

Unlike regulated compounds, emissions of unregulated compounds are not always measured on a chassis dynamometer. Based on the correlation equations given in Figure 4, it is therefore possible to estimate the emission factors of benzene, toluene, xylene, formaldehyde and acetaldehyde with HC and CO measurements for the Euro 4–6 diesel vehicles. However, these correlations only give an approximate estimation that takes into account the large standard deviation due to the high variability of emissions of regulated and unregulated compounds during cold start.

2.4. Preliminary PCA analysis

Principal component analysis (PCA) is performed as a preliminary method to study the impacts of driving conditions, aftertreatment, and engine technologies on pollutant emissions by analyzing the variable main trends. PCA was performed with emission factors of various gaseous and particulate pollutants measured in this study for two Euro 6 diesel and gasoline vehicles, as well as for four Euro 5 vehicles and two Euro 4 vehicles measured in previous study (*15*). The technical characteristics of these eight vehicles are given in the Table S4 in the Supporting Information. To build the PCA, we used either the five driving conditions (Artemis urban with cold start, urban with hot start, road, motorway and NEDC) or the eight tested vehicles as individuals, with the 32 pollutant emissions for each case (as variables) (Section 2.4 herein). The SPAD8 software was then used to perform the PCA analysis of the data set. The results showed that the first two dimensions set by PCA account for the bulk of the total variance. Therefore, in these two cases, only two dimensions were used for this preliminary study.

2.4.1. Impacts of driving conditions on pollutant emissions

The impacts of driving conditions on pollutant emissions are studied using the PCA analysis with emission factors measured under the Artemis urban cold and hot start, Artemis road, Artemis motorway, and NEDC driving cycles. Two PCA analysis were performed, one for the Euro 4–6 diesel vehicles and one for the Euro 4–6 gasoline vehicle.

For the Euro 4–6 diesel vehicles, the urban cold start driving condition produces the most important emissions of various pollutants (PN, BTEX and carbonyl compounds…) compared to other driving conditions. For the Euro 4–6 gasoline vehicles, the impacts of the driving conditions on pollutant emissions are shown in the figure 5. Figure 5a shows the projection of the variables, the measured emission factors in this case, on the two principal axes. They account for 85% of the total variance, with a strong Axis 1 (49% of the variance). Figure 5b shows the projection of the driving cycles (individuals) in the same two dimensions.

A cluster comprising BTEX, black carbon, and carbonyl compounds can be seen on the right portion of the correlation circle (Figure 5a). These compounds follow the same emission pattern and are at the same position as the Artemis urban driving cycle with cold start (Figure 5b). This observation indicates that the cold urban driving condition produces highest emissions of these compounds. Similar results were observed by Caplain et al. (*26*) and Louis et al. (*14*). Another cluster,

located in the upper left portion of the correlation circle and corresponding to the Artemis motorway driving cycle, comprises particles, and CO. The motorway driving condition at high speed produces highest particle, and CO emissions. Finally, the NEDC driving cycle is in the middle of the four Artemis driving cycles of the factorial plan. This observation indicates that cycle emissions are not correlated with the two principal axes.

(a)

(b)
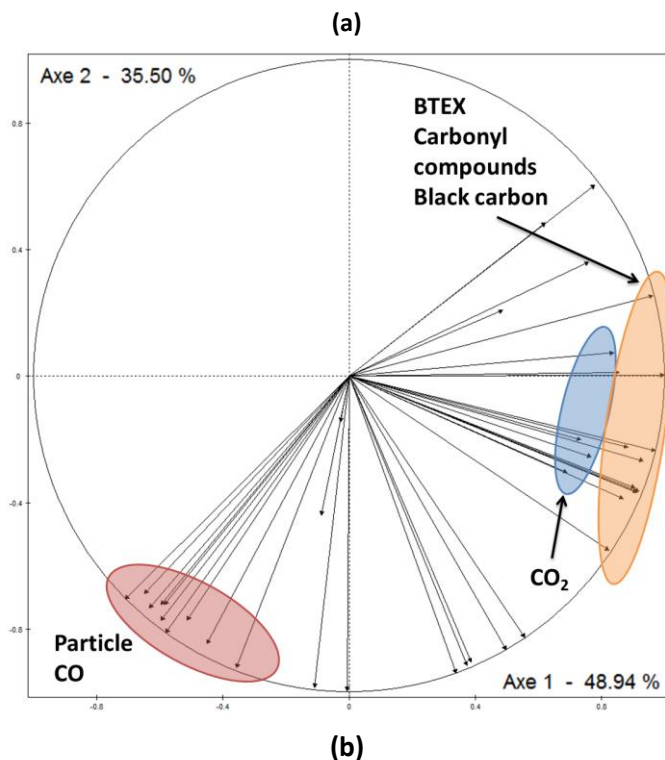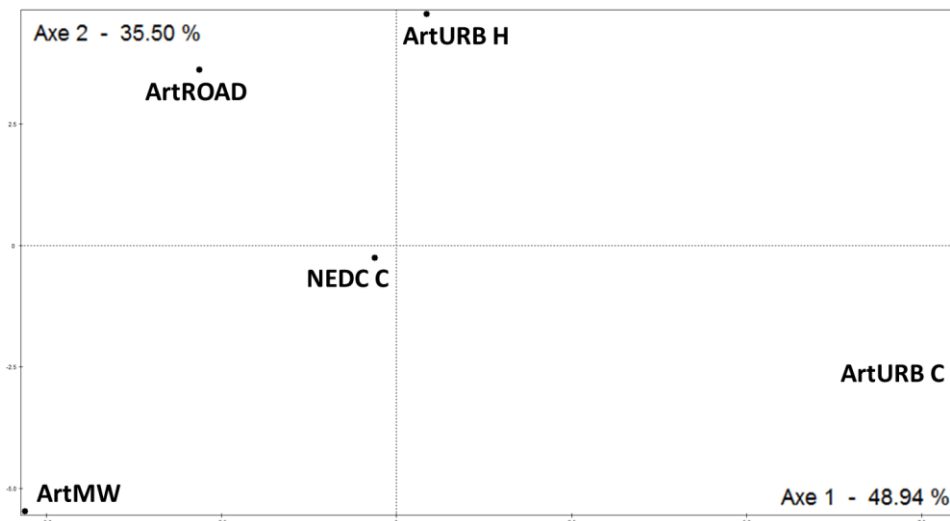
Figure 5. PCA performed for all the driving cycles for the Euro 4–6 gasoline vehicles, with (a) the projection of emission factors and (b) the projection of cycles.

2.4.2. Impacts of aftertreatment and engine technologies on pollutant emissions

The eight vehicles tested were fitted with six different aftertreatment and engine technologies. All three of gasoline vehicles in this study were fitted with TWC. However, they had different engine

technologies. The Euro 4 vehicle used an indirect injection technology, the Euro 5 vehicle used a direct injection technology and the Euro 6 used a direct injection technology with propulsion engine (located at the rear). All six diesel vehicles were fitted with DOC. Apart from this common system, the aftertreatment technologies were different. One Euro 4 vehicle and one Euro 5 vehicle had a catalyzed DPF, two Euro 5 vehicles had an additive DPF (add DPF), and one Euro 6 vehicle had a catalyzed DPF (cat DPF) and NO_X trap.
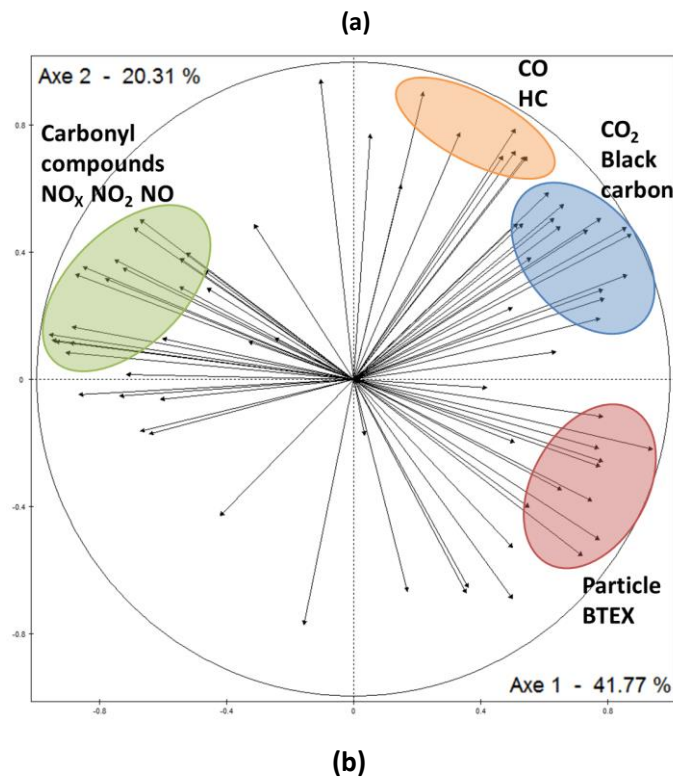
(a)

(b)

Figure 6. PCA performed for all the driving cycles and all the vehicles, with (a) the projection of emission factors and (b) the projection of vehicles.

To study the effects of vehicle technologies on the pollutant emissions, we performed PCA using the emission factors measured for all the vehicles with all the Artemis and NEDC driving cycles as

13

378 variables, and the eight tested vehicles as individuals. Figure 6 shows the projection of the variables
379 (Figure 6a) and individuals (Figure 6b) on the two principal axes. They account for 62% of the total
380 variance, with a strong Axis 1 (42% of the variance). On the factorial plan, the diesel and gasoline
381 vehicles are separated into two clusters. The gasoline vehicles are in the right portion of the plan and
382 the diesel vehicles are in the left portion. In the case of the diesel vehicles, the two Euro 5 with
383 additive DPF were clustered together and located at left bottom of the vehicle projection. In
384 contrary, the three diesel vehicles with catalysed DPF located at top left of the plan. All three
385 gasoline vehicles tested were located at different places: Euro 6 DI at right bottom; Euro 4 at right
386 axis; and Euro 5 DI at top right.

387 The cluster on the left portion of the correlation circle comprises NO_X and carbonyl compounds.
388 They correspond to the diesel vehicles fitted with a catalyzed DPF that meet Euro 4–6 standards
389 which are characterized by higher emissions of these compounds. The Euro 6 Catalyzed DPF diesel
390 vehicle with NO_X trap is located at the leftmost portion of the plan, indicating that this vehicle
391 produces higher NO_X emissions. Such high emissions were also observed Ntziachristos et al. (*35*)
392 under the WLTC cycle and PEMS measurements, between 100 and 1100 mg/km with high
393 uncertainties. Two clusters at the upper right portion comprise CO and HC and black carbon and CO_2,
394 respectively. The cluster at the lower right portion comprises particles and BTEX. These various
395 compounds are emitted in greater quantities by the Euro 4–6 gasoline vehicles compared to the
396 diesel vehicles.

397 This preliminary PCA analysis shows the possibility of studying the impacts of driving conditions
398 and technologies on emissions using a statistical method. However, the number of samples remains
399 small and does not comprise all vehicle technologies. A detailed discussion is presented in the
400 Section 4 herein.

2.5.Discussion

402 This paper aims to measure emissions of unregulated compounds from Euro 6 vehicles that are
403 never measured in order to improve knowledge about their emissions under different driving
404 conditions, and to supplement the first data for the emission factor inventory used by various
405 emission models (HBEFA, COPERT IV). This paper also attempts to show whether it is possible to use
406 PCA statistical analysis to investigate the impacts of aftertreament technologies and driving
407 conditions on vehicle emissions.

408 One Euro 6 diesel vehicle and one gasoline vehicle were tested on a chassis dynamometer for
409 real-world Artemis, WLTC, and NEDC driving cycles. Emission factors of particles, black carbon, NO_2,
410 BTEX, PAH and carbonyl compounds for these vehicles were determined. The results show that diesel
411 produces 200 to 5000 times more of NO_2 emissions and 4 to 4500 times less of PN emissions than
412 gasoline vehicle. Moreover, the Euro 6 diesel vehicle emits four times more carbonyl compounds
413 than the Euro 6 gasoline vehicle. Compared to the Artemis urban hot start, Artemis urban cold start
414 produces 100, 9–16, 2.5, and 10 times more PN, BTEX, carbonyl compounds, and BC emissions,
415 respectively, and three times less NO_2 emissions than Artemis urban hot start for both the diesel and
416 gasoline vehicles. Compared to the WLTC approval cycle, diesel emission levels of PN, BC, NO_2, BTEX
417 and carbonyl compounds are similar under the Artemis average cycles (urban cold start + road +
418 motorway). For the gasoline vehicle, all the pollutant emissions are similar between the average
419 Artemis and WLTC cycles. The only exception is BTEX: the WLTC cycle induced 4 to 13 times more
420 emissions than average Artemis cycle. However, only two vehicles in this study were tested using the

WLTC cycle. Further testing will have to be conducted to confirm the impact of the WLTC driving condition on emissions of unregulated pollutants. Positive linear correlations have been observed for Euro 4–6 diesel vehicles between emissions of regulated compounds (HC and CO) and unregulated compounds (black carbon, benzene, toluene, xylene, formaldehyde and acetaldehyde). These correlations show that is possible to estimate some of the unregulated compounds that are not always measured as a function of regulated compound emissions. These correlations only provide an approximate estimation that takes into account the large standard deviation.

PCA statistical analysis has been used as a preliminary method to see the possibility to investigate the impact of aftertreatment device and driving condition on pollutant emissions of eight vehicles with seven different technologies tested in this work and our previous work. With our PCA analysis, we show that the Euro 4–6 gasoline vehicles are characterized by higher particle number emission and lower NOx emission comparing to Diesel DPF vehicles. This statistical analysis with our data set is in agreement with Bach et al. (*13*), Alves et al. (*23*) and Louis et al. (*15*). They observed that Euro 4–5 gasoline vehicles emit around 100 times more particles and around 10 times less NOx comparing to the Euro 4–5 diesel equipped with DPF. The PCA analysis of the driving conditions showed that the urban driving conditions with cold start produce significant PN, BTEX, and carbonyl compound emissions compared to hot start for the Euro 4–6 diesel vehicles. This is confirmed by the results of Louis et al. (15), Caplain et al. (26) and Joumard et al. (21). The PCA showed that high-speed driving conditions (motorway) produce significant CO and PN emissions compared to low-speed driving conditions (urban) mainly induce by the gasoline vehicles. This is in agreement with Huang et al. (22). They observed that the urban driving condition with cold start emits around 2 to 150 times more BTEX and around two times more carbonyl compounds compared to the urban driving condition with hot start. For the impacts of aftertreatment and engine technologies, the PCA showed that diesel vehicles equipped with additive and catalyzed DPF emit few particles. Two different DPF technologies exhibit slightly different emission behaviors. The Euro 6 vehicle fitted with a NO_X trap emitted the most NO_X. The three gasoline vehicles, which are located opposite the diesel vehicles on the factorial plan, emit little NO_X, but more particles, black carbon, BTEX, CO, HC, and CO_2. Due to different engine technologies – indirect injection for Euro 4, direct injection for Euro 5 and direct injection with a propulsion engine for Euro 6 – the three gasoline vehicles exhibit different emission behaviors. These preliminary tests showed that different vehicle technologies or driving conditions can be characterized by some key pollutants. . However, these tests included a relatively low sample number and did not cover all vehicle technologies. To complete our PCA analysis, we attempted to integrate results from other studies. For example: Caplain et al. (*26*) tested pre-Euro to Euro 3 diesel and gasoline vehicles. They monitored 11 aldehydes and 2 ketones as pollutants under urban with hot start and motorway driving conditions. Rehn (*25*) tested Euro 2 to Euro 4 diesel and gasoline vehicles by measuring HC, NO_X, CO, PAHs in particulate phase, BTEX, aldehydes and acetone under Artemis urban with hot and cold start, and road driving conditions. Alves et al. (*23*) tested Euro 3 to Euro 5 diesel and gasoline vehicles. They monitored HC, CO, NO_X, and BTEX under Artemis urban with hot and cold start, and road driving conditions. However, none of the pollutants monitored in these studies were measured for all Artemis driving conditions. Moreover, the particle number, black carbon, and several organic compound emission factors were not measured for Pre-Euro to Euro 3 Diesel and gasoline vehicles. We therefore lack all the necessary data to complete our PCA data set for the same pollutants under all driving conditions or for all vehicles. The PCA analysis with integration of literature data shows that the missing data, which introduced significant bias to the

465 PCA analysis, should be included in a future study so as to extend this statistical method to a larger
466 vehicle population.

467 **Acknowledgments**

470 **Supporting information available**

471 Fuel composition for all tested vehicles (Table S1); Analytical methods for BTEX, carbonyl
472 compounds, and PAH samples in the gas and particulate phases with quantification limit and
473 uncertainty (Table S2); Emission factors for unregulated pollutant from Euro 6 diesel and gasoline
474 vehicles (Table S3); Technical characteristics of the eight diesel and gasoline vehicles used for
475 statistical analyses (Table S4). This material is available free of charge via the Internet at
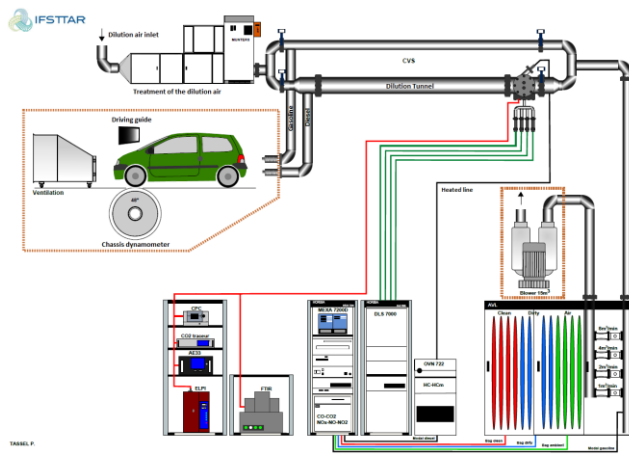476 http://pubs.acs.org.

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