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1 *Impact of fuel ethanol content on regulated and non-regulated*
2 *emissions monitored by various analytical techniques over flex-*
3 *fuel and conversion kit applications*

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10

11 **KEYWORDS**

12 Ethanol, regulated emissions, non-regulated emissions, WLTC cycle, exhaust gases,
13 chromatography, mass spectrometry

14 **ABSTRACT**

15 This study evaluates the impact of ethanol content on both regulated and non-regulated emissions
16 with recent vehicle technologies. The three vehicles used here are complying with EU6d-temp or
17 EU6c emission standards and are adapted to variable ethanol concentrations, either through flex-
18 fuel or E85 conversion kit. Both regulated and non-regulated emissions are characterized to

19 highlight the fuel and vehicle technology impacts. The analysis of non-regulated pollutants in
20 exhaust gases is performed with three different techniques to evaluate their advantages or
21 limitations and assess time-resolved emission levels. HPLC coupled to UV detection to measure
22 aldehydes and ketones. GC-MS was used for PAHs characterization. GC-FID was used to measure
23 VOCs (C1 to C12) on the first phase of the WLTC. FTICR-MS was used to assess time-resolved
24 emission levels. Results indicate a negligible impact on the emissions for ethanol content from 10
25 to 20 % vol. Nevertheless, a significant emission composition variation is observed at 50 % vol.
26 and this is even more pronounced with 85 % vol. of ethanol. Expected trends based on the
27 literature review are confirmed for all vehicles and this includes an increase in unburned ethanol
28 and aldehydes emissions with higher ethanol content while in this condition lower aromatics
29 contribute to reduce particulate matters emissions. The use of varying amounts of ethanol in recent
30 and diverse Euro 6d-temp vehicle technologies shows that the increase in ethanol content is
31 unaffected by the reduction in particulate emissions and the increase in the finest. However, the
32 results indicate a risk of increased NOx emissions for Euro 6d-temp IC engines, which should be
33 confirmed on other vehicles of similar technology. This study results also indicate that most
34 pollutants are emitted in the engine and exhaust warm-up phase. All analytical techniques
35 exhibited similar trends.

36 **1. Introduction**

37 Vehicle transportation is under fast transformation. The European Union aims at a Green Deal
38 net zero greenhouse gas emission target by 2050, which requires a rapid reduction in emissions
39 from road transport. To reach this objective, different decarbonization pathways were identified
40 and are to be implemented with both short- and long-term impact. Switching away from internal
41 combustion engine (ICE) to battery electric vehicle (BEV) has been identified as one of

42 prospective path towards such goal. Many carmakers are already committed to a zero emission,
43 electric future. However, even with extremely aggressive and proactive policies towards
44 electrification, given the average age of the vehicle fleet in Europe (according to ACEA¹, 11.5
45 years for passenger cars and getting older), in 2030, ICEs will still be a majority. Considering
46 therefore the large contribution of ICE for transportation, the integration of advanced low carbon
47 fuels is mandatory to decarbonize the sector with immediate effect on the existing fleet. In addition,
48 the full life cycle analysis for carbon dioxide emissions tends to support the development of
49 advanced fuels compared to the full electrification strategy (JEC V5²). In this context, different
50 options may be identified for developing alternative sustainable fuels.

51 One of these options is related to the use of ethanol. As a well-established bio gasoline
52 component (half the countries of the European Union propose E10, and a quarter propose E10 in
53 almost 100 % of gas stations³), ethanol is available at large scale. Advanced production capacities
54 may be reaching 1 MT/year worldwide within the next few years. According to JEC V5, advanced
55 bioethanol has one of the most promising carbon dioxide (CO₂) reduction potentials in a vehicle
56 cradle to grave basis. Ethanol is present up to a level of 10 % vol. in Unleaded 95-E10 and is
57 accepted by most spark ignition engines with no necessary modification. The use of Superethanol-
58 E85 (65 to 85 % vol. of ethanol) is authorized on original flex-fuel vehicles, or on certain vehicles
59 fitted with approved E85 conversion kit.

¹ <https://www.acea.be/statistics/article/average-age-of-the-eu-motor-vehicle-fleet-by-vehicle-type>

² JEC Well-to-Wheels analysis of future automotive fuels and powertrains in the European context, EUR 30284 EN, 2020

³ <https://www.epure.org/about-ethanol/fuel-market/fuel-blends/>

60 Ethanol's physical and thermal properties are quite interesting for gasoline application. Its
61 composition allows lower CO₂ emissions, and its high-octane rating gives it better combustion
62 efficiency and performance. Indeed, produced mainly from conventional (i.e. competition with
63 food) feedstocks, corn, wheat and sugar beet, its widespread use and potential could foster the
64 development of advanced bioethanol production paths using lignocellulosic biomass or different
65 organic residues. However, its lower heat of combustion, reduced vaporization under cold
66 operation and risk of oil dilution are disadvantages associated to the use of ethanol [1,2].

67 The impact of different ethanol-gasoline blends has been investigated several times in the
68 literature. It included blends from 0 to 85% vol. of ethanol with gasoline passenger car compliant
69 with Euro 3 to Euro 6. Most of these studies aim at evaluating the impact of ethanol on emissions.
70 Roller test bench is the most common experimental facility used and it is combined with several
71 driving cycles: Federal Test Procedure cycle (FTP-75), California Unified cycle (LA92), Common
72 Artemis Driving Cycle (CADC), New European Driving Cycle (NEDC) and Worldwide
73 harmonized Light-duty vehicles Test Cycle (WLTC).

74 These studies lead to several observations regarding the regulated and unregulated emissions.
75 Observed effects are varied. This is most related to different fuel matrix, engine, and after-
76 treatment calibrations as well as different driving cycles used. First of all, it has been demonstrated
77 that the oxygen content increase associated to ethanol generally tends to reduce carbon monoxide
78 (CO) emissions [3–8]. However, the reported reduction percentage varies among the different
79 studies.

80 Regarding unburned hydrocarbons (HC), the impact of ethanol content is not always clear. On
81 the one hand, some studies shown that HC emissions are reduced with increasing ethanol [5,6,9].

82 One the other hand, some studies shown that HC emissions exhibit a minimum at intermediate
83 level of ethanol, about 25-35 % lower (E20) than for E0 and E80 [1,10].

84 A decrease in nitrogen oxides (NO_x) emissions is generally found with additional ethanol
85 content [3,6,11]. However, this result is not consistent among studies. Indeed, this may depend on
86 the engine hardware (e.g. direct or indirect injection), the adaptability of the engine calibration to
87 operate highly oxygenated fuels (e.g. limited adaptability may lead to leaner combustion
88 operation), and the driving conditions.

89 The vast majority of the studies shown a decrease in particulate matter with increasing ethanol
90 content [6,12,13] and others shown the opposite effect [14], notably due to an increase in fine
91 particulate matter (below 30 nm) [15].

92 Regarding the unregulated emissions, ethanol addition may lead to a reduction of monoaromatic
93 species [13] and polyaromatic hydrocarbons (PAHs) [12]. It has also been shown that higher
94 ethanol concentrations in fuel blends may lead to higher emissions of certain aldehydes [13,16,17].
95 These molecules are presented by the authors as potentially carcinogenic compounds to humans
96 and may contribute to impact air quality through ozone formation. High ethanol content also
97 contributes to increase unburned ethanol emissions. The amount is especially significant during
98 cold start when the catalyst is not active [11].

99 Both light alcohols and aldehydes are volatile organic compounds (VOCs) and such emissions
100 are usually measured using flame ionization detector (FID). It is well documented [18] that the
101 FID response is proportional to the carbon atom concentrations for hydrocarbons. The response
102 for oxygenates, however, is significantly lower. Indeed, previous studies have shown a different
103 selectivity of FID towards oxygenated compounds, such as ethanol, acetaldehyde, and
104 formaldehyde, which are commonly found in the exhaust of ethanol-fueled engines [19,20]. The

105 importance of the measurements of these compounds is emphasized when nonmethane
106 hydrocarbons (NMHC) emissions are compared to nonmethane hydrocarbons (NMOG) emissions.
107 Relying exclusively on FID readings result in an underestimation of the real emissions. The
108 magnitude of underestimation depends on the proportion and oxygenate type. More recent studies
109 have compared different analytical techniques including High Resolution Fourier transform
110 infrared spectrometry (FTIR), proton transfer reaction-mass spectrometry (PTR-Qi-ToF-MS),
111 photoacoustic spectroscopy (PAS) and gas chromatography (GC) to assess the feasibility of the
112 online measurement of ethanol and aldehydes emissions. A comparison of these techniques led to
113 a good agreement regarding the oxygenates identification and quantification [18]. Given the low
114 sensitivity of FID for measuring oxygenated compounds, one of these techniques could be used to
115 calculate real NMOG emissions.

116 Given the possibility of having high ethanol concentration in fuel blends, it is therefore crucial
117 to study the emissions for not only the regulated gases, but also the unregulated ones. While there
118 is some information available in the literature about the effects of ethanol-gasoline blends on
119 exhaust emissions in flex-fuel spark-ignition vehicles, there is limited information on IC engine
120 and hybrid vehicles equipped with adapted E85 conversion kits. Furthermore, information on the
121 time resolved emissions of non-regulated compounds are not widely available in the literature for
122 recent engine technologies combined with ethanol content variation.

123 Therefore, this study evaluates the impact of varying ethanol blends concentrations (from 0 to 85%
124 vol of ethanol) on the tailpipe regulated and non-regulated emissions from one Euro 6c flex-fuel
125 passenger car, one Euro 6d-temp IC engine and one Euro 6d-temp hybrid vehicle fitted with
126 approved E85 conversion kit. The impact of the fuel variability on current control strategies has
127 also been investigated. Two driving cycles are used: WLTC [21] and CADC [22]. The latter is

128 considered as more realistic because it is based on statistical analysis of a large database of
 129 European real-world driving patterns. In the present study three analytical techniques were
 130 combined. High-performance liquid chromatograph (HPLC) coupled to ultraviolet (UV) detection
 131 to measure aldehydes and ketones. Gas chromatography coupled to mass spectrometry (GC-MS)
 132 was used for PAHs characterization. GC-FID was used to measure VOCs (C1 to C12) on the first
 133 phase of the WLTC, the most emissive part. To assess the impact of ethanol transient speciation
 134 of emitted VOCs, emissions were recorded in real-time by Fourier transform ion cyclotron
 135 resonance mass spectrometry (FTICR-MS) over the whole driving cycle. This was to include
 136 higher load and transient conditions which are not recorded by offline chromatography.

137 **2. Materials and Methods**

138 **2.1 Fuel matrix definition**

139 The tested fuel matrix aims to cover a set of different formulation cases that may be encountered
 140 when standard commercial fuels E10 and E85 are mixed in the tank. Tested fuels are listed in Table
 141 1. Fuels E10 and E85 are defined under the homologation requirements. Fuels E20 and E50 are
 142 blends of the earlier to attain a 20 % and a 50% vol of ethanol respectively for E20 and E50.

143 **Table 1.** Fuel matrix

Fuel	Formulation	Standard
E10	10 % vol of ethanol (fuel that meets Euro 6 certification specifications)	EN 228
E20	20 % vol of ethanol (mixture of E10 and E85)	EN 228 ⁴
E50	50 % vol of ethanol (mixture of E10 and E95)	EN 228 ⁵
E85	85 % vol of ethanol (fuel that meets Euro 6 certification specifications)	EN 15293

⁴ All specifications are met except for ethanol content.

⁵ All specifications are met except for ethanol content.

144

145 The study focused on three vehicles having recent engine technologies representative of the
146 French market. The vehicles selected were:

- 147 • Vehicle A, a EURO 6d-temp gasoline passenger car (gasoline direct injection - GDI, fitted
148 with gasoline particle filter - GPF)
- 149 • Vehicle B, a EURO 6d-temp gasoline hybrid passenger car (gasoline indirect injection -
150 GII)
- 151 • Vehicle C, a EURO 6c flexi-fuel passenger car (GDI)

152 Vehicles A and B were tested with E10 and E20 fuels at the original configuration. Then, they
153 were fitted with E85 conversion kit, and the four matrix's fuels were evaluated. In addition, a cross
154 test with a second conversion kit technology was carried out over E10 and E85 fuels. The full fuel
155 matrix was also evaluated on the flexi-fuel vehicle EU6c. Table 2 shows an overview. The tests
156 allowed the assessment of the impact of ethanol fuel-content over regulated and non-regulated
157 emissions for different technological solutions and recent vehicle technologies.

158

Table 2. Configurations tested

Vehicle	Configuration tested		
		E85 conversion kit #1	E85 conversion kit #3
Vehicle A GDI + GPF	E10	E10	E10
	E20	E20	
		E50	
		E85	E85
	E85 conversion kit #2		E85 conversion kit #4
Vehicle B Hybrid GII	E10	E10	E10
	E20	E20	
		E50	
		E85	E85

Vehicle C	E10, E20, E50, E85
Flexi-fuel GDI	

159 **2.2 Testing installation**

160 The tests were carried out on a roller bench (Table 3) over WLTC and CADC driving cycle. The
 161 chassis dynamometer is located into a conditioned chamber maintained at $23\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$. Figure 1
 162 shows the schema of implantation of the various analytical apparatuses on the roller test bed. The
 163 exhaust gas emissions were collected and measured either directly online by mass spectrometry or
 164 according to the Constant Volume System (CVS) based on a full flow dilution tunnel. Each fuel-
 165 vehicle configuration was tested twice, and a 2 % CO₂ repeatability was verified.

166 **Table 3.** Roller bench technical characteristics

Power (kW)	55
Speed (km/h)	160
Type	Bi roller
Ventilation maximum speed	120 km/h
Temperature	$23\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$
Hygrometry	$45\text{ } \% \pm 10\text{ } \%$

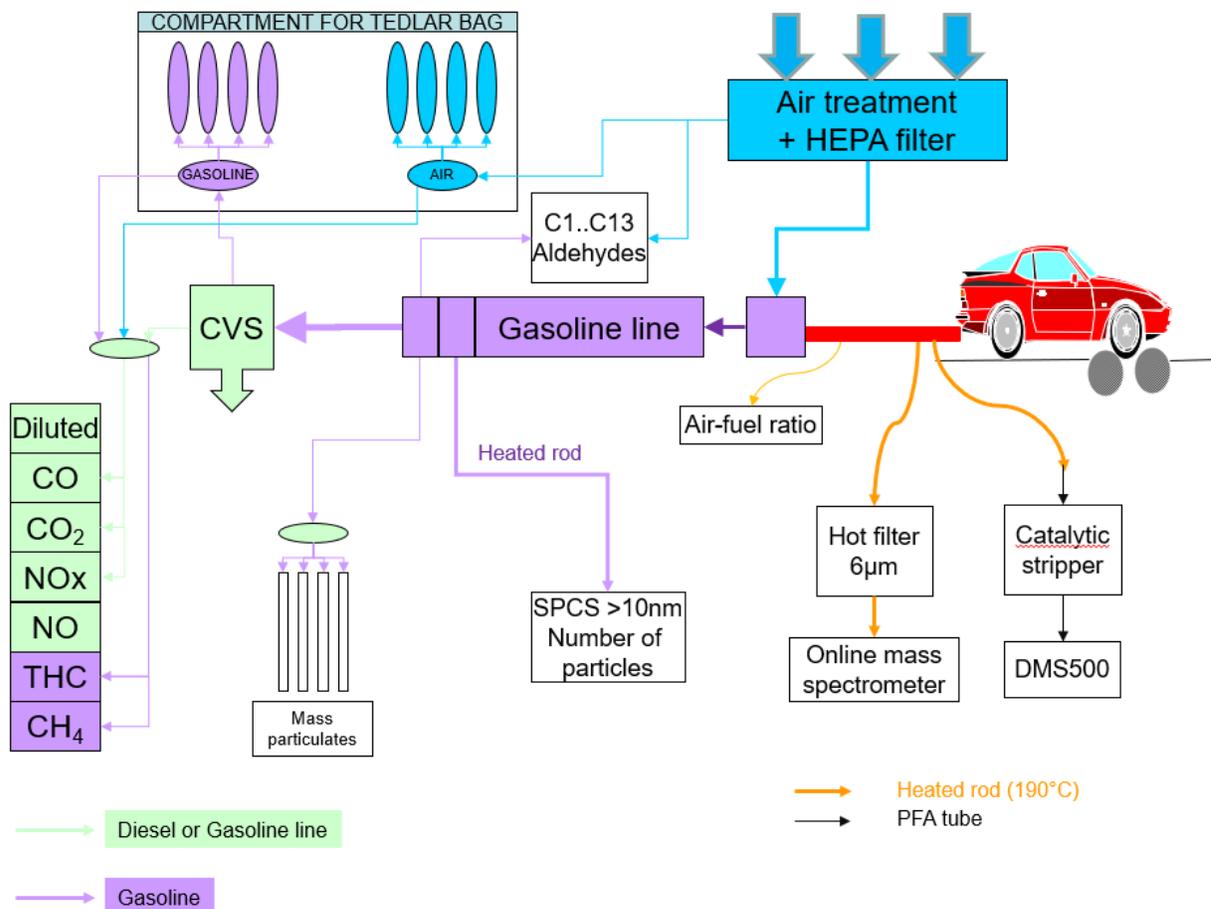


Figure 1. Exhaust gas conditioning and measuring apparatus available at roller bench.

2.2.1. Regulated emissions

Standard instrumentation used for characterization of regulated pollutants from Euro 6 vehicles was used, except for the extension of particle size down to 10 nm:

- Diluted gas analyzer allowing the characterization of HC, CO, CO₂, NO_x emissions,
- Gravimetric sampling system for the determination of the mass of particles emitted (PM), collected after dilution and conditioning. No significant effect of ethanol on PM was found. Measured values are low and are within the margin of error for the measurement; therefore, the mass of particles emitted was not considered for further interpretation,

177 • Standardized counting system for the determination of the total number of particles
178 emitted (diameter > 10 nm) (PN), collected after dilution and conditioning.

179 In addition, a DMS500 was used for size distribution analysis of particles emitted.

180 The analytical methods employed to measure gaseous emissions, particles mass and number are
181 described in Table 4.

182 **Table 4.** Analytical methods

183

Compound	Analytical method
CO / CO ₂	Non Dispersive Infra-Red (NDIR)
NO / NO _x	Chemiluminescence Analysis (CLA)
HC / CH ₄	Flame Ionisation Detector (FID)
Particles mass	Pallflex® filter
Particles number	SPCS (Solid Particle Counting System)

184

185 2.2.2. Non-regulated emissions

186 Three different families of non-regulated compounds were analyzed in the framework of this
187 study: aldehydes and ketones, polycyclic aromatic hydrocarbons (PAHs) and other volatile organic
188 compounds (VOCs). Very low amounts of PAHs were found; therefore, these compounds were
189 not considered for further interpretation.

190 **Aldehydes and ketones**

191 Exhaust gas samples, extracted after dilution and conditioning, were collected over cartridges
192 containing silica grafted with DNPH (Dinitrophenylhydrazine). Aldehydes and ketones are thus
193 sampled as hydrazone derivatives. Cartridges are then eluted with a mixture of organic solvents
194 (water/acetonitrile 35/65, HPLC grade) to recover the analytes. The extract is analyzed with high-
195 performance liquid chromatography (Prominence LCD-20ADXR from Shimadzu) coupled to a
196 UV detector (SPD-20A from Shimadzu) operated at 365 nm. The method is calibrated with a
197 certified reference standard (TO11/IP-6A Aldehyde/Ketone-DNPH Mix) provided by Sigma-
198 Aldrich.

199 **Volatile organic compounds**

200 Diluted exhaust gases are sampled in Tedlar® bags and injected in a custom configuration
201 consisting of two gas chromatographs (Varian 450) equipped with three different columns
202 (Porapak Q, Plot Alumina and DB1) and three FID detectors for the quantification of methane, C2
203 to C6 and C6 to C12 hydrocarbons. A pre-concentration system with adsorbents cooled with liquid
204 nitrogen (Sample Preconcentration Traps, SPT) enables to greatly improve the sensitivity of the
205 technique (around ppb).

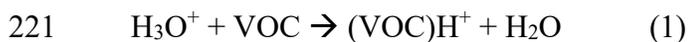
206 Blank levels are determined by regular analyses of the dilution air used in the roller test bed. The
207 overall amounts of non-regulated compounds determined by analysis (expressed in ppm) are then

208 converted into mg/km thanks to several experimental factors from the roller test bed, as are the
209 volume sampled, the distance, and the dilution factors.

210 The whole experimental protocol (sampling, dilution, and analysis) was validated with a
211 certified gas mixture of C2-C6 hydrocarbons. Briefly, the chromatogram obtained directly from
212 an injection of the gas was compared to the one from the gas having undergone the whole process.
213 The overlay of both chromatograms did not highlight any modification through the process, which
214 was thus validated.

215 **Analysis of VOCs by real time mass spectrometry**

216 The BTrap instrument is a Fourier Transform Ion Cyclotron Resonance Mass Spectrometer
217 (FTICR-MS) in which the species present in the analyzed sample are ionized using a chemical
218 reaction [23,24]. H_3O^+ ions are prepared in the ICR cell and react by proton transfer with the
219 sample. In this way only the Volatile Organic Compounds (VOC) present in the gas exhaust are
220 ionized



222 Because their proton affinity is smaller than for H_2O , the small molecules present in air, as N_2 ,
223 O_2 , CO_2 , and CH_4 , are not ionized. The selectivity of this chemical ionization technique ensures a
224 good sensitivity. Moreover, the analysis of the mass spectra is straightforward since each VOC
225 present in the sample appears as a protonated ion. The full sequence of precursor ion formation,
226 reaction with the vehicle exhaust gas sample, and detection of the complete mass spectrum takes
227 only a few seconds. Concentrations for all VOCs are obtained in real time. The species are
228 identified on the mass spectra by the mass of the protonated molecules. The precision of the mass
229 measurements allows the attribution of a molecular formula to all the observed species (however

230 isomers cannot be distinguished by their mass). Due to the precise and fast sampling technique,
231 the BTrap was placed at the exhaust line, before gas dilution.

232 Reaction (1) is realized under well controlled reaction time and pressure conditions. The sample
233 gas pressure is integrated over reaction time, the result being named PxT [23,24]. VOCs
234 concentrations expressed in ppm are obtained from the recorded ion intensities, the PxT value and
235 the bi molecular rate coefficient for the ionization reaction using the following formula:

$$236 \quad [VOC] = \frac{\ln\left(\frac{Sum}{I_{H3O^+}}\right) * I_{VOCH^+} * 10^6}{(Sum - I_{H3O^+}) * k * PxT * 3.21}$$

237 Where Sum is the sum of all ions intensities on the spectrum, I_{H3O^+} and I_{VOCH^+} the intensities of
238 the precursor ion H_3O^+ and of the protonated VOC respectively. k is the bimolecular reaction rate
239 coefficient for reaction (1), PxT the sample pressure integrated over reaction time.

240 **Complementarity**

241 Both approaches (online FTICR-MS and offline laboratory analysis by chromatography) provide
242 complementary information. Online mass spectrometry gives valuable information on the time
243 resolved emission of the compounds. Moreover, the online spectrometry allows measuring the full
244 driving cycle, to include higher load and acceleration conditions not recorded by the offline
245 chromatography which is done on the first part of the cycle. However, some compounds cannot be
246 seen with this technique, either because they are not protonated like CH_4 for example, or because
247 they are present at very low concentrations. The comparison of techniques relying on different gas
248 conditioning and principles is advantageous to cross-validate the results and distinguish between
249 physical phenomena and analytical artifacts. **Table 5** summarizes the differences and
250 complementarities of both approaches.

251 **Table 5.** Features of each analytical strategy deployed in the current study

	Offline chromatographic analysis	Online FTICR-MS
Sampling point	Diluted exhaust gas	Undiluted exhaust gas
Sampling duration	First phase of WLTC cycle	Instantaneous
Type of information	Averaged	Instantaneous
Type of compounds that can be measured	CH ₄ , VOC to C ₁₂ , aldehydes, ketones, ethanol...	VOC including aldehydes, ketones, alcohols, aromatics, olefins, NH ₃ ...

252

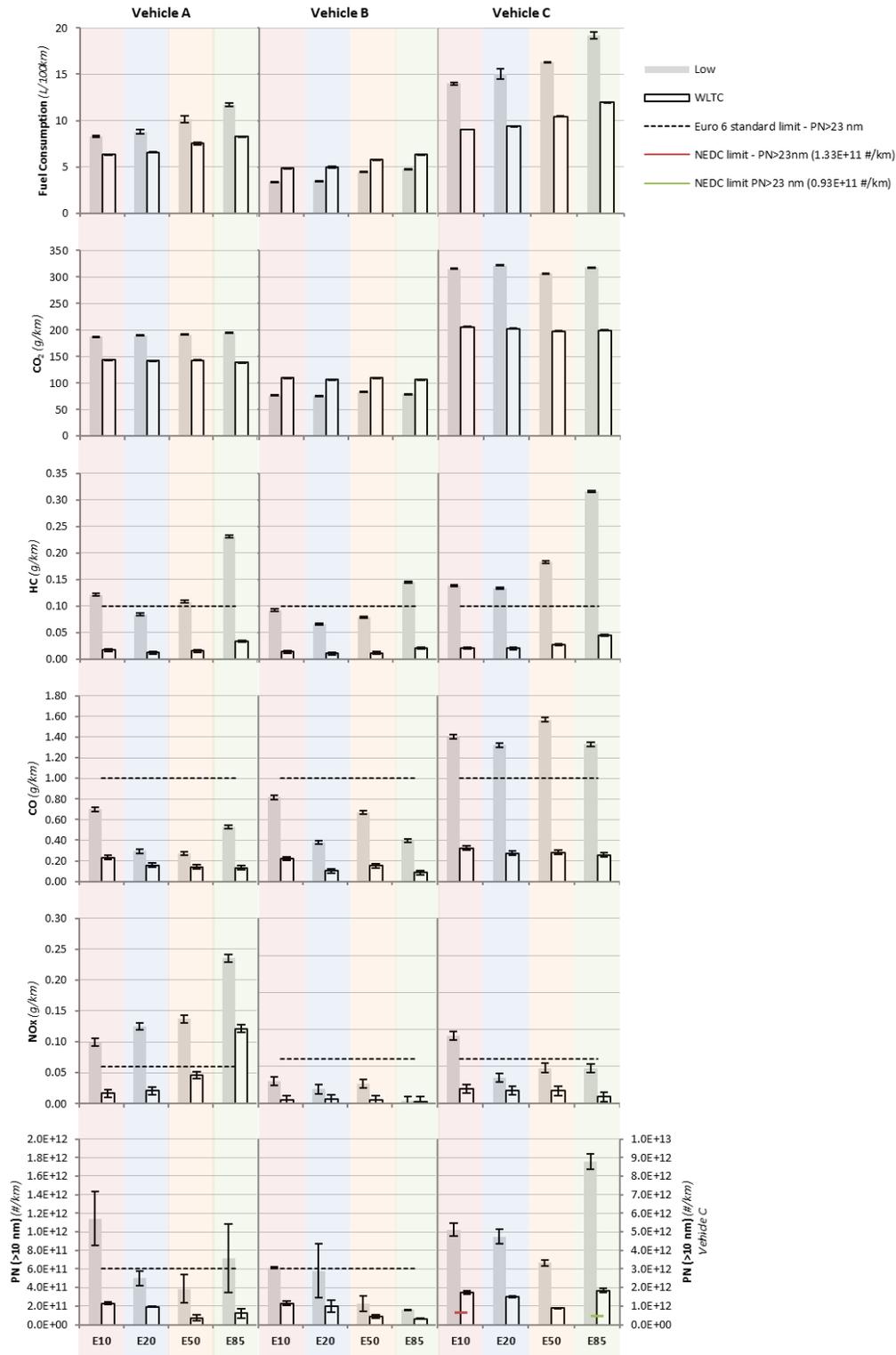
253 **3. Results and Discussion**

254 Similar tendencies were found between the two driving cycles; therefore, only test results in
 255 WLTC were considered for further interpretation.

256 **3.1 Driving cycle, regulated emissions, particles**

257 Gaseous emissions, particles, and fuel consumption (FC) results for the testing of the three
 258 vehicles are presented in the following figures. The results for each vehicle/fuel combination
 259 represent the average of two test runs. The error bars represent the measurement uncertainty for
 260 gaseous emissions or one standard deviation for fuel consumption and total number of particles.
 261 The former is provided for each emission discussed below.

3.1.1. Cold start emissions and global emissions



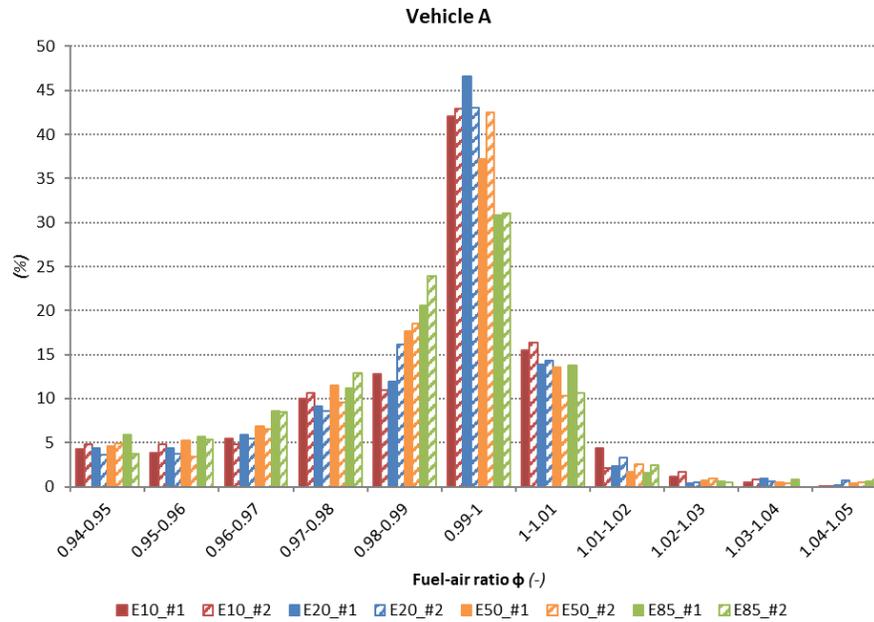
264 **Figure 2.** Regulated gaseous emissions, particles, and fuel consumption results over the
265 complete WLTC driving cycle for the testing of Vehicle A (GDI), Vehicle B (hybrid) and
266 Vehicle C (flex-fuel) with E10, E20, E50 and E85. Gaseous emissions are reported with their
267 corresponding measurement uncertainty. Fuel consumption and total number of particles are
268 reported with their standard deviation. Results for low phase are also highlighted with gray bars.

269 A comparison of the results obtained for all fuels tested is shown in Figure 2 for the three
270 vehicles. Results for the Low phase are also highlighted. This part of the cycle, which represents
271 the urban driving conditions and engine warmup phase, is the most emissive.

272 As expected, a clear fuel consumption increase trend is observed, starting at 20 % vol of ethanol.
273 Consumption increases up to 32 % with E85. This increase is attributed to the lower Low Heating
274 Value (LHV) of ethanol. Moreover, consumption is higher in the Low phase where the fuel mixture
275 is enriched and that catalyst warmup strategies are required during the first few minutes. Greater
276 dispersion is also present in this phase for all vehicles. Regarding CO₂ emissions, all vehicles show
277 a slightly but consistently reduction with ethanol content, reaching 3 % with E85. This result is
278 consistent with the fact that all energy from the fuel is derived from the combustion of carbon and
279 hydrogen, the somewhat higher ratio of hydrogen to carbon in E85 versus E10 results in the slightly
280 lower emissions of CO₂ for the same amount of energy expended [3,25]. While an increase up to
281 3.5 % is observed on the Low phase for vehicles A and B, original flexi-fuel calibration seems to
282 be favorable to the reduction of CO₂ emissions in cold-start conditions. As far as HC emissions
283 are concerned, although emissions are low, a decrease trend is observed with E20 for all vehicles.
284 Addition of ethanol up to 20 % vol seems to improve combustion quality by increasing O/C fuel
285 ratio [1]. Indeed, thanks to ethanol oxygen content, the engine benefits from better combustion,
286 which favors oxidation reactions and consequently reduces exhaust emissions. Above 20 % vol,

287 the ethanol positive effect on combustion seems to be inhibited, as an increase in HC emissions is
288 observed, irrespective of the vehicle technology. While trends of decreasing HC emissions with
289 increasing ethanol content have generally been seen in studies utilizing larger fleets of vehicles
290 [5,6,8,10], this increasing trend was also observed by G. Karavalakis et al. [9] and M.B. Celik [25].
291 One hypothesis is that at high ethanol content, the poor evaporation of ethanol in cold conditions
292 is source of increased liquid spray penetration [26] This induces walls wetting, which leads to an
293 increase in unburnt HC. It should be noted that this effect is most visible from 50 % vol. The
294 increase varies from 54 % to more than 100 % with E85. Most important increase is found over
295 the Low phase when catalyst has not attained maximum efficiency. Nevertheless, cycle results
296 remain below the regulation limit of 0.1 g/km for all fuels. CO emissions show a clear reduction
297 trend, starting at 20 % v/v of ethanol for all vehicles. There is a 42 %, 61 %, and 20 % gain for
298 respectively vehicle A, B and C with E85. The general trend of decreasing CO emissions with
299 increasing ethanol content is consistent with previous studies [3–8], and reductions may be
300 ascribed to the fuel-borne oxygen, which leans the air–fuel ratio and improves oxidation during
301 combustion and over the catalyst. NO_x emissions results show that fuel impact on NO_x emissions
302 varied by vehicle. No clear dependance on ethanol fuel content is found for vehicles B and C;
303 emissions results are within the repeatability range. However, NO_x emissions decrease up to 87%
304 on Low phase with E85. Regarding vehicle A, a clear NO_x emissions increase is observed, starting
305 at 50 % vol of ethanol. The regulation limit of 0.06 g/km is largely exceeded with E85. Increasing
306 NO_x emissions with increasing ethanol content may be due to differences in catalyst technology,
307 aging, or effectiveness. Previous studies with larger vehicle fleets have also shown trends of
308 increasing NO_x emissions with increasing ethanol content [5,9]. Indeed, higher fuel oxygen
309 content in the fuel can lean out the air–fuel mixture, which, in turn, can lead to higher NO_x

310 emissions. Other studies have shown no changes, inconsistent changes, or even decreases in NOx
311 emissions due to the lower adiabatic flame temperature of ethanol than gasoline [3,6,11]. To
312 discuss NOx results of vehicle A (GDI), the fuel-air ratio (ϕ) was monitored, and results show that
313 the addition of ethanol shifts the fuel-air ratio distribution towards areas of lean mixture ($\phi < 1$)
314 (Figure 3). The difference is less pronounced between E10 and E20 fuels but becomes more
315 pronounced with E50 and E85 fuels. The hypothesis is that, due to the lower calorific value of
316 ethanol, the corrections made to the injection time to guarantee the torque are not sufficient to
317 ensure good monitoring of the stoichiometric fuel-air mixture and lead to slightly lean combustion,
318 which is favorable to NOx emissions. In addition, the presence of oxygen in the fuel, and a possible
319 increase in combustion temperatures due to ethanol's higher RON and latent heat of vaporization,
320 which allow for greater ignition timing at high loads, are also factors that can favor NOx
321 production. As observed for a vast majority of study [6,12,13], the number of particle emissions
322 show a reduction with E85 for vehicles A and B. No clear trend in the impact of ethanol content
323 is found for vehicle C, except in the warm-up phase where there is an increase of 72 % with E85.



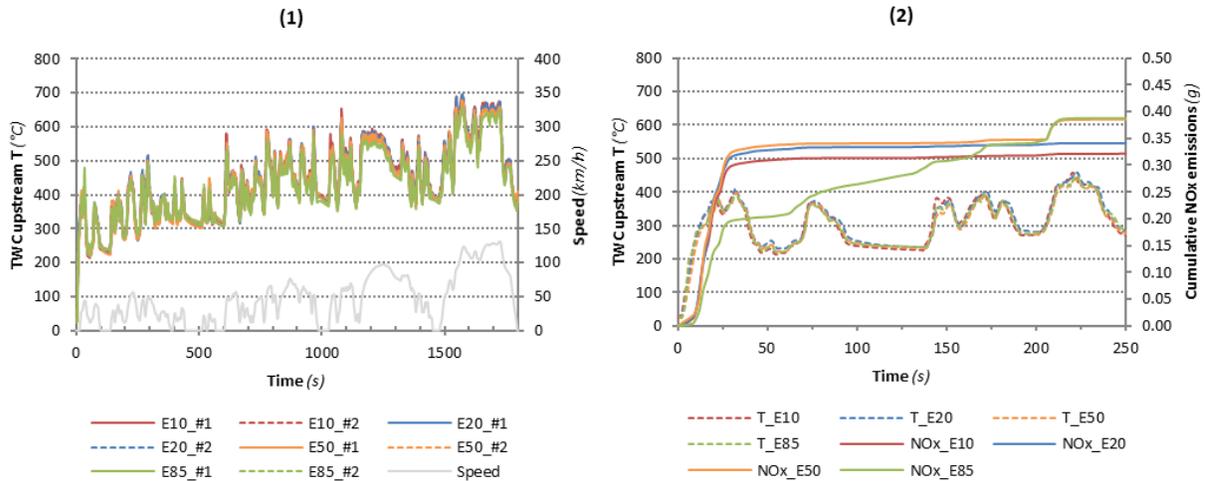
324

325 **Figure 3.** Fuel-air ratio ϕ distribution over WLTC for vehicle A (GDI) with E10, E20, E50 and
 326 E85. The two test runs are presented for each fuel.

327 3.1.2. After-treatment system analysis

328 **Three-way catalyst (TWC)**

329 By analyzing the TWC upstream temperature (Figure 4), it would appear that the addition of
 330 ethanol has no significant impact on the TWC upstream temperature in the first part of the cycle.
 331 However, in the second part of the cycle, i.e. in the areas of highest load, where there are hardly
 332 any emissions, a significant drop in the upstream temperature of the catalyst is seen as the ethanol
 333 content in the fuel increases. Indeed, the upstream catalyst temperature is 50 °C lower in E85.



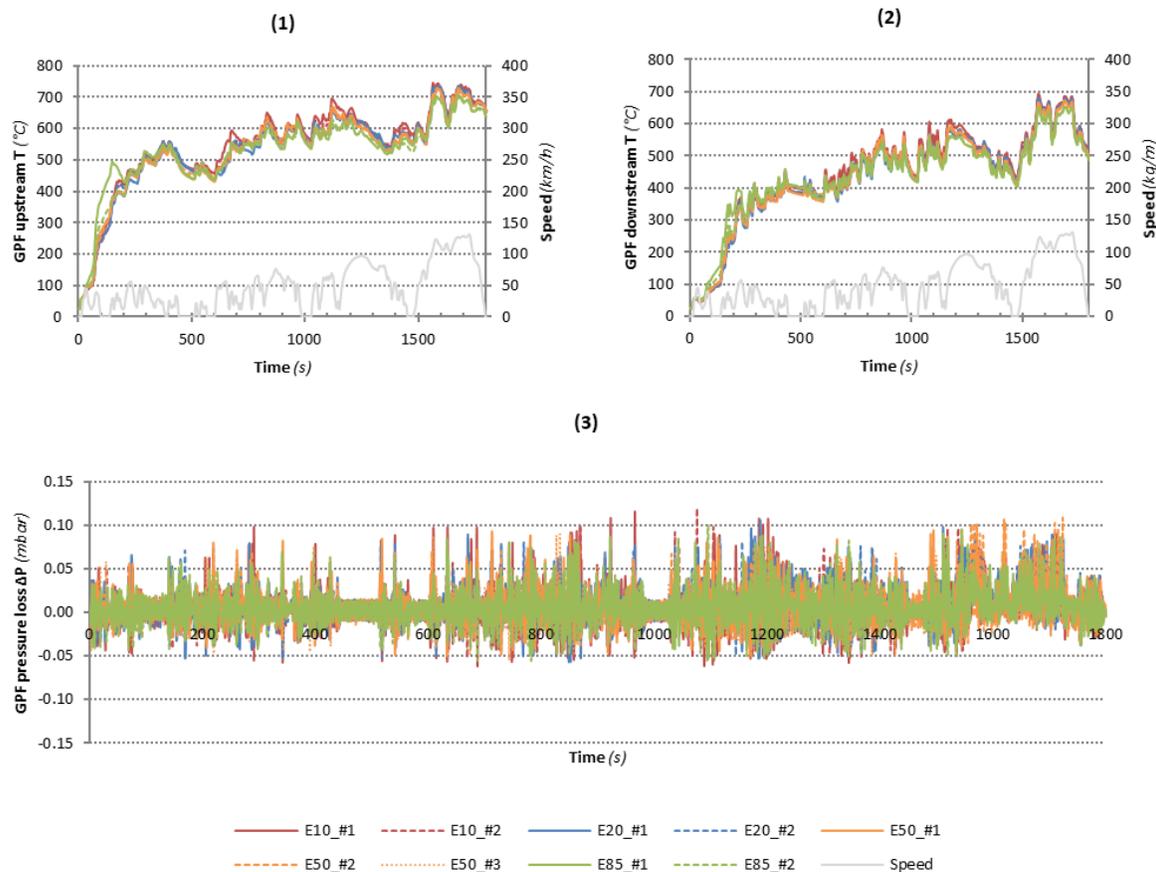
334

335 **Figure 4.** TWC upstream temperature (1) and catalyst light-off delay (2) over WLTC for vehicle
 336 A (GDI) with E10, E20, E50 and E85. The two test runs are presented for each fuel.

337 In terms of catalyst lighting off (Figure 4), the addition of ethanol to the fuel does not appear to
 338 have an impact on the TWC light-off temperature and activation time. However, some studies have
 339 shown that the light-off temperature marginally shifts to lower temperatures, with increasing levels
 340 of ethanol, but the effect is small [27]. Regarding TWC activation time, some authors have
 341 observed that the addition of ethanol delays the ignition of the TWC [28].

342 Gasoline particle filter (GPF)

343 By analyzing the GPF upstream and downstream temperature (Figure 5), it can be seen that the
 344 GPF upstream/downstream temperature increase with the ethanol content over the first phase of
 345 the cycle, the phase in which the majority of the particulate matter is emitted. However, from 400
 346 seconds, the GPF upstream/downstream temperature decreases ($\Delta_{E10 \rightarrow E85}$ by about 50°C) as the
 347 ethanol content of the fuel increases.



348

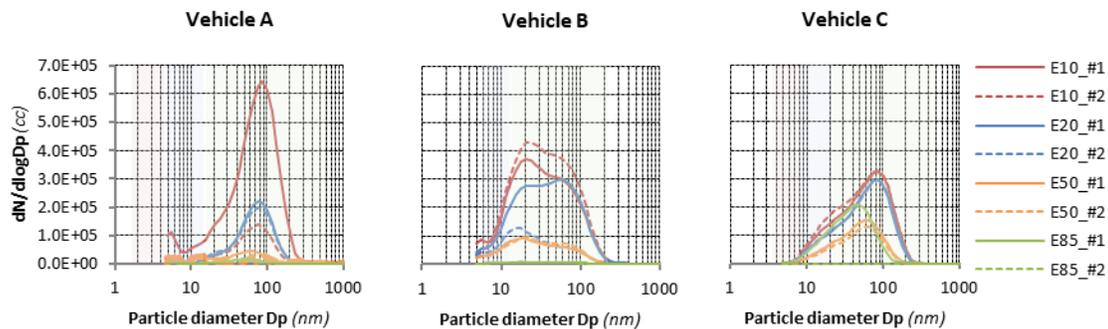
349 **Figure 5.** GPF upstream (1) and downstream temperature (2) and GPF pressure loss (3) time
 350 evolution by fuel for the vehicle A (GDI) with E10, E20, E50 and E85. The two test runs are
 351 presented for each fuel.

352 Under the test conditions, the addition of ethanol from E10 to E85 does not appear to impact the
 353 already relatively low-pressure loss (< 15 mbar) significantly at any time in the cycle (Figure 5).

354 3.1.3 Particle size distribution analysis

355 To discuss the effect of ethanol on the size of the emitted particles, the particle size distribution
 356 was analyzed for the four fuels by considering the particles over the whole WLTC driving cycle
 357 (Figure 6). For most fuels, the particle size distributions showed bimodal profiles, consisting of a
 358 nucleation mode (10–23 nm) and an accumulation mode (23–100 nm).

359 The addition of ethanol from 10 to 20% vol does not show a clear trend in particle size
 360 distribution for vehicle A (Euro 6d-temp IC engine) fitted with a GPF; the impact of ethanol
 361 appears to be neutral on fine particles (size < 23 nm). However, above 20% vol, the production of
 362 particles larger than 23 nm decreases significantly with the addition of ethanol. Accumulation
 363 mode is centered at around 70-90 nm regardless the fuel. Regarding vehicle B (Euro 6d-temp
 364 hybrid), despite high variability in particle size distribution between trials, ethanol addition seems
 365 to have a positive impact on all particle sizes; there is an overall decrease. For vehicle C (Euro 6c
 366 flex-fuel), there is a trend towards the medium and smaller particle size distribution, and a
 367 reduction in the number of particles of size 70 nm and above with increasing ethanol content.
 368 Results are consistent with previous studies showing that, with increasing alcohol content, peak
 369 particle number concentrations and particle size are decreased [6].



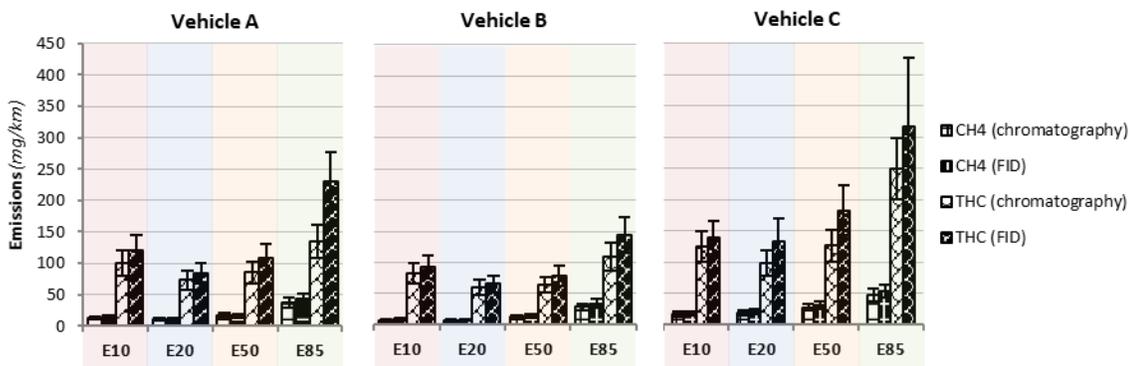
370
 371 **Figure 6.** Particle size spectral density over WLTC for vehicle A (GDI), vehicle B (hybrid) and
 372 vehicle C (flex-fuel) with E10, E20, E50 and E85. The two test runs are presented for each fuel.

373 **3.2 Non-regulated emissions**

374 Non-regulated emissions analysis through chromatography techniques were carried out only on
 375 Low phase of the WLTC as concentration levels in other phases was close to detection limits.

376 3.2.1. Comparison of methane and total hydrocarbon measurement

377 Methane and total hydrocarbon (THC) were measured both directly on roller test bed by
378 standardized gas analyzers, and by gas chromatography (total hydrocarbons being obtained by
379 summation of all VOCs detected). Therefore, the amounts obtained by both techniques could be
380 compared in various conditions (three vehicles, four ethanol contents) and are presented on Figure
381 7. This comparison was helpful to cross-validate the results.



382

383 **Figure 7.** Methane and total hydrocarbon emissions on Low phase of the WLTC for vehicle A
384 (GDI), vehicle B (hybrid) and vehicle C (flex-fuel) with E10, E20, E50 and E85.

385 Chromatography results are reported with their error bars, which represent the maximal value
386 between 20% uncertainty, and the standard deviation obtained between two independent
387 measurements. FID results are reported with their corresponding measurement uncertainty.

388 Both for methane and total hydrocarbons, concentrations measured by chromatography and FID
389 are in very good agreement with the measurements with chromatographic separation. This comfort
390 the use of these measurements for quantitative evaluation of the various emissions.

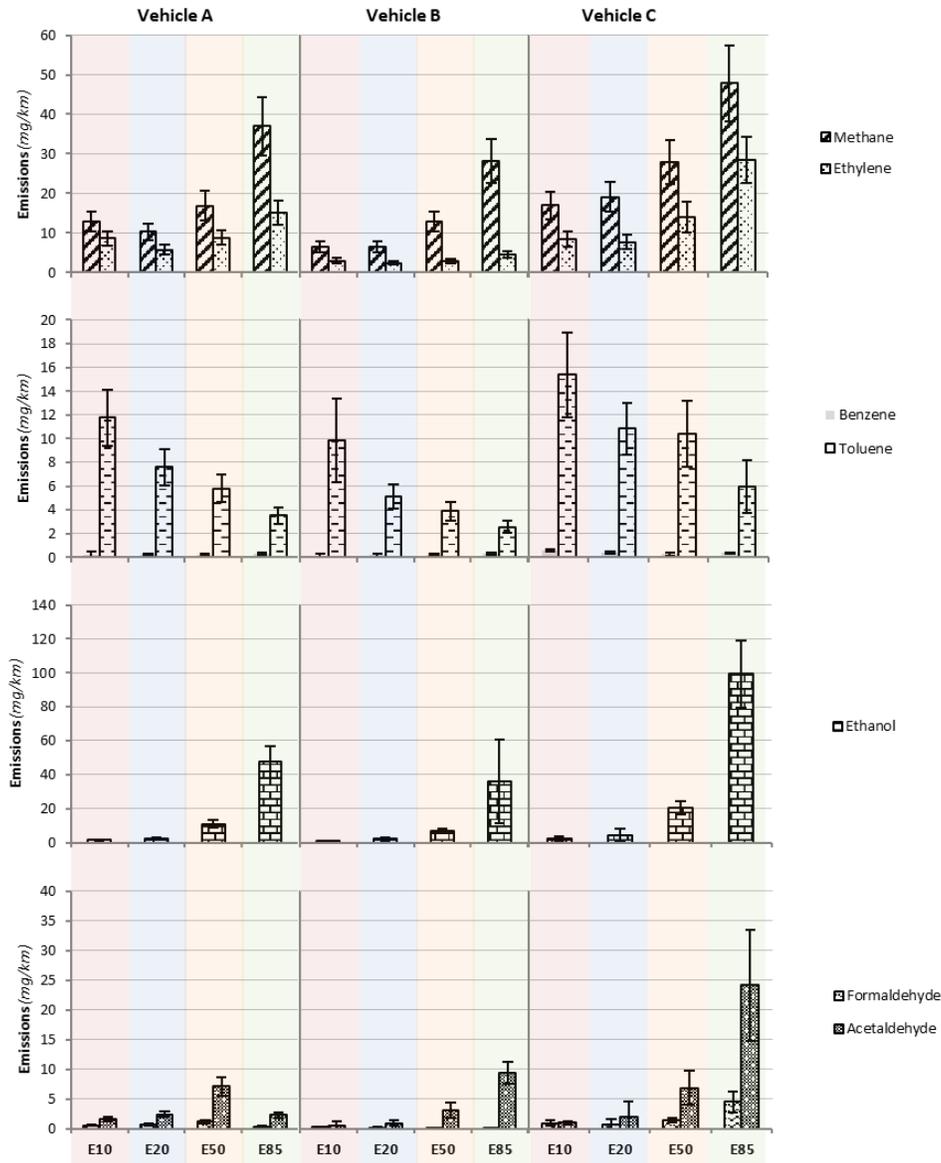
391 3.2.2. Choice of non-regulated compounds analyzed

392 Among all results that were obtained on VOCs, it was decided to focus here on a selection of
393 relevant molecules to simply gather most of information. They were selected for their higher
394 concentration or for their known pollution and health impacts. The compounds that were
395 considered are: methane and ethylene (significant concentrations and particular behaviors towards
396 increasing ethanol content), benzene and toluene (known toxicity and surrogates for aromatics),
397 ethanol (constituent of variable amount in the fuels), formaldehyde and acetaldehyde (known
398 toxicity and expected by-products of ethanol combustion).

399 3.2.3. Emissions results

400 The impact of fuel ethanol content on non-regulated emissions was investigated (

401 Figure 8).



402

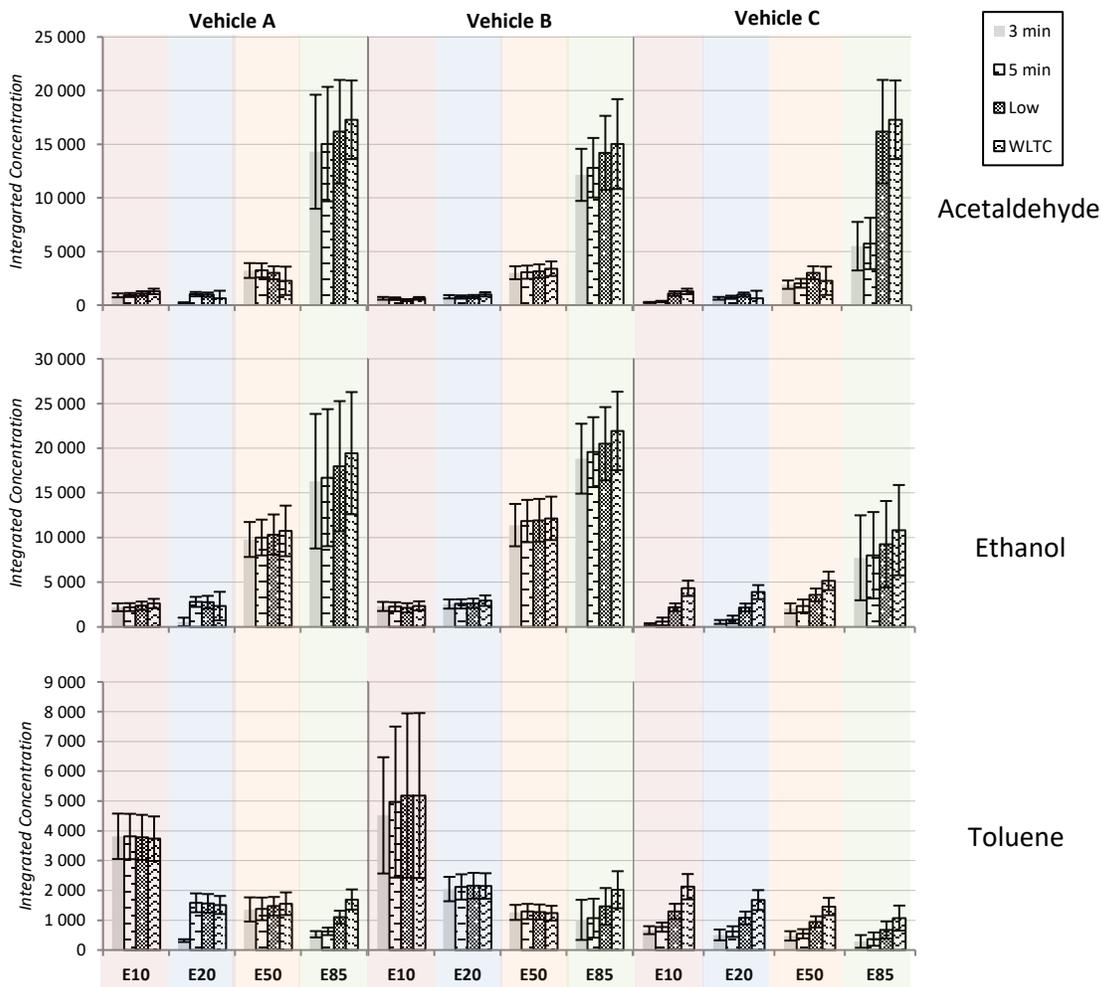
403 **Figure 8.** Emissions of selected compounds measured by chromatography on Low phase of
 404 WLTC for vehicle A (GDI), vehicle B (hybrid), vehicle C (flex-fuel) with E10, E20, E50 and
 405 E85. Emissions results are reported with their error bars, which represent the maximal value
 406 between 20% uncertainty, and the standard deviation obtained between two independent
 407 measurements.

408 It appears that there is no strong impact of an increase of ethanol content from 10% to 20%
409 (E10 and E20) over non-regulated emissions, and this is the case for all vehicle technologies. This
410 result was also observed by several authors [9,11]. With a fuel containing 85% ethanol (E85), an
411 increase of methane, ethanol, ethylene, and acetaldehyde emissions can be detected for all vehicle
412 technologies, except for vehicle A where acetaldehyde emissions with E85 are similar with E10.
413 Moreover, higher formaldehyde emissions are also detected on vehicle C. The vehicle C, even if
414 it should be fully optimized for a fuel composition with 85% ethanol, emits quite high amounts of
415 methane (48 mg/km), ethylene (28 mg/km), ethanol (99 mg/km) and aldehydes (5 mg/km for
416 formaldehyde and 24 mg/km for acetaldehyde). This observation is of particular concern, even
417 more as formaldehyde emissions even exceed US regulation (2.5 mg/km).

418 Concerning total VOCs, Figure 7 also highlights the same trend (almost same emission levels
419 for E10 and E20, and significant increase with E85) for both vehicles. Total VOCs emissions are
420 increasing with high ethanol content, despite a reduction in aromatic compounds.

421 3.2.4. Real time analysis of exhaust emissions

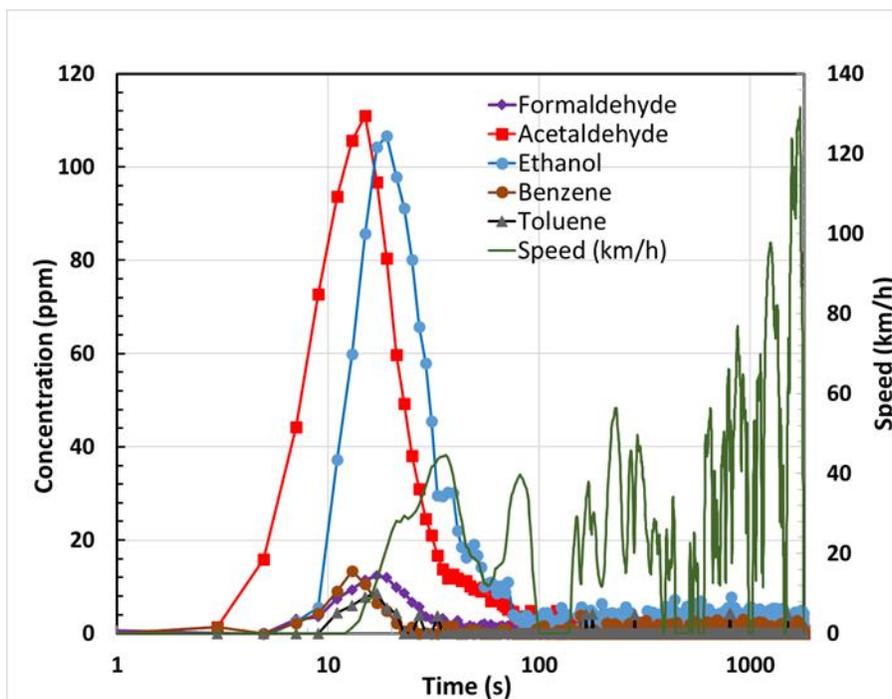
422 The analysis is performed in real time. Emissions of non-regulated compounds occur mostly
423 during the Low phase of the WLTC cycle and for the volatile compounds measured by FTICR-
424 MS the most important emissions occur generally during the first three minutes. This is illustrated
425 in Figure 9 for acetaldehyde, ethanol, and toluene where the emissions integrated over different
426 time windows are displayed.



427
 428 **Figure 9.** Non-regulated emissions for 3 selected compounds: (a) acetaldehyde (b) ethanol (c)
 429 toluene measured by mass spectrometry over different time windows: during the first 3 minutes,
 430 the first 5 minutes, the Low phase of the WLTC cycle and over the full WLTC cycle. The
 431 reported error bars are the maximal value between 20% uncertainty and the standard deviation
 432 obtained between two independent measurements.

433 More precisely in Figure 10 is shown the real time measurement by mass spectrometry of five
 434 selected compounds with a time resolution of a few seconds in the case of vehicle C with E85. The
 435 time scale used is logarithmic to emphasize that the main emissions occur at the beginning of the
 436 WLTC cycle, during the first three minutes when the after-treatment system is warming up. The

437 temporal structure differs slightly for the different compounds. We can notice for example that the
438 response for acetaldehyde is almost immediate whereas the response for ethanol is somewhat
439 delayed.



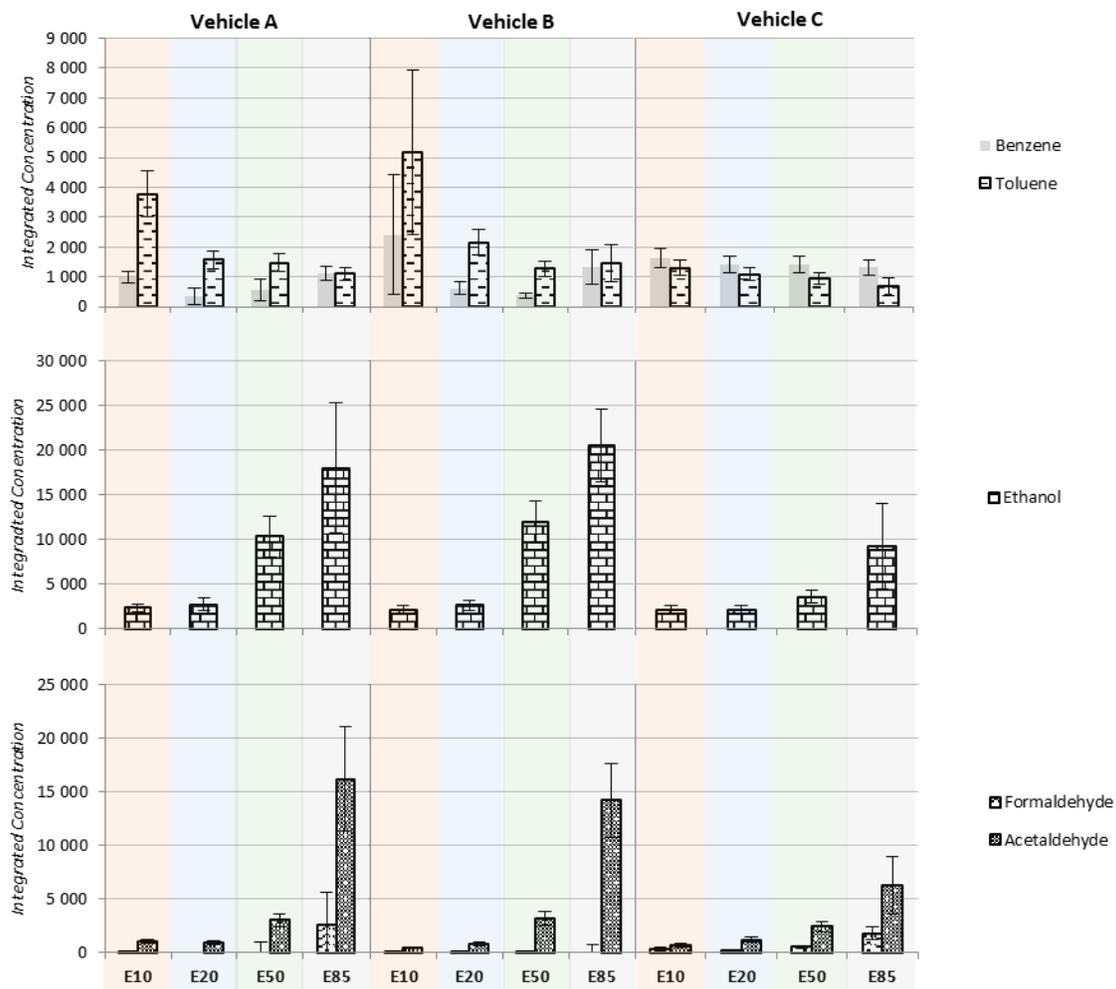
440
441 **Figure 10.** Measurement by mass spectrometry of the time evolution for the concentrations of 5
442 selected compounds (formaldehyde, acetaldehyde, ethanol, benzene, toluene) for the vehicle C
443 (flex-fuel) with E85 over WLTC. The time scale is logarithmic to emphasize the cold start
444 emissions. The reported intensities are those of the protonated ions from the mass spectrometry
445 real time analysis.

446 To compare with the results obtained by chromatography given earlier on Figure 8, the mass
447 spectrometric real time measurements were integrated over the Low phase of the WLTC cycle.
448 Methane and ethylene were not measured by real time FTICR-MS as they are not ionized with the
449 chemical ionization technique used in the mass spectrometer. Figure 11 gives the result of this

450 integration for 5 compounds (ethanol, benzene, toluene, formaldehyde, acetaldehyde). The
451 integration is done after conversion of the intensities of the ions into concentrations of the
452 corresponding neutral and subtraction of the level measured during a blanc measurement (mean
453 value observed before the beginning of the WLTC cycle).

454 The results of this integration are less reliable than the measurements obtained by
455 chromatography which is the reference technique for such measurements, and we must also point
456 out that the integration over time of the concentrations obtained by mass spectrometry don't give
457 the total amount emitted in mg/km as with chromatographic measurements. However, we can see
458 that the same trends are observed with mass spectrometry and chromatography when going from
459 E10 to E85. Indeed, for ethanol and aldehydes the emission levels obtained with E10 and E20 are
460 quite comparable whereas for E50 and E85 we observe a significant increase. For the aromatics,
461 benzene, and toluene a decrease is observed when going from E10 to E85.

462 The main discrepancy is the overall levels which are lower for vehicle C in the mass
463 spectrometric measurements for vehicle C. We have no definite explanation for the decrease in
464 sensibility for these measurements. This could be linked to a change in the reaction conditions in
465 the mass spectrometer.



466

467 **Figure 11.** Emissions of selected compounds (ethanol, benzene, toluene, formaldehyde,
 468 acetaldehyde) measured by mass spectrometry on Low phase of WLTC for vehicle A, B and C
 469 with E10, E20, E50 and E85. The error bars are the maximal value between 20% uncertainty and
 470 the standard deviation obtained between two independent measurements.

471 3.2.5. Analytical measurements discussion

472 Both analytical techniques (sampling and gas chromatography vs. time-resolved mass
 473 spectrometry) exhibit similar trends concerning the impact of ethanol on non-regulated emissions.
 474 As presented on Figure 8 and Figure 11, the presence of ethanol causes an increase in the emission
 475 of oxygenated compounds and a decrease of aromatics.

476 Both techniques are not sampled on the same location on the roller bench (Table 5). B-Trap
477 analysis is carried out on undiluted exhaust gases, while sampling and chromatographic analysis
478 is done on diluted gases. With pollution levels being always lower, one perspective for future
479 studies would be to implement both analyzer on undiluted exhaust gases. Otherwise, even with a
480 pre-concentration step, sensitivity limits of chromatographic analysis will be reached. This
481 coupling of techniques is indeed valuable because on the one hand the chromatographic analysis
482 provides insight into the molecular speciation, facilitating the molecular identification after
483 FTICR-MS analysis. On the other hand, B-Trap analysis enables to gain information on the
484 kinetics of the emissions, which is not reachable with an offline sample averaged over the whole
485 driving cycle.

486 **4. Conclusion**

487 This study evaluates the impact of varying ethanol blends concentrations (from 0 to 85% vol of
488 ethanol) on the tailpipe regulated and non-regulated emissions from one Euro 6c flex-fuel
489 passenger car, one Euro 6d-temp IC engine and one Euro 6d-temp hybrid vehicle fitted with
490 approved E85 conversion kit. Two driving cycles are used: WLTC and CADC. In addition to
491 standard instrumentation used for characterization of regulated emissions, three analytical
492 techniques were combined for characterization of non-regulated pollutants. High-performance
493 liquid chromatograph (HPLC) coupled to ultraviolet (UV) detection to measure aldehydes and
494 ketones. Gas chromatography coupled to mass spectrometry (GC-MS) was used for PAHs
495 characterization. GC-FID was used to measure VOCs (C1 to C12) on the first phase of the WLTC,
496 the most emissive part. To assess the impact of ethanol transient speciation of emitted VOCs,
497 emissions were recorded in real-time by Fourier transform ion cyclotron resonance mass

498 spectrometry (FTICR-MS) over the whole driving cycle. This was to include higher load and
499 transient conditions which are not recorded by offline chromatography.

500 The results show that the impact of high ethanol content is broadly similar amongst the different
501 tested technologies (E85 conversion kits and flex-fuel). It was concluded that at 50% vol of ethanol
502 in the fuel and above, the emissions of total unburnt hydrocarbons increase with an exponential
503 trend. The use of varying amounts of ethanol in recent and diverse Euro 6d-temp vehicle
504 technologies shows that the number and size of particles are unaffected by the by the increase in
505 fuel ethanol content. However, the results indicate a risk of increased NO_x emissions for Euro 6d-
506 temp IC engines, which should be confirmed on other vehicles of similar technology. The main
507 identified trends for non-regulated emissions were confirmed for all vehicles. Ethanol content of
508 50% vol and above lead to an increase of aldehyde emissions, ethylene, methane, and ethanol. The
509 later represent near 50 % of total non-regulated emissions.

510 Both analytical techniques (sampling and gas chromatography vs. time-resolved mass
511 spectrometry) exhibited similar trends concerning the impact of ethanol on non-regulated
512 emissions. Time-resolved mass spectrometry is carried out on undiluted exhaust gases, while
513 sampling and chromatographic analysis is done on diluted gases. This coupling of techniques is
514 indeed valuable because on the one hand the chromatographic analysis facilitates the molecular
515 identification and, on the other hand, time-resolved mass spectrometry enables to identify
516 emissions profiles during the driving cycle. Future work is necessary to confirm the observed
517 trends in different operating conditions including aged vehicles and after-treatment. The ethanol
518 impact on GPF temperature is poorly discussed in the literature and the temperature increase
519 observed in this study once ethanol is added may have a variable impact depending on the system
520 condition. Both sampling and gas chromatography and time-resolved mass spectrometry analyzers

521 could be implemented on undiluted exhaust gas so as not to face with the sensitivity limits of the
522 chromatographic analysis as pollution levels are always lower.

523 **5. Declaration of Competing Interest**

524 The authors declare that they have no known competing financial interests that could have
525 appeared to influence the work reported in this paper.

526 **6. Acknowledgements**

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