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Impact of ethanol containing gasoline blends on emissions from a flex-fuel vehicle tested over the Worldwide Harmonized Light duty Test Cycle (WLTC)

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HIGHLIGHTS

- Hydrous and anhydrous ethanol blends show similar regulated and unregulated emissions.
- Low temperature leads to higher emissions for all tested blends.
- E85 and E75 blends resulted in higher emissions of acetaldehyde and ethanol.
- Higher emissions of acetaldehyde and ethanol yield higher OFP.

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ABSTRACT

Regulated and unregulated emissions from a Euro 5a flex-fuel vehicle tested with nine different hydrous and anhydrous ethanol containing fuel blends at 23 and −7 °C over the World harmonized Light-duty vehicle Test Cycle and the New European Driving Cycle, were investigated at the Vehicle Emission Laboratory at the European Commission Joint Research Centre Ispra, Italy. The experimental results showed no differences on the regulated and unregulated emissions when hydrous ethanol blends were used instead of anhydrous ethanol blends. The use of E85 and E75 blends (gasoline containing 85% and 75% of ethanol, respectively) resulted in a reduction of NO_x emissions (30–55%) but increased the emissions of carbon monoxide, methane, carbonyls and ethanol compared to E5, E10 and E15 blends (gasoline containing 5%, 10% and 15% of ethanol, respectively). The increase of the acetaldehyde and ethanol emissions (up to 120% and 350% at 23 °C and up to 400% and 390% at −7 °C, for acetaldehyde and ethanol, respectively) caused a severe increment of the ozone formation potential. Most of the studied pollutants presented similar emission factors during the tests performed with E10 and E15 blends. The emission factors of most unregulated compounds were lower over the NEDC (with ammonia as an exception) than over the WLTC. However, when taking into consideration only the cold start emissions, emission factors over the WLTC were observed to be higher, or similar, to those obtained over the NEDC. Low ambient temperature caused an increase of the emissions of all studied compounds with all tested blends.

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1. Introduction

Vehicular emissions significantly influence the composition of the atmosphere and have a strong impact on climate change [1]. The use of alternative fuels has been promoted in the EU as a measure to decrease greenhouse gases (GHG) emissions and also to meet what at the time was a growing demand of energy for transport use [2]. Biofuels have been seen as a measure to reduce emissions of GHGs from road transport because they were considered CO_2 neutral fuels. The EU has set a 10% renewable energy requirement for the transport sector, to be complied with by 2020 (2009/28/EC) [3]. In 2010, the use of renewable energy by the transport sector was 4.70%, 91% of which was covered by biofuels [4]. In the United States, the Environmental Protection Agency (EPA) has implemented a series of initiatives to promote the introduction of renewable fuels, with a target of 136 billion liters of renewable fuel to be blended with gasoline by 2022 [5]. So far, ethanol is the main renewable fuel used for transportation

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in the US [6,7]. Blending mandates exist in 52 countries around the world having such requirements. China has a biofuels mandate of 10% by 2020. India, expects to cover 20% of its fuel demand with ethanol by 2017. Brazil, where ethanol has been used in different fuel blends since the mid-70s, mandates that 20% of the gasoline demand has to be supplied by ethanol by 2022. This target has already been reached.

In Europe, the latest version of the principle European gasoline (EN228) standards allows blending up to E10 (gasoline containing up to 10% of ethanol). Hydrous ethanol containing fuel blends have been proposed as an alternative to the anhydrous ethanol blends. By skipping the drying step after distillation of the fuel ethanol one can avoid the capital and energy cost associated with these drying units, which makes hydrous ethanol cheaper than anhydrous ethanol [8]. Brazil uses hydrous ethanol (ethanol with up to 4.9% vol/vol of water) in E100 for flex-fuel vehicles.

The high targets set on the use of renewable fuel will likely lead to a further increase of the ethanol concentration in gasoline. With the fuel composition undergoing continuous changes, it is crucial to have a deep understanding of the impact that these new fuels will have on vehicular emissions. The present study was set up on that frame.

Few studies have examined the impact that the different concentrations of ethanol in the fuel blend have on the exhaust emissions of modern spark ignition engines [9,10] or how different ethanol containing blends affect the emissions of modern flex-fuel vehicles (FFV) [8,10–13]. FFVs operate with standard gasoline and any ethanol (hydrous and anhydrous) containing blend. In Europe, FFVs can run on standard gasoline (hereinafter E5, gasoline containing 5% ethanol) or on blends of ethanol and gasoline containing up to 85% ethanol during the summer (also known as E85) or 75% during winter (E75, winter blend). Modern gasoline vehicles can run on blends containing up to 15% of ethanol [14].

Previous studies [7,11,12,15] have suggested that an increase in the ethanol content in the fuel blends reduces the emissions of some regulated gases (CO and total hydrocarbons (THC)) and CO_2. Those studies did not show strong trends for NO_x emissions. As opposed to the promising benefits in the emissions of regulated compounds and CO_2, an increase in the ethanol concentration in a fuel blend led to higher emissions of formaldehyde and acetaldehyde [7,11,12,15]. These carbonyl compounds are highly toxic and potentially carcinogenic [16–18]. They are also known for their impact on air quality, as they are precursors of ozone and peroxyacetyl nitrates (PAN) [15,19–21]. Therefore, given the current push to increase the ethanol concentration in motor fuel blends, it is crucial to study the emissions from FFVs for not only the regulated gases, but also the unregulated ones.

In the present study, gaseous emissions were directly measured at the raw exhaust with a High Resolution Fourier Transform Infrared spectrometer (FTIR) at a 1 Hz acquisition frequency. Gaseous compounds (e.g., CO, NO, acetaldehyde, ethanol, etc.) were monitored in real-time over the New European Driving Cycle (NEDC), which is currently used for type approval of light-duty vehicles (LDVs) in Europe, and over the World harmonized Light-duty Test Cycle (WLTC) that will soon be used for type approval of LDVs in the European Union and potentially other countries who are signatories to the United Nations Economic Commission for Europe (UNECE) [22]. This is, to our knowledge, the first study that investigates not only the effect of different anhydrous ethanol fuel blends (AHE), but also the effect of different hydrous ethanol blends (HE) on vehicular emissions. Furthermore, for the first time, the regulated and unregulated compounds emitted by a FFV over the WLTC are compared to those emitted over the NEDC. The effect of low temperature was also studied for the winter fuel blends (AHE75 and HE75) in comparison with the standard gasoline, E5. The analysis of a series of relevant ozone precursors measured in the vehicles' exhaust by FTIR was carried out for all blends tested. Finally, the impact of the cold engine start on the emissions of formaldehyde, acetaldehyde, ammonia, ethanol, nitrous oxide and methane was evaluated.

2. Experimental

In the present study a Euro 5a flex-fuel light duty vehicle (FFV) equipped with a three way catalyst (TWC) and a turbo charged air intake system (see technical details in Table 1) was tested at 23 and −7 °C over the WLTC and NEDC using nine different ethanol containing fuel blends. The tests were carried out in the Vehicle Emission Laboratory (VELA) at the European Commission Joint Research Centre Ispra, Italy. The facility includes a climatic test cell with controlled temperature and relative humidity (RH) to mimic different European ambient conditions (temperature range: −10 to 35 °C; RH range: 50–80%). The tests were performed on a chassis dynamometer (inertia range: 454–4500 kg), designed for two and four-wheel drive LDVs (two 1.22 m roller benches – MAHA GmbH, Germany). The exhaust was fed, as defined by the regulation (70/220/EEC) and its following amendments [23], to a Constant Volume Sampler (CVS, HORIBA, Japan) using a critical Venturi nozzle to regulate the flow (CVS flow range: 3–30 m^3/min). Gaseous emissions were analyzed from a set of Tedlar bags. The bags were filled with diluted exhaust from the CVS (Automatic Bag Sampler, CGM electronics) and CO, total hydrocarbons (THC), NO_x, and CO_2 concentrations were measured using an integrated measurement system (MEXA-7400HTR-LE, HORIBA), as described in Section 2.3. A series of thermocouples monitored the temperature of the oil, cooling water, exhaust, and ambient conditions. A universal exhaust gas oxygen (UEGO) type sensor was connected to the tailpipe, upstream of the catalyst, to monitor the air to fuel ratio. Vehicles were kept inside the climatic cell under the described conditions for a 24 h soaking period prior to each emission test. For the test cell configuration, see Fig. 1.

2.1. Fuel blends

Nine fuel blends were tested in the present study. A certified reference gasoline containing 5% anhydrous ethanol (E5) was used during the tests performed at 23 and −7 °C. Four fuel blends containing 10%, 15%, 75% and 85% hydrous ethanol and four blends containing anhydrous ethanol in the same ratio were used during the tests. The fuel blends were provided by Argos (The Netherlands) and prepared by mixing certified reference E5 gasoline with anhydrous ethanol and, in the case of hydrous ethanol, with anhydrous ethanol and demineralized water. For all fuel blends the same E5 base gasoline, anhydrous ethanol and demineralized water were used. The nomenclature of the blends applied is as follows: blends containing hydrous ethanol have the prefix HE, while blends containing anhydrous ethanol are designated with AHE. The number that follows the prefix indicates the volume fraction of

Table 1
Vehicle specifications.

Features	FFV
Combustion type	Spark ignition
Year of registration	2012
EU emission standard	Euro 5a
After-treatment	TWC[a]
Fuel system	Direct injection
Engine power (kW)	132
Engine displacement (cm^3)	1596
Odometer (km)	24334

[a] TWC (three way catalyst).

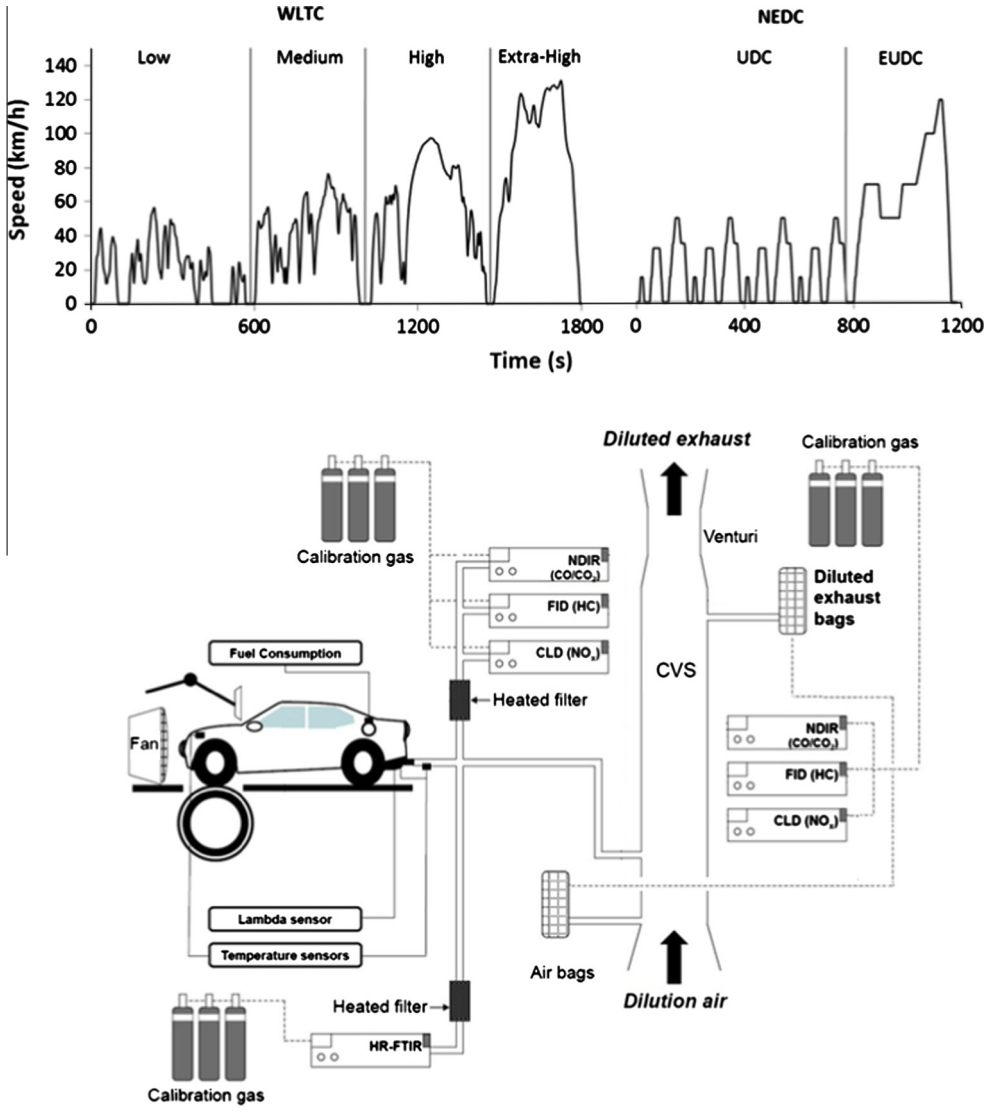

Fig. 1. Driving cycles performed (top) and schematic diagram of the experimental setup (bottom).

the ethanol + water in the blend. Hence, AHE15 is an anhydrous blend containing 15% ethanol and HE75 is a hydrous blend containing 75% ethanol including the water. Table 2 provides a full description of the blends used. The typical ethanol concentration of the winter fuel blend is 75%. Therefore, the two blends containing 75% ethanol, AHE75 and HE75, were only used during the test performed at −7 °C. The E5, used as a reference gasoline, was tested at both 23 and −7 °C and the other fuel blends (AHE10, AHE15, AHE85, HE10, HE15 and HE85) were tested at 23 °C.

2.2. Test cycles

The FFV was tested using the nine described fuels over the Worldwide harmonized Light-duty driving Test Cycle (WLTC) and

Table 2
Fuels specifications.

Parameter	Method	Unit	E5	AHE10	AHE15	AHE75	AHE85	HE10	HE15	HE75	HE85
RON	ISO 5164	–	94.0	96.4	96.3	102.9	104.0	96.2	98.0	107.0	108.0
MON	ISO 5163	–	84.2	85.4	86.4	88.4	89.0	85.6	85.0	91.0	90.7
Density at 15 °C	ASTM D 4052	kg/m^3	746.5	748.8	751.1	777.0	793.0	749.	753.1	792.7	795.7
DVPE at 100F	ASTM D 5191	kPa	57.5	57.6	57.1	40.1	30.1	60.1	60.1	40.7	34.4
Distillation evaporated at 70 °C	ASTM D 86	vol%	33.7	46.5	49.5	11.6	3.2	46.4	48.5	8.6	4.7
Gross calorific value	Calculated	kcal/kg	11.280	11.272	11.263	11.168	11.147	11.206	11.148	10.493	10.386
Sulphur (S)	ASTM D 5453	mg/kg	4.8	4.2	4.0	0.9	0.6	4.0	4.0	1.0	0.4
Carbon	ASTM D 9291	mass%	61.1	66.6	62.3	50.0	52.2	60.5	63.8	48.1	48.4
Hydrogen	ASTM D 9291	mass%	8.5	9.8	9.5	10.5	11.0	9.3	10.1	11.4	12.0
Nitrogen	ASTM D 9291	mass%	<0.75	<0.75	<0.75	<0.75	<0.75	<0.75	<0.75	<0.75	<0.75
Oxygen	Calculated	mass%	30.4	23.6	28.2	39.5	36.0	30.2	26.1	40.5	39.6
Water	ASTM D 1364	mass%	0.074	0.087	0.106	0.137	0.137	0.652	1.070	5.660	6.450

over the New European Driving Cycle (NEDC) at 23 or −7 °C. Duplicate tests were performed for each fuel blend over the WTLC and one test per fuel blend was performed over the NEDC. The WLTC [22,24] is a cold start driving cycle, i.e., the vehicle and its components (oil, coolant, catalyst, etc.) are at 23 or −7 °C, ±1 °C, at the beginning of the test cycle. The WLTC consists of four phases with different speed distributions (see Fig. 1), and it is designed to be representative of real world driving conditions based on real world vehicle trips from several countries. The length of the entire cycle is 1800 s and it is comprised of the low speed (589 s), medium speed (433 s), high speed (455 s) and extra-high speed (323 s) phases. It reaches a maximum speed of 131.3 km/h and is about 23.3 km long.

Three different WLTC driving cycles have been developed on the basis of the vehicle's power-to-mass ratio and its maximum speed, to represent three different vehicle classes. The vehicle tested in the present study pertains to class 3 (power/mass > 34 kW/ton and maximum speed > 120 km/h), which is the highest power and speed class. Figure 1 illustrates the version WLTC 5.3 of the speed profile applicable for this class of vehicle.

The NEDC is also a cold start driving cycle. It includes first an urban phase (urban driven cycle, UDC) of 780 s followed by an extra-urban phase (extra-urban driving cycle, EUDC) of 400 s. The low temperature emission test for spark ignition LDVs, known as type VI test, is limited to the urban part of the cycle (UDC) and only regulates CO (15 g/km) and THC (1.8 g/km) emissions (Directive 98/69/EC).

The tests were conducted at test cell temperatures of 23 and −7 °C, ±0.1 °C, and at 50 ± 2% RH. The temperature refers not only to the cell temperature, but also to the vehicle's oil temperature, ±1 °C, at the beginning of each test (see Fig. 1).

The cold start period of the vehicle was defined based on the legislation for heavy duty vehicles (EC No 582/2011) [25], which considers the period elapsing from the start of the test until the vehicle's coolant temperature reaches 70 °C for the first time as the cold start. This period lasted around 200–220 s (1–1.2 km) at 23 °C and 620–670 s (3.1–3.7 km) at −7 °C.

2.3. Analytical instrumentation

The regulated gaseous emissions were measured using standard methodologies defined by the related regulation [23] using an integrated setup (MEXA-7400HTR-LE, HORIBA) that analyzes diluted gas from the CVS using the following techniques (see Fig. 1): non-dispersive infrared (for CO/CO_2), a chemiluminescence (for NO_x) and a heated (191 °C) flame ionization detector (FID; for THC). The analyses were done in conformity with directive 70/220/EEC and its amendments for the tests performed over the NEDC or following the world-harmonized light-duty vehicle test procedure (WLTP) [24] for the tests carried out over the WLTC.

More than twenty exhaust gas compounds (e.g., NO, N_2O, CH_4, NH_3, HCHO, CH_3CHO) were monitored from the vehicle raw exhaust at 1 Hz acquisition frequency by a High Resolution Fourier Transform Infrared spectrometer (FTIR-MKS Multigas analyzer 2030-HS, Wilmington, MA, USA). The method is described in more detail in the literature [26,27], therefore, only a brief description is given here. The device consists of a silicon carbide source (at 1200 °C), a multipath cell (optical length: 5.11 m), a Michelson interferometer (spectral resolution: 0.5 cm^{-1}, spectral range: 600–3500 cm^{-1}) and a liquid nitrogen cooled mercury cadmium telluride detector (MCT).

A second set of analyzers, similar to the one used for gaseous regulated emission measurement was directly connected to the vehicle's exhaust pipe, allowing for time-resolved (at 1 Hz) measurement of THC, NO_x and CO/CO_2 from the raw exhaust. CO, CO_2 and NO_x measurements from these analyzers were used to synchronize the FTIR time-resolved signal (for more information see Clairotte et al. [26]).

The volumetric flow rate of the exhaust (m^3/s) was determined by subtracting the variable dilution flow entering the tunnel to the constant total flow inside the tunnel. Mass flows were derived from the exhaust gas flow rates (m^3/s) and from the measured concentration (ppmV). Emission factors (mg/km) were calculated from the integrated mass flow and the total driving distance of the cycles.

Previous studies have pointed out a lack of selectivity of the heated FID towards oxygenated hydrocarbon compounds emitted in the exhaust from engines fuelled with high ethanol blended mixtures [28,29]. Therefore, the time-resolved THC volumetric concentration measured with the FID were corrected using the concentrations measured with the FTIR of ethanol, methanol, formaldehyde and acetaldehyde, and the FID response factor for each of them, as described by Clairotte et al. [11].

The European Air Quality Directive on Ozone, 2002/3/EC [30] requires the analysis of 30 volatile organic carbons (VOCs), including 29 C_2–C_9 hydrocarbons and formaldehyde (see Table S1), as they are considered, together with nitrogen oxides, the main ozone precursors in urban air. Several of the compounds that are recommended for measurements were, below the limit of detection (below ppm levels) or, otherwise not quantifiable. The measurable hydrocarbons as well as a selection of compounds that are considered efficient ozone precursors, namely carbonyl compounds and ethanol, were monitored by the FTIR in order to estimate the ozone formation potential (OFP) of the vehicle's emissions (see Table 3). The OFPs of these compounds were calculated in accordance to the maximum incremental reactivity concept (MIR) [31]. The MIR concept is based on a scenario where optimum conditions of precursor/NO_x ratios yield maximum ozone formation. The OFP is presented as the sum of the ozone produced from each precursor emitted over the whole cycle (see Table 3, Fig. 6).

3. Results and discussion

3.1. Regulated gases emissions

The emission factors (EFs) of the regulated gases obtained for a Euro 5a FFV tested using nine fuel blends over the NEDC and WLTC at 23 or −7 °C are summarized in Table 3 and also in Fig. 2. Notice that Euro 5a regulation requires the vehicle to be tested over the NEDC; therefore, only the EFs obtained over the NEDC (or over phase 1 of the NEDC (i.e., UDC) for the low temperature test) are compared with the Euro 5a emission limits. The FFV showed THC and non-methane hydrocarbons (NMHC) emissions above the Euro 5a emission limits for the reference fuel E5 at 23 °C. The NHMC emissions were also above the limits for the AHE85 blend. The vehicle complied with the emission standards for all the other fuel blends. The FFV also complied with the low temperature emission test at −7 °C (see Table S1) with the winter blends, AHE75 and HE75, and the reference fuel (E5).

The measured emissions are discussed considering the five main variables present in the framework of the study, namely: the ethanol concentration (5%, 10%, 15%, 85% and 75%), the ambient temperature (23 *vs* −7 °C), the cycle (WLTC *vs* NEDC), the cold start emissions (cold start emissions *vs* total emissions) and the water content in the fuel blends (anhydrous (AHE) *vs* hydrous (HE)).

In general, higher emissions were observed when testing the vehicle at −7 °C over either cycle. At 23 °C, the regulated compound EFs are higher for the E5 blend than those of any other blend. The exception is that CO emissions are similar for all fuels over the NEDC, which is consistent with previous findings [10,12,17,32], while CO emissions were higher for the E85 blends

Table 3
Regulated and unregulated emission factors in mg/km (CO_2* emission factor in g/km) over the NEDC and WLTC for the nine tested fuels at 23 and/or −7 °C.

	E5	AHE10	AHE15	HE10	HE15	AHE85	HE85	AHE75-7C	HE75-7C	E5-7C
NEDC mg/km										
THC	147	42	60	57	34	101	76	385	357	212
NMHC	126	34	48	49	25	72	40	229	208	197
CO	363	389	368	345	407	373	367	888	922	932
NO_x	10	13	10	9	10	6	8	23	19	25
CO_2*	169	172	170	171	171	156	163	187	188	164
Formaldehyde	1	1	1	1	1	2	2	4	4	2
Acetaldehyde	3	4	5	4	4	21	15	62	65	3
NH_3	4	11	9	8	10	13	15	19	14	5
N_2O	0.4	0.6	0.5	0.4	0.4	0.4	0.3	1.9	1.8	1.6
CH_4	5	6	7	5	7	18	19	46	54	20
EtOH	12	1	5	4	2	9	39	225	223	10
Ethane	2	1	1	1	1	1	1	4	5	3
Ethene	4	3	4	3	3	6	6	31	38	15
Propene	2	2	2	2	2	1	1	4	4	7
Acetylene	2	3	4	6	6	9	7	19	17	9
Isopentene	2	4	11	12	5	8	4	15	13	7
MeOH	0	2	2	1	1	3	1	5	2	0
Benzene	4	2	2	1	1	1	0	3	4	3
Toluene	17	5	5	4	2	3	1	9	11	15
OFP [mg O_3/km]	167	129	181	168	129	270	249	1099	1160	353
WLTC mg/km										
THC	93	42	39	40	43	71	69	202	198	139
NMHC	82	33	31	33	32	34	29	113	118	121
CO	394	469	400	363	423	735	606	1291	1248	932
NO_x	62	42	51	41	39	19	23	38	35	76
CO_2*	151	156	155	157	156	144	146	151	168	169
Formaldehyde	1	0	0	1	0	1	1	2	2	1
Acetaldehyde	1	3	3	3	3	10	11	31	35	2
NH_3	6	16	14	10	14	26	22	34	24	13
N2O	0.6	0.6	0.4	0.6	0.5	0.5	0.4	1.5	1.3	1.6
CH_4	7	7	7	6	6	26	24	56	60	17
EtOH	7	1	2	1	1	37	21	119	137	8
Ethane	1	1	0	0	0	1	1	3	3	3
Ethene	3	2	2	2	2	5	5	23	25	9
Propene	1	2	2	2	3	3	3	5	5	5
Acetylene	1	3	3	4	6	7	7	13	18	5
Isopentene	2	7	8	8	7	3	2	12	13	4
MeOH	0	2	2	1	1	1	2	1	1	0
Benzene	5	2	1	4	1	1	0	5	5	11
Toluene	15	5	4	11	2	2	1	14	14	22
OFP [mg O_3/km]	128	128	127	151	127	242	211	738	804	280

Euro 5a spark ignition emission limits (mg/km) at 22 °C: THC = 100; NMHC = 68; CO = 1000; NO_x = 60.

over the WLTC. While THC and NMHC emissions tended to be higher over the NEDC than over the WLTC, NO_x and CO were higher over the WLTC for most of the blends (see Supplementary Material Text S1). High ethanol content reduced NO_x and increased CO emissions at both temperatures. Similar THC and NMHC EFs were observed for E75 and E5 at −7 °C. Results show no particular trend when using HE blends instead of AHE blends.

Figs. S1 and S2 illustrates the emission factors broken down by cycle phase, i.e., 4 phases during the WLTC (low, medium, high and extra high speed) and 2 phases during the NEDC (UDC and EUDC). It is shown that emissions of regulated compounds are mainly produced during the first phase of each cycle, with the exception of the NO_x over the WLTC at 23 °C, which, is evenly distributed along the cycle.

3.2. Unregulated gases emissions

Figs. 3 and 4 illustrate the EFs (mg/km) of a number of unregulated compounds that are atmospherically relevant, obtained by FTIR analysis using the nine fuel blends, over the WLTC and NEDC, and at 22 and −7 °C. A comprehensive analysis of the exhaust emissions of: formaldehyde (HCHO) and acetaldehyde (CH_3CHO), classified, respectively, as a human carcinogen and as a probable carcinogen by the US Department of Health and Human Services [33]; ammonia (NH_3), which is a precursor of atmospheric secondary aerosols [34,35] and is also classified under the European dangerous substances directive (67/548/EEC) [36] as toxic, corrosive and dangerous for the environment; ethanol (CH_3CH_2OH), which is a precursor of acetaldehyde and PAN in the atmosphere [37,38]; and three of the most important greenhouse gases (GHG), carbon dioxide (CO_2), nitrous oxide (N_2O) and methane (CH_4), was performed. The emissions of these unregulated compounds were sub-classified as air toxics emissions (formaldehyde, acetaldehyde, ammonia and ethanol; air toxics emission factors are shown in Fig. 3) and GHG emissions (carbon dioxide, nitrous oxide and methane; GHGs emission factors are illustrated in Fig. 4). A summary of the results can be found in Table 3.

In general, the EFs of the unregulated compounds for the hydrous and anhydrous ethanol fuel blends containing the same ethanol concentration showed no, or little, differences (see Table 3 and Fig. 3). Trends of increased EFs during the cold start and cold ambient temperature were observed with all fuel blends and cycles (see Fig. S3). The exception was ammonia, the emissions of which were lower before catalyst light-off. In fact, ammonia formation on the TWC is triggered right after the catalyst light-off [39–41] (see Section 3.2.1). Once the catalyst reached its optimal operating temperature, the other unregulated compounds were essentially under

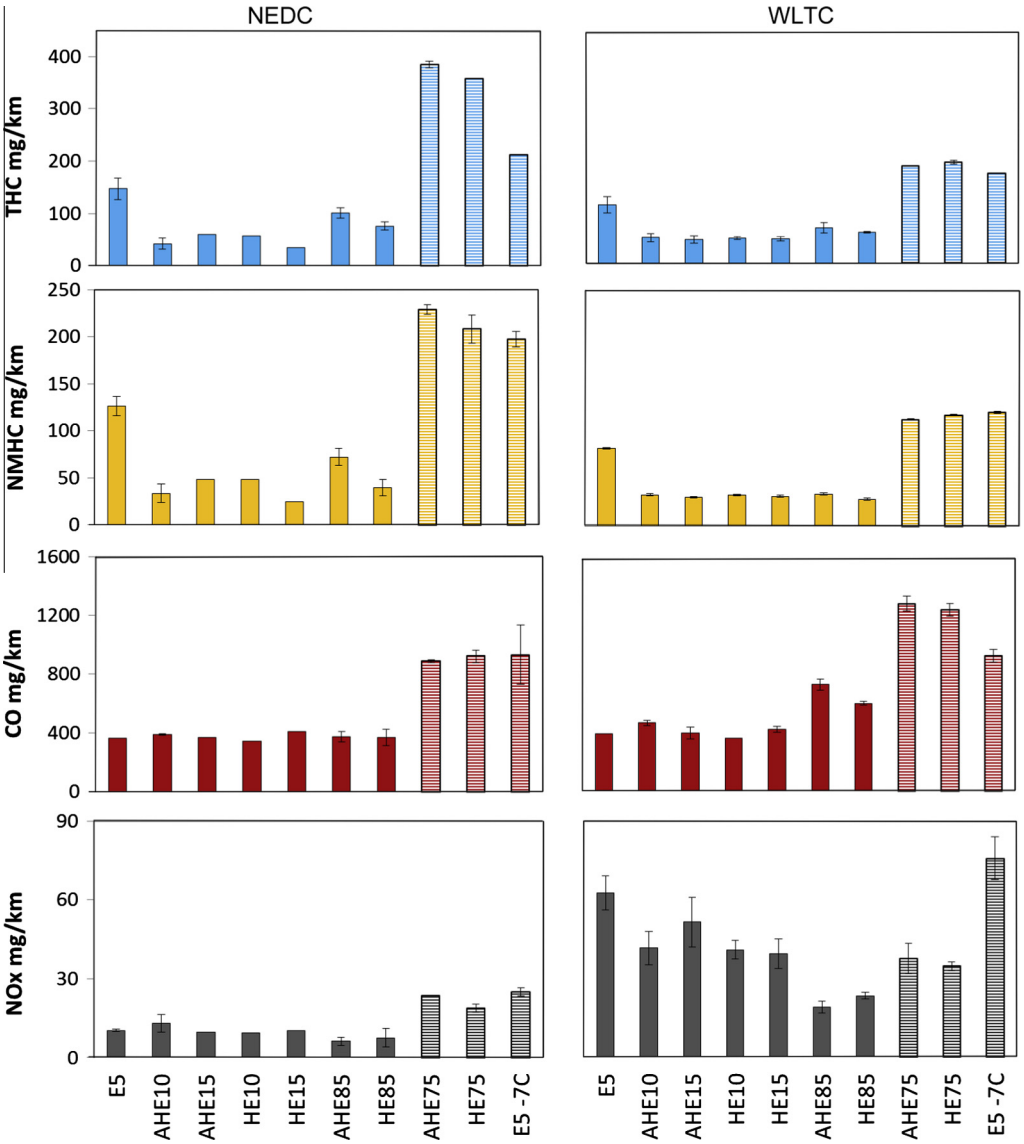

Fig. 2. Regulated compounds emission factors (mg/km) over the NEDC (left barplots) and over the WLTC (right barplots). Hatched areas refer to experiments performed at −7 °C.

the limits of detection. An example of the emission profiles can be seen in Figs. S5e and S6e.

The total emissions (g) of the unregulated compounds, measured over the entire cycle, were higher over the WLTC than over the NEDC for all fuels and temperatures (see Fig. S4 in the Supplementary Material). Furthermore, the emissions during the cold start, which lasted the same distance for both cycles (1.0–1.2 km at 23 °C and 3.1–3.7 km at −7 °C), were higher over the WLTC than over the NEDC. Hence, on cold start, when most of the emissions take place, the FFV emitted more over the WLTC than over the NEDC (see Fig. S4).

3.2.1. Air toxics emissions

Fig. 3 shows EFs for the selected air toxics. In general, the air toxics emissions for E5, E10 and E15 blends were similar. The results show that EFs of the carbonyl compounds measured, formaldehyde and acetaldehyde, were two times higher over the NEDC than over the WLTC for seven of the nine used blends at the two studied temperatures. The exceptions were the AHE10 and HE10, which had EFs that were about the same over the two cycles (see Table 3). Carbonyl EFs increased for high ethanol content fuels, E75 and E85. Formaldehyde EFs were 2–4 times higher for the E85 and E75 compared to the other blends. Since ethanol is the main precursor of acetaldehyde in vehicular emission, an increase of acetaldehyde emissions with higher ethanol content fuels was expected. In fact, acetaldehyde EFs were four times higher for the E85 blends than for the other blends. The EFs for the E75 blends, used at −7 °C, were three times higher than those obtained for the E85 blends and one order of magnitude higher than those obtained for the other blends, including the E5 used at −7 °C. As already observed by Clairotte et al., for a Euro 4 and a Euro 5 flex-fuel vehicles [11], acetaldehyde EFs were boosted at −7 °C compared to formaldehyde, suggesting a different formation pathway and a different precursor [11]. As shown in previous studies, no changes in formaldehyde and acetaldehyde emissions as a function of ethanol content were observed for the E5–E15 blends [10]. Fig. 3 illustrates that ethanol emissions were more pronounced when a higher ethanol content fuel blends, i.e. E85, were used. Tests at low temperature resulted in higher ethanol emissions which were, as stated above, mainly manifested in the cold start emissions. Ethanol emissions were not a strong function of the ethanol content for E5–E15 blends. Over the WLTC, the emitted

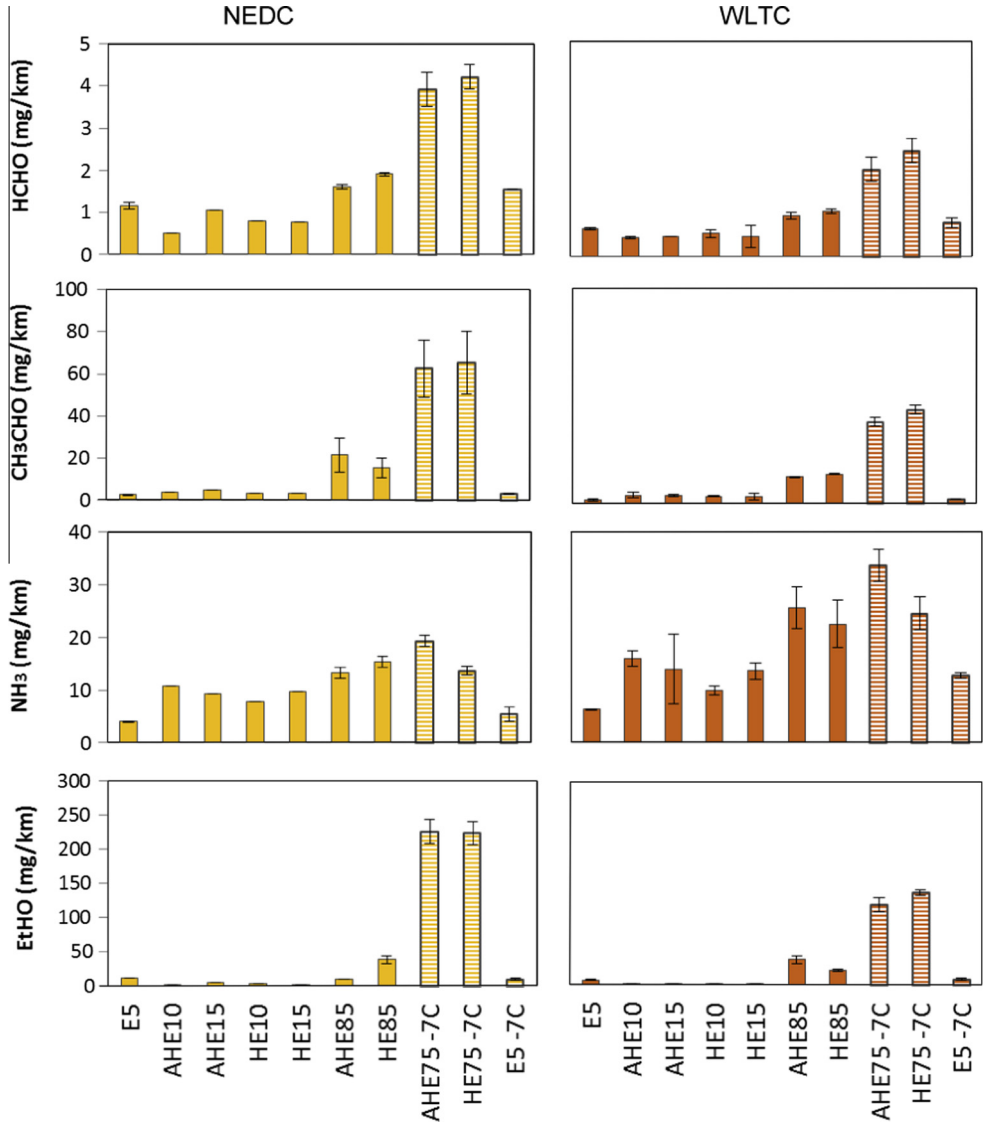

Fig. 3. Air toxics gases emission factors (mg/km) over the NEDC (yellow) and WLTC (orange). Hatched areas refer to experiments performed at −7 °C. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

ethanol was 3 to almost 30 times higher for E85 than for E5–E15 blends and about 15 times higher for E75 than for E5 at −7 °C (see also Table 3). Ethanol EFs for E5 and E85 were in good agreement with the EFs reported in previous studies [11,12]. However, the EFs obtained when the FFV was run with the E75 blends at −7 °C were 50–70% lower than those reported by Clairotte et al. [11].

In spark ignition vehicles, NH_3 is formed in the three way catalyst (TWC) after catalyst light-off, through a mechanism that involves NO and H_2 [41] or via steam reforming from hydrocarbons [39]. NH_3 formation over the catalyst is enhanced at low air/fuel ratios, also known as rich combustion, where conditions are reductive and higher concentrations of CO and H_2 are present [39,42]. These are typical conditions during the accelerations, which explain the higher emissions of NH_3 during the acceleration events present in the cycles (see Figs. S5e and S6e). NH_3 emissions therefore depend on the driving mode. Higher NH_3 emissions are expected for an aggressive or dynamic driving style, where there are a lot of accelerations (rich combustion) and decelerations (lean combustion) [40]. As illustrated in Fig. 1 the WLTC is more dynamic than the NEDC. As a consequence, the NH_3 emissions were higher over the WLTC than over the NEDC. The obtained NH_3 EFs were in line with what can be found in the literature for other Euro 5 spark ignition vehicles [43–45].

Previous studies suggested that CO emissions from gasoline vehicles are indicative of NH_3 formation over the catalyst [40,43–45]. Therefore, the correlation between the CO and NH_3 EFs for all the fuel blends, together with those used by Suarez-Bertoa et al., [45] was analyzed and proved to be excellent at the two ambient temperatures (see Fig. 5).

The emissions of NH_3 were affected by low ambient temperatures. The vehicle then runs under rich conditions for a longer period (see Fig. S7). As consequence, the emissions of NH_3 at −7 °C were higher than at 23 °C. The increase of NH_3 at low temperature was more pronounced over the WLTC.

3.2.2. Greenhouse gases emissions

Fig. 4 shows EFs for the selected GHGs. CO_2 EFs were higher over the NEDC compared to WLTC. No trends were observed in CO_2 emissions as a function of ethanol content for E5–E15 blends in either cycle. The CO_2 emissions tended to increase at low temperatures. At 23 °C, CO_2 emissions are lower for the E85 blends.

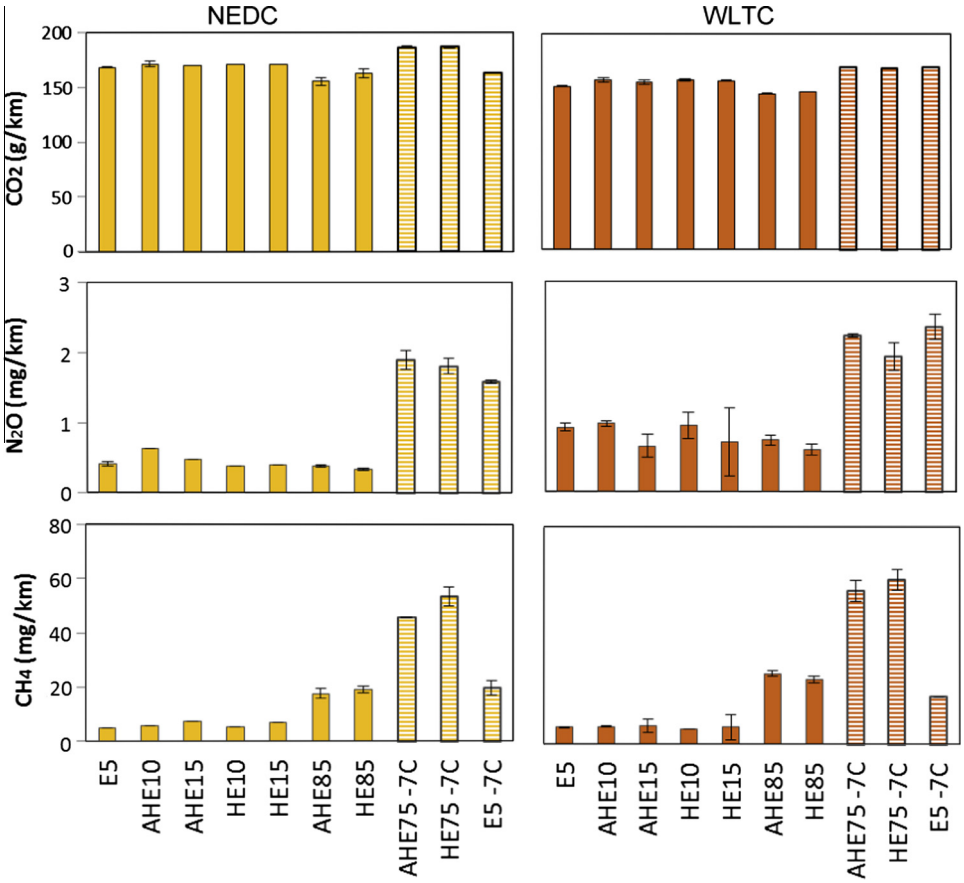

Fig. 4. Greenhouse gases emission factors (mg/km) over the NEDC (yellow) and WLTC (orange). The hatched areas refer to experiments performed at −7 °C. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

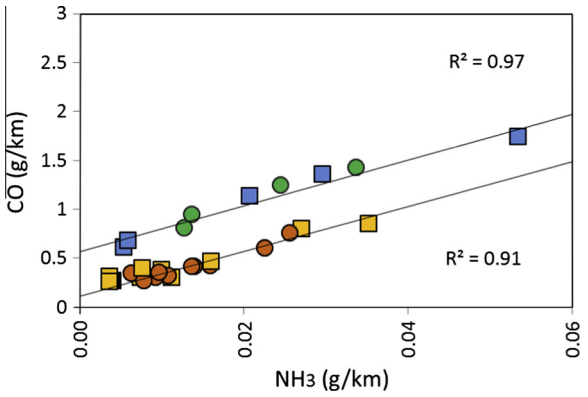

Fig. 5. Correlation of NH_3 and CO emissions. Emission factors (g/km) of CO and NH_3 emitted by the studied FFV using different fuels (circles) and those from previous studies (squares) at 23 (yellow and orange) and −7 °C (blue and green). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 4 illustrates that N_2O emissions were similar when working at 23 °C with any of the tested fuels. N_2O is catalytically produced, especially at cold catalyst temperature, consistently with larger observed emissions during the cold start. The emissions were affected by the ambient temperature, increasing by up to 200% at −7 °C, which is in agreement with previous studies [12]. Similar N_2O EFs were reported by Clairotte et al. at 22 °C [11]. However, they reported no differences in N_2O emissions at the two temperatures (22 and −7 °C).

The emissions of CH_4 were affected by the high concentration of ethanol present in the E85 and E75 blends and also by low ambient temperatures. CH_4 EFs were approximately 4 times higher for the E85 blends than for other blends tested at 23 °C and 3 times higher for the E75 blends compared to E5 at −7 °C.

The CO_2 emissions for E85 blends are lower than those of E5–E15 blends even when the CO_2 emissions are calculated taking into consideration the CH_4 and N_2O emissions as CO_2 equivalents (global warming potential over 100 years for CH_4 and N_2O are 25 and 298 eq. g CO_2, respectively), i.e., $CO_{2\ Total} = CO_2 + CH_4 * 25 + N_2O * 298$.

3.3. Ozone formation potential (OFP)

The estimated OFPs (mg O_3/km), calculated in accordance to the maximum incremental reactivity concept (MIR) [31], and the percentage contributions of the listed compounds for the FFV tested with the nine fuels over the NEDC and WLTC at 22 and −7 °C are illustrated in Fig. 6. The columns in the top panel of Fig. 6 represent the total OFP and the contributions of all compounds that were taken into consideration. Although slightly higher OFPs were calculated for the tests performed over the NEDC, similar trends were observed for both cycles. Besides CO, the compounds used for the estimation of these OFPs are mainly emitted during the cold start. The OFPs were affected by the high concentration of ethanol present in the E85 and E75 blends and also by low ambient temperatures. In fact, at 23 °C, the OFPs of the E85 blends were two times higher than those of the E5–E15 blends and at −7 °C, OFPs of E75 were three times higher than those of E5.

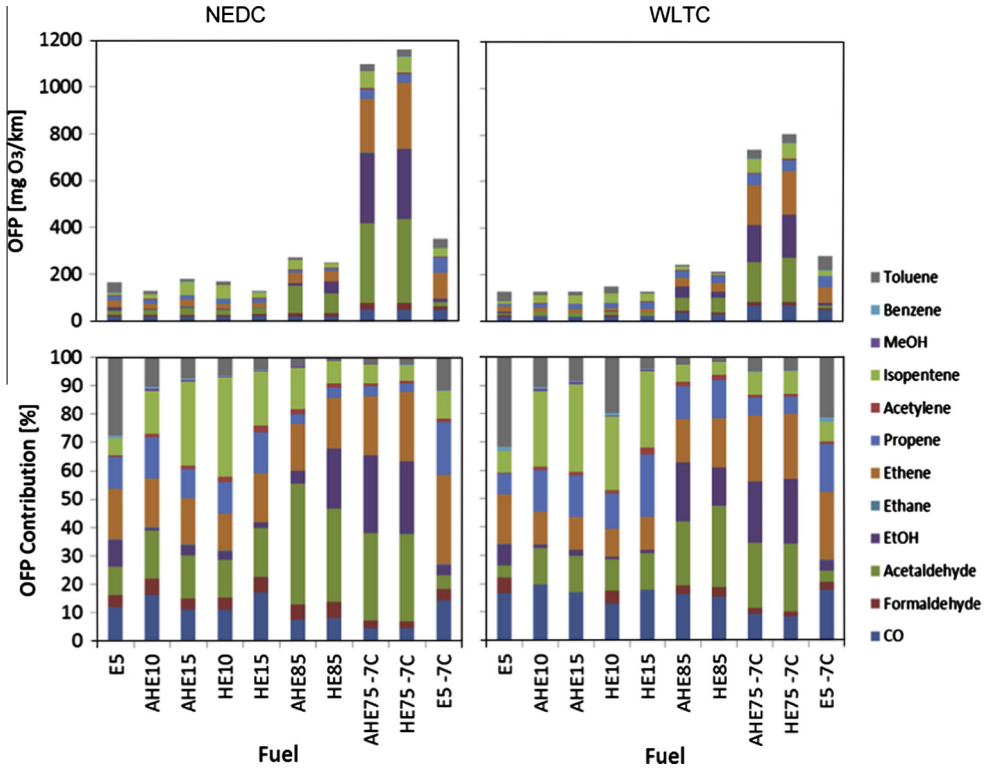

Fig. 6. Estimated OFPs (mg O_3/km) (Top) and the percentage contributions (Bottom) over the NEDC and WLTC.

As illustrated in the bottom panel of Fig. 6, in general, similar contributions were observed for both cycles. Hydrocarbons represented 60–70% of the total contributions for the low ethanol containing blends (E5–E15), whereas, acetaldehyde, ethene and their precursor, ethanol, were the main contributors for the high ethanol containing blends (E85 and E75), accounting for up to 80% of the total contribution. Toluene is an important contributor for the E5 at both temperatures (up to 32% and 21% at 23 and −7 °C, respectively).

The European Ozone Directive 2002/3/EC specify the analysis of 29 C_2–C_9 hydrocarbons, formaldehyde and nitrogen oxides, as they are considered the main ozone precursors in urban air [30]. This list does not include acetaldehyde or ethanol, which are typically found in the exhaust of vehicles that run with high ethanol contain blends (see above). However, acetaldehyde is the fourth main ozone precursor in Rio de Janeiro as a result of the increase of ethanol concentration in the fuel blends [46], and in the atmosphere ethanol is oxidized to acetaldehyde [37,38]. Therefore, extensive use of E85 and/or E75 blends could further undermine the urban air quality where ethanol blends were not commonly used.

4. Conclusions

The composition of fuels has been subjected to numerous modifications in recent years. It is crucial that the introduction and use of these new fuels be accompanied by a thorough assessment of their impact on the vehicle emissions. For that reason, regulated and unregulated emissions from a Euro 5a flex-fuel light duty vehicle (FFV), tested at 23 and −7 °C over the WLTC and NEDC using nine different ethanol containing fuel blends, were investigated.

The results suggest that there are no marked differences in the regulated and unregulated emissions when hydrous ethanol blends are used instead of anhydrous ethanol blends. Moreover, most of the studied pollutants showed similar EFs during the tests performed using E10 and E15 (gasoline containing 10% and 15% of ethanol, respectively) blends.

The ethanol fuel content did not result in a particular trend in CO_2 emissions. However, when run on E85, the vehicle emitted nearly 6% less CO_2 than with E5–E15 blends. The high concentration of ethanol in the E85 and E75 blends reduced emissions of NO_x by 30–55% but increased the emissions of CO, CH_4, formaldehyde, acetaldehyde and ethanol (nearly 65%, 150%, 100%, 120% and 350% at 23 °C and 35%, 185%, 100%, 400% and 390% at −7 °C) compared to the E5, E10 and E15 blends. The rise of the acetaldehyde and ethanol emissions led to a sharp rise in the OFP for the higher ethanol blends. Low temperature led to an increase in the emissions of all studied compounds, and therefore of the OFP. If combined with the high ethanol content in the E75 blends, the low temperature effect was more pronounced for compounds like acetaldehyde, CH_4 and NH_3.

NH_3 emissions, formed after catalyst light-off, were well correlated with CO emissions, and were higher during the more dynamic WLTC.

Cold start emissions accounted for up to 80% of the total unregulated emissions. Hence, more effort should be placed on the reduction of cold start emissions in order to reduce the impact that vehicular unregulated emissions have on the environment and health.

Finally, in the case of an extensive introduction of high ethanol containing blends into the European market, the list of compounds under European Ozone Directive 2002/3/EC should be updated to specify that acetaldehyde and ethanol should also be monitored. Including these compounds would help to provide a better understanding of ozone formation and dispersion processes in urban areas, as well as an improvement of photochemical models.

Disclaimer

The opinions expressed in this manuscript are those of the authors and should in no way be considered to represent an official opinion of the European Commission.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2014.10.076.

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