Impact of cold temperature on Euro 6 passenger car emissions☆

Ricardo Suarez-Bertoa[*], Covadonga Astorga[**]

European Commission Joint Research Centre, Directorate for Energy, Transport and Climate, Sustainable Transport Unit, 21027 Ispra, VA, Italy

ABSTRACT

Hydrocarbons, CO, NOx, NH3, N2O, CO2 and particulate matter emissions affect air quality, global warming and human health. Transport sector is an important source of these pollutants and high pollution episodes are often experienced during the cold season. However, EU vehicle emissions regulation at cold ambient temperature only addresses hydrocarbons and CO vehicular emissions. For that reason, we have studied the impact that cold ambient temperatures have on Euro 6 diesel and spark ignition (including: gasoline, ethanol flex-fuel and hybrid vehicles) vehicle emissions using the World-harmonized Light-duty Test Cycle (WLTC) at -7 °C and 23 °C. Results indicate that when facing the WLTC at 23 °C the tested vehicles present emissions below the values set for type approval of Euro 6 vehicles (still using NEDC), with the exception of NOx emissions from diesel vehicles that were 2.3–6 times higher than Euro 6 standards. However, emissions disproportionally increased when vehicles were tested at cold ambient temperature (-7 °C). High solid particle number (SPN) emissions ($>1 \times 10^{11}$ # km^{-1}) were measured from gasoline direct injection (GDI) vehicles and gasoline port fuel injection vehicles. However, only diesel and GDI SPN emissions are currently regulated. Results show the need for a new, technology independent, procedure that enables the authorities to assess pollutant emissions from vehicles at cold ambient temperatures.

Harmful pollutant emissions from spark ignition and diesel vehicles are strongly and negatively affected by cold ambient temperatures. Only hydrocarbon, CO emissions are currently regulated at cold temperature. Therefore, it is of great importance to revise current EU winter vehicle emissions regulation.

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1. Introduction

Winter season is associated with high pollution episodes (Custódio et al., 2016; Wang et al., 2017). Recent seasonal studies have shown that in some urban areas the highest levels of NOx, NH3, CO and PM occur in the cold season (Hofman et al., 2016; Hama et al., 2017). Those studies, as well as the recent report presented by the European Environment Agency (EEA, 2014), indicate that transport sector is one of the main sources of these air pollutants. Moreover, they are (themselves or as precursors) among the most problematic pollutants in terms of harm to human health in Europe: PM, ground-level O3 and nitrogen dioxide (NO2) (EEA, 2015).

Urban PM composition is strongly influenced by vehicle exhaust (Custódio et al., 2016; Giorio et al., 2015; Jeong et al., 2016; Pey et al., 2010). Vehicles contribute to both organic and inorganic fraction of the PM via: i) primary PM emissions and ii) emission of precursors of secondary organic aerosols (SOA) and secondary inorganic aerosols, such as volatile organic compounds (VOCs), NOx or NH3 (Amanatidis et al., 2014; Gordon et al., 2014; Link et al., 2017; Platt et al., 2014, 2017). Moreover, transport sector is one of the dominant sources of NOx, CO and non-methane volatile organic compounds (NMVOC) in Europe; pollutants that together with methane are the main ground-level ozone precursors (EEA 2014). Road transport emissions account for 40.5% NOx, 26.5% CO and 14.6% NMVOC of the total emissions in EEA-33.

European vehicle emissions regulation has become more stringent over the years aiming at improving Europe's air quality. Emissions of THC, NMHC, CO, NOx, solid particle number (SPN; solid particles with a diameter >23 nm) and particle mass (PM) are now a days regulated under the Type 1 test for Euro 6 vehicles. Furthermore, with the implementation of the new regulation in EU

(EC, 692/2008), this test will be performed following the WLTP, where tests must be performed at 23 ± 5 °C using the worldwide harmonized light-duty driving test cycle (WLTC) (UNECE, GTR 15). However, emission limits and testing procedure at cold ambient temperature have not seen significant changes since it first introduction in 1998 (EC, 98/69).

The Type 6 test (name commonly used in EU to refer to the cold temperature test) was introduced "as a measure against air pollution by emissions from motor vehicles at cold ambient temperatures". The test is carried out only on positive-ignition light-duty vehicles on a chassis dynamometer at -7 ± 3 °C over the Urban Driving Cycle (UDC; first of the two phases constituting the New European Driving Cycle, NEDC), and only foresees the analysis of CO and THC. It is worth noticing that CO and THC emissions must be, respectively, lower than 15 g km^{-1} and 1.8 g km^{-1}, which are more than 15 times higher than those allowed during Type 1 test performed at 23 ± 5 °C.

Similar procedures are applied at cold temperature in the USA (CFR 1066 Subpart H) (US. EPA), South Korea (MOE, 2014) and China (China 6, 2017). They present a number of similarities with the European Type 6 test, including the temperature at which the test is performed (-7 °C) and the determination of the road-load (which can be either determined at -7 °C or adjusting the driving resistance by decreasing 10% the coast-down time), but there are important differences as well. For instance, while the procedures applied in USA and China require petrol and diesel vehicles to be tested al low temperature, those in force in EU and Korea only apply to positive-ignition vehicles. Moreover, China has been the first country to include NOx measurements and emission limits at cold temperature (China 6, 2017).

A new and representative procedure that enables the authorities to assess the emissions from vehicles at low ambient temperatures needs to be defined and the present work addresses a number of important issues that should be considered in the future low temperature testing procedure in EU. Issues such as: The use of WLTC, a cycle that is more representative of real world driving; the use of a procedure that is fuel and technology independent applied to spark-ignition, compression-ignition and hybrid light-duty vehicles; the measurement of criteria pollutant emissions present in vehicle exhaust, other than THC and CO, namely: NOx and SPN.

Vehicle emissions of NH$_3$ - a precursor of secondary inorganic aerosol in the atmosphere (Kim et al., 2000; Phan et al., 2013) - and nitrous oxide (N$_2$O) - a powerful greenhouse gas and the single most important ozone-depleting substance (ODS) (Ravishankara et al., 2009)- have been related to the use of catalytic converters such as: as Three-Way Catalyst (TWC), NOx Storage Catalyst (NSC), Diesel Oxidation Catalyst (DOC), Selective Catalytic Reduction (SCR) and Lean NOx Trap (LNT) (Guan et al., 2014; Ko et al., 2017; Suarez-Bertoa et al., 2014; Suarez-Bertoa and Astorga 2016a; Wallington and Wiesen, 2014). NH$_3$ vehicle emissions are regulated in Korea (MOE, 2014), and N$_2$O emission standards have recently been introduced by the U.S. Environmental Protection Agency (EPA) under the Clean Air Act (EPA, 2015) and in China with the introduction of China 6 (China 6, 2017). However, NH$_3$ and N$_2$O emissions from passenger cars are not regulated in EU. Therefore, the use modern vehicles equipped with these after-treatments brings new environmental and health concerns since unknown amounts of NH$_3$ and N$_2$O will be emitted. For that reason, in addition to criteria pollutants (CO, THC, NOx, SPN) and CO$_2$, emissions of NH$_3$ and N$_2$O at -7 °C and 23 °C are also discussed here. The presented results are of great interest to help extending and updating vehicle emission inventories and databases which often lack of data for cold temperature emissions or rely on those obtained using the off-dated UDC, which is not representative of realistic driving conditions.

2. Experimental section

Twelve passenger cars from the European market (see Table 1), were tested at the Vehicle Emission Laboratory (VELA) of the European Commission Joint Research Centre (EC-JRC) Ispra, Italy. The facility includes a climatic test cell with controlled temperature and relative humidity (RH) to simulate ambient conditions (temperature range: -10 to 35 °C; RH: 50%). Duplicated tests were performed at 23 and -7 °C on a chassis dynamometer (inertia range: 454–4500 kg), designed for two and four-wheel drive light-duty vehicles (two 1.22 m roller benches – Maha GmbH, Germany). The emissions were fed to a Constant Volume Sampler (CVS, Horiba, Japan) through a heated transfer-line (~90 °C). A critical Venturi nozzle was used to regulate the flow (CVS flow range: 3–30 m^3 min^{-1}). A series of thermocouples monitored the temperature of the oil, cooling water, exhaust, and ambient conditions.

The selected fleet features a wide range of engine power, displacement, mileage and after-treatment systems, typical of the modern European fleet. It included: Five Euro 6 diesel vehicles (3 equipped with SCR (DV1-DV3) and 2 equipped with LNT (DV4 and DV5)); five Euro 6 gasoline vehicles (GV1-GV5; all equipped with TWC and one (GV3) also equipped with NSC); one Euro 6 gasoline hybrid (HV; equipped with TWC); and one Euro 5 flex-fuel vehicle (FFV; equipped with TWC).

Tests were performed using the WLTC at 23 and -7 °C ambient temperature. The WLTC (UNECE, GTR 15) was designed to be representative of real world driving conditions based on real world vehicle trips from several countries (Tutuianu et al., 2015). It is a cold start driving cycle consisting of four phases with different speed distributions: low speed (589 s), medium speed (433 s), high speed (455 s) and extra-high speed (323 s) phases (see Fig. 1). It reaches a maximum speed of 131.3 km h^{-1}, lasts 1800 s and is ~23.3 km long. Before being tested, vehicles were kept inside the climatic cell under the needed temperature (23 or -7 °C) for at least 6 h.

As indicated in the different regulations, vehicle road-load needs to be adjusted for low temperature testing. In this study, driving resistance was adjusted decreasing the coast-down time estimated at 23 °C by 10% for all the tests at -7 °C, including those with the hybrid vehicle, HV.

CO$_2$ emissions from hybrid and common diesel and gasoline vehicles are calculated following different procedures at 23 °C (UNECE, GTR 15). The high voltage battery of a hybrid vehicle can be at different state of charge (SOC) at the beginning of the test. For that reason, a series of tests under the so-called charge sustaining protocol are needed to calculate a correction factor for CO$_2$ emissions from hybrid vehicles (UNECE, GTR 15). In this study HV was tested using the hybrid vehicles protocol at 23 °C and at -7 °C.

Vehicles were tested using reference fuels as stated in Global Technical Regulation 15 (GTR 15) for tests at 23 °C and UNECE Regulation 83 for tests at -7 °C. EU regulation does not prescribe a reference diesel for test at low temperature because this test is not applicable for diesel vehicles. Grade D (Cold Filter Plugging Point (CFPP) -10 °C) winter diesel was then chosen for tests at -7 °C. Besides being tested on E5, FFV was tested on E85 (summer blend, containing 85% vol ethanol and 15% vol gasoline) at 23 °C and on E75 (winter blend, containing 75% vol ethanol and 25% vol gasoline) at -7 °C.

Regulated gaseous emissions were measured using an integrated setup (MEXA-7400HTR-LE, HORIBA) that analysed diluted gas from the CVS. Gaseous emissions were analysed from a set of Tedlar bags. The bags were filled with diluted exhaust from the CVS (Automatic Bag Sampler, CGM electronics) and concentrations were measured using non-dispersive infrared (for CO/CO$_2$), a chemiluminescence (for NOx) and a heated (191 °C) flame ionization

Table 1
Vehicles specifications.

	Engine type	After-treatment	Engine displacement (cm^3)	Engine power (kW)	Odometer (km)	Euro Standard
DV1	CI HDi	DOC + DPF + SCR	1560	73	4792	6
DV2	CI HDi	DOC + DPF + SCR	1997	110	14365	6
DV3	CI TDI	DOC + DPF + SCR	2987	140	32178	6
DV4	CI TDI	DOC + DPF + LNT	1422	55	6229	6
DV5	CI TDI	DOC + DPF + LNT	1968	110	24473	6
GV1	SI GDI	TWC	998	76	3520	6
GV2	SI GDI	TWC	999	81	4200	6
GV3	SI GDI	TWC + NSC	1991	155	11211	6
GV4	SI GDI	TWC	1242	51	10523	6
GV5	SI PFI	TWC	1368	57	7723	6
FFV	SI PFI	TWC	1596	132	25098	5
HV	SI GDI	TWC	2494	114	9558	6

CI Compression ignition; HDi high-pressure direct injection; TDI Turbo diesel injection; SI Spark ignition; GDI Gasoline direct injection; PFI Port fuel injection; DOC Diesel Oxidation Catalyst; DPF Diesel particle filter; Selective Catalytic Reduction; LNT Lean-NOx Trap; TWC Three-Way Catalyst; NSC NOx Storage Catalyst.
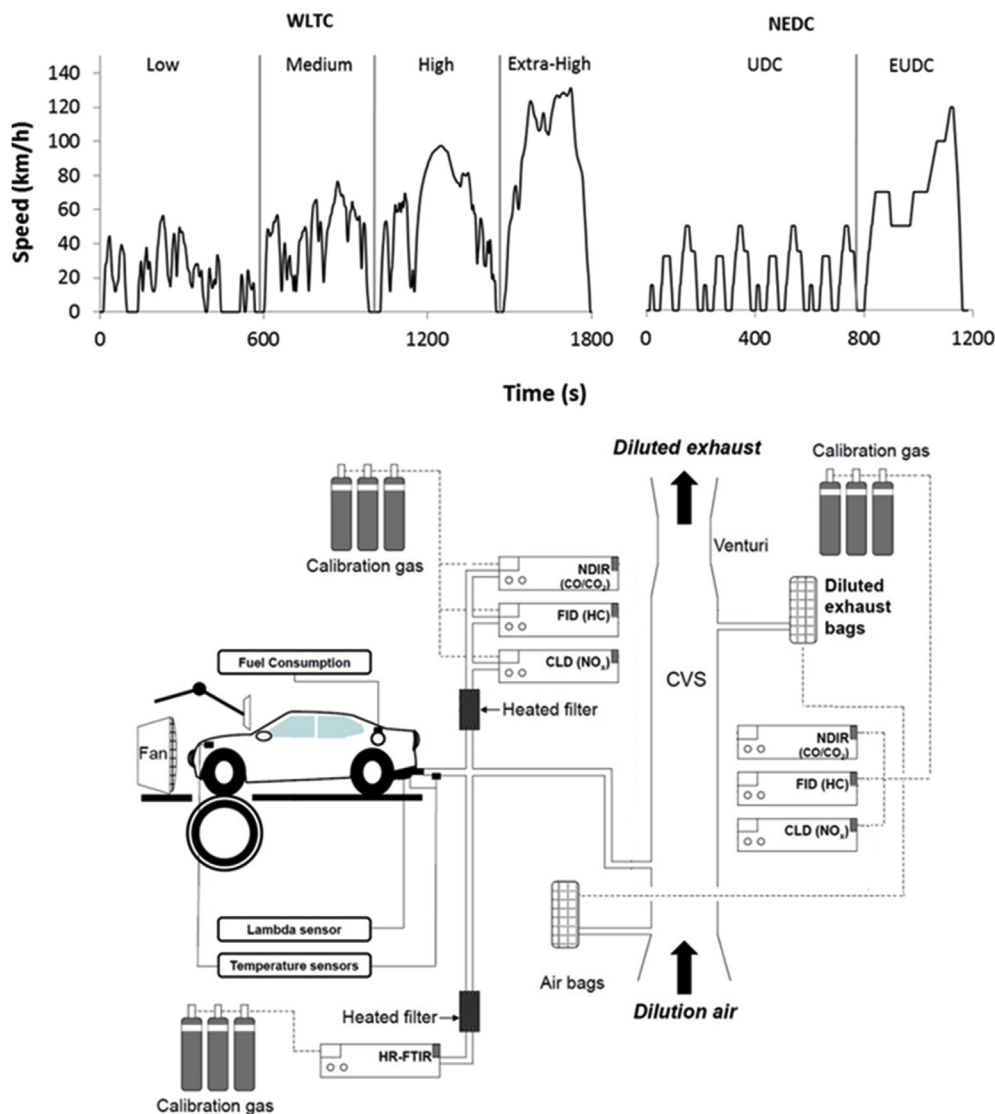
Fig. 1. Driving cycles (top) and schematic diagram of the experimental setup (bottom).

detector (FID; for THC). A solid particle number (SPN) measurement system (AVL APC 489), with particle diameter cut-off of 23 nm ($d_{50\%} = 23$), compliant with the light-duty vehicles Regulation 83 (UNECE Regultaion 83), was used at the CVS to measure SPN. In order to estimate the cumulative mass emitted during the tests, criteria pollutants were also measured in real-time (at 1 Hz resolution) from the raw exhaust using a second set of analysers, i.e., non-dispersive infrared, FID and chemiluminescence detector.

A number of gaseous compounds contained in the raw exhaust (including NH_3, N_2O, NO, NO_2, CO and CO_2) were monitored at 1 Hz acquisition frequency by a high resolution Fourier Transform Infrared spectrometer (FTIR — MKS Multigas analyzer 2030-HS, Wilmington, MA, USA). The method and instrumentation are described more in detail in the literature (Suarez-Bertoa et al., 2015a). The raw exhaust was sampled directly from the tailpipe of the vehicles using a heated PTFE (polytetrafluoroethylene) line and a pumping system (flow: ca. 10 L min^{-1}, T: 191 °C) to avoid condensation and/or adsorption of hydrophilic compounds (e.g., NH_3). The residence time of the undiluted exhaust gas in the heated line before the FTIR measurement cell was less than 2 s. The temperature of the gas cell of the FTIR was set to 191 °C. CO and NOx measurements from the previously described non-dispersive infrared and chemiluminescence detector analysers were used to synchronize the FTIR signal.

The volumetric flow rate of the exhaust $m^3 s^{-1}$ 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 corrected for the flow uptake of the instruments connected at the tailpipe ($m^3 s^{-1}$) and from the measured concentration (parts per million by volume). Emission factors (mg km^{-1}) were calculated from the integrated mass flow and the total driving distance of the WLTC (23.3 km).

3. Results

Table 2 and Table 3 summarize the emission factors from twelve passenger cars — Gasoline (GV1-GV5), diesel (DV1-DV5), flex-fuel (FFV) and gasoline-hybrid (HV) vehicles (see Table 1 for vehicles description) — tested at −7 and 23 °C using the WLTC in the Vehicle Emission Laboratory (VELA) at the EC-JRC.

CO, THC, NOx and SPN emissions from all studied spark ignition vehicles (common gasoline, flex-fuel and hybrid vehicles) at 23 °C using the WLTC were below the values set for type approval of Euro 6 vehicles, using NEDC (THC 100 mg km^{-1}; CO 1000 mg km^{-1}; NOx 60 mg km^{-1}; PN 6×10^{11} # km^{-1}) (EC 692/2008), with the exception of the CO emissions from GV4 (see Table 2). On the other hand, diesel vehicles tested at 23 °C using the WLTC resulted in CO and SPN emissions that were below the Euro 6 standards (CO 500 mg km^{-1}; PN 6×10^{11} # km^{-1}) but their NOx emissions were, in all cases, higher than the values set for type approval of Euro 6 vehicles using NEDC (NOx 80 mg km^{-1}) (EC 692/2008). Although diesel vehicles presented relatively low THC emissions, THC + NOx emissions were also above the Euro 6 standards (THC + NOx 170 mg km^{-1}) for all the diesel vehicles tested. The emissions of criteria pollutants were disproportionally higher when spark

ignition and diesel vehicles were tested at cold temperature (−7 °C; Table 3). These differences will be discussed in the following sections.

Although the common gasoline, the hybrid and the flex-fuel vehicles, fall all under the spark ignition type, the emissions factors from HV and FFV (fuelled with E85 and E75) were not included in the calculations of average emissions from gasoline vehicles to avoid bias related to other variables, such as fuel (for the flex-fuel tested with the E85 and E75 blends) or the use of the electrical powertrain or regenerative braking (in the case of the hybrid).

3.1. THC and CO emissions

THC emission factors (EFs) from gasoline vehicles at 23 °C ranged from 12 mg km^{-1} (GV2) to 54 ± 6 mg km^{-1} (GV1). THC emissions from gasoline vehicles were on average 6.5 times [1.9–13.1 times] higher at −7 °C than at 23 °C. THC EFs at low temperature varied from 117 ± 1 mg km^{-1} (GV2) to 184 ± 3 mg km^{-1} (FFV-E5). In the case of CO, EF at 23 °C varied from 154 ± 52 mg km^{-1} (GV2) to 5766 mg km^{-1} (GV4). Emissions at −7 °C were on average 2.6 times [1.4–5.8 times] higher than those measured at 23 °C. CO EFs at −7° C ranged from 206 ± 18 mg km^{-1} (GV2) to 10111 ± 1149 mg km^{-1} (GV4). GV4 run often on a rich air-fuel mixture to be able to follow the dynamic WLTC, resulting in the high CO emissions measured.

THC EFs from diesel vehicles were around one order of magnitude lower than those reported for gasoline vehicles at the two studied temperatures. CO emissions from diesel vehicles were also substantially lower than those observed for gasoline (Table 3). THC and CO emissions from diesel vehicles were on average 1.5 times and 1.8 times higher at −7 °C than at 23 °C ([1.1–2 times] and [1.1–3 times] for THC and CO respectively). THC EFs at 23 °C varied from 2 ± 1 mg km^{-1} (DV2) to 19 ± 4 mg km^{-1} (DV5). At cold temperature THC EFs ranged from 4 ± 1 mg km^{-1} (DV2) to 20 ± 1 mg km^{-1} (DV5). While CO EFs at −7 °C varied from 30 ± 8 mg km^{-1} (DV4) to 199 ± 22 mg km^{-1} (DV1), at 23 °C varied from 22 ± 3 mg km^{-1} (DV4) to 126 ± 6 mg km^{-1} (DV1).

THC and CO emissions from the FFV were in line with those from common gasoline vehicles (Tables 2 and 3). Hence, FFV's THC and CO emissions were respectively 39 ± 8 mg km^{-1} and 427 ± 40 mg km^{-1} at 23 °C, and 193 ± 39 mg km^{-1} and 1066 ± 258 mg km^{-1} at −7 °C.

THC and CO emissions from the HV increased respectively 12 and 18 times going from 23 °C (THC 13 ± 1 mg km^{-1}; CO 128 ± 53 mg km^{-1}) to −7 °C (THC 158 ± 14 mg km^{-1}; CO 2235 ± 557 mg km^{-1}). While HV's THC emissions at −7 °C (158 ± 14 mg km^{-1}) were similar to those from the gasoline

Table 2
Average emission factors (mg km^{-1}; CO_2 g km^{-1} and PN # km^{-1}) over the WLTC at 23 °C. Errors refer to maximum semi-dispersion of the two tests, except for HV who performed 5 tests.

	THC	CO	CO_2	PN(x 10^{11})	NOx	NO_2	N_2O	NH_3
DV1	4 ± 0	126 ± 6	138 ± 0	0.05 ± 0.03	148 ± 5	5 ± 1	11 ± 1	24 ± 7
DV2	2 ± 1	46 ± 6	154 ± 9	0.09 ± 0.01	476 ± 15	73 ± 1	8 ± 5	7 ± 2
DV3	7 ± 1	41 ± 1	337 ± 2	0.06 ± 0.01	238 ± 15	83 ± 4	14 ± 0	9 ± 0
DV4	13 ± 0	22 ± 3	146 ± 1	0.09 ± 0.04	484 ± 23	167 ± 16	8 ± 1	0 ± 0
DV5	19 ± 4	41 ± 22	173 ± 1	2.4 ± 0.5	183 ± 1	28 ± 1	12 ± 3	2 ± 0
GV1	54 ± 6	567 ± 124	117 ± 1	24 ± 1	34 ± 3	N.A.	1 ± 0	17 ± 3
GV2	12 ± 0	154 ± 52	145 ± 3	–	21 ± 6	N.A.	1 ± 0	9 ± 0
GV3	13 ± 0	158 ± 10	177 ± 2	11.0 ± 0.1	18 ± 1	1 ± 0	14 ± 0	46 ± 8
GV4[a]	$25 \pm /$	$5766 \pm /$	$142 \pm /$	–	$9 \pm /$	N.A.	$2 \pm /$	$34 \pm /$
GV5	24 ± 1	972 ± 4	152 ± 5	2.1 ± 0	27 ± 4	N.A.	1 ± 0	17 ± 0
FFV-E5	97 ± 16	319 ± 23	164 ± 2	23.1 ± 0.4	70 ± 15	N.A.	1 ± 0	6 ± 0
FFV-E85	39 ± 8	427 ± 40	156 ± 4	2.4 ± 0	20 ± 0	N.A.	1 ± 0	11 ± 1
HV	13 ± 1	128 ± 53	203 ± 4	6 ± 1	4 ± 1	N.A.	1 ± 0	4 ± 2

[a] Only one test was performed; N.A = below limit of detection.

Table 3
Average emission factors (mg km^{-1}; CO$_2$ g km^{-1} and PN # km^{-1}) over the WLTC at −7 °C. Errors refer to maximum semi-dispersion of the two tests, except for HV who performed 5 tests.

	THC	CO	CO$_2$	PN($\times 10^{11}$)	NOx	NO$_2$	N$_2$O	NH$_3$
DV1	8 ± 0	199 ± 22	160 ± 3	0.3 ± 0.2	1066 ± 28	247 ± 52	11 ± 3	0 ± 0
DV2	4 ± 1	138 ± 53	185 ± 8	0.07 ± 0.05	1142 ± 3	430 ± 0	10 ± 0	3 ± 1
DV3	8 ± 1	88 ± 4	368 ± 1	0.2 ± 0.1	803 ± 15	326 ± 5	17 ± 0	8 ± 3
DV4	17 ± 7	30 ± 8	175 ± 1	0.8 ± 0.6	839 ± 118	267 ± 74	12 ± 2	0 ± 0
DV5	20 ± 1	45 ± 1	199 ± 2	0.46 ± 0.04	393 ± 32	73 ± 7	12 ± 3	2 ± 0
GV1	146 ± 11	791 ± 115	120 ± 4	38.2 ± 0.6	43 ± 3	N.A.	1 ± 0	26 ± 5
GV2	117 ± 1	206 ± 18	160 ± 2	–	24 ± 4	N.A.	3 ±/[a]	12 ±/[a]
GV3	170 ± 52	920 ± 23	175 ± 1	28 ± 3	82 ± 20	N.A.	9 ±/[a]	51 ±/[a]
GV4	153 ± 7	10111 ± 1149	153 ± 2	–	7 ± 1	N.A.	4 ± 0	55 ± 1
GV5	133 ± 1	2604 ± 87	187 ± 2	12.2 ± 0.5	35 ± 0	N.A.	1 ± 0	25 ± 3
FFV-E5	184 ± 3	806 ± 67	181 ± 1	65 ± 1	86 ± 16	N.A.	2 ± 0	13 ± 1
FFV-E75	193 ± 39	1066 ± 258	167 ± 3	12 ± 1	29 ± 2	N.A.	1 ± 0	20 ± 2
HV	158 ± 14	2235 ± 557	264 ± 2	23.5 ± 0.5	14 ± 4	N.A.	1 ± 0	21 ± 1

[a] FTIR not present in the second test; N.A = below limit of detection.

vehicles (e.g., GV1, GV3, GV4), CO emissions (2235 ± 557 mg km^{-1}) were among the highest measured for GDI vehicles. This indicates a very strong influence of the temperature on the emissions of this type of vehicles. THC and CO emissions from HV at 23 °C were in line to those recently reported for a Euro 5 hybrid and a Euro 5 plug-in hybrid vehicle (Suarez-Bertoa and Astorga 2016b).

3.2. NOx and NH$_3$ emissions

NOx EFs from gasoline vehicles at 23 °C ranged from 9 mg km^{-1} (GV4) to 70 ± 15 mg km^{-1} (FFV-E5). At −7 °C, NOx emissions were on average 1.7 times [0.8–4.6 times] higher than at 23 °C. At cold temperature, NOx EFs ranged from 7 ± 1 mg km^{-1} (GV4) to 86 ± 16 mg km^{-1} (FFV-E5). FFV tested on E85/E75 blends presented slightly higher NOx at −7 °C (29 ± 2 mg km^{-1}) than at 23 °C (20 mg km^{-1}). HV's NOx emissions were 4 ± 1 mg km^{-1} at 23 °C and 14 ± 4 mg km^{-1} at −7 °C. Higher NOx emissions from spark ignition vehicles may be related to the lower catalytic efficiency and longer periods to reach light-off temperature at cold ambient temperatures (Heck et al., 2002; Suarez-Bertoa et al., 2015b).

NOx emissions from diesel vehicles were 20 times higher than those measured for gasoline vehicles. Diesel NOx emissions increased on average 3.4 times going from 23 °C down to −7 °C [1.7–7.2 times]. NOx EFs at 23 °C ranged from 148 ± 5 mg km^{-1} (DV1) to 484 ± 23 mg km^{-1} (DV4), and at −7 °C varied from 393 ± 32 mg km^{-1} (DV5) to 1142 ± 3 mg km^{-1} (DV2). These results are in good agreement with Ko et al., who recently studied a Euro 6 LNT-equipped diesel vehicle using the WLTC (Ko et al., 2017). Ko et al. reported NOx emissions 7 times higher at − 5 °C (~700 mg km^{-1}) than at 23 °C (~100 mg km^{-1}) and linked the high NOx emissions at low temperature to the longer ignition delay time, and a decrease on the operation of the EGR.

NH$_3$ EFs from spark ignition vehicles at 23 °C ranged from 6 mg km^{-1} (FFV-E5) to 46 ± 8 mg km^{-1} (GV3). NH$_3$ emissions from these vehicles increased on average 1.5 times [1.1–1.6 times] as temperature decreased from 23 to −7 °C. Average NH$_3$ EF at −7 °C was 26 ± 16 mg km^{-1}, going from 12 mg km^{-1} (GV2) to 55 ± 1 mg km^{-1} (GV4). HV emitted 4 ± 2 mg km^{-1} of NH$_3$ at 23 °C and 5.3 times more at −7 °C (21 ± 1 mg km^{-1}).

Average NH$_3$ emissions from diesel vehicles decreased from 8 mg km^{-1} at 23 °C down to levels below the limit of detection at −7 °C. While the average NH$_3$ EF from SCR-equipped diesel vehicles at −7 °C was 4 ± 2 mg km^{-1} [0–8 mg km^{-1}], for DV4 and DV5 (LNT-equipped) they were 0 and 2 mg km^{-1}, respectively. At 23 °C, NH$_3$ emissions from SCR-equipped diesel vehicles ranged from 7 ± 2 mg km^{-1} to 24 ± 7 mg km^{-1}. SCR systems, present in DV1 − DV3, seemed to be deactivated at cold temperature, resulting in

very low NH$_3$ and very high NOx emissions (see the example of DV2 in Fig. 4). No NH$_3$ emissions were observed from DV4 at −7 °C, which is in agreement with what observed by Ko et al. at the cold start phase using the WLTC at −5 °C (Ko et al., 2017).

3.3. GHG emissions

CO$_2$ EFs from gasoline vehicles at 23 °C ranged from 117 ± 1 g km^{-1} (GV1) to 177 ± 2 g km^{-1} (GV3). CO$_2$ emissions from the tested gasoline vehicles were on average 9% higher [0–23%] at −7 °C than at 23 °C. At cold temperature, CO$_2$ emissions varied from 120 ± 4 g km^{-1} (GV1; GDI) to 187 ± 2 g km^{-1} (GV5; PFI). HV's CO$_2$ emissions were on average 30% higher at −7 °C (264 ± 2 g km^{-1}) than at 23 °C (203 ± 4 g km^{-1}), being the largest difference of all the studied vehicles.

CO$_2$ emissions from the tested diesel vehicles were on average 15% higher [9–20%] at −7 °C than at 23 °C. CO$_2$ emissions at cold temperature ranged from 160 ± 3 g km^{-1} (DV1) to 368 ± 1 g km^{-1} (DV3; vehicle with the largest engine displacement in this study), and at 23 °C ranged from 138 g km^{-1} (DV1) to 337 ± 2 g km^{-1}.

N$_2$O emissions from gasoline vehicles were 1.6 times higher at −7 °C than at 23 °C. However, N$_2$O emissions from diesel vehicles were similar (DV1 and DV5) or slightly decreased (DV2-DV4) when tested at cold temperature. While, spark ignition average N$_2$O EF at −7 °C was 3 ± 2 mg km^{-1} [1–9 mg km^{-1}], diesel average N$_2$O EF at −7 °C was 12 ± 3 mg km^{-1} [10–17 mg km^{-1}]. At 23 °C, spark ignition N$_2$O EFs ranged from 1 mg km^{-1} to 14 mg km^{-1}, and diesel vehicles' N$_2$O EFs ranged from 8 mg km^{-1} to 14 mg km^{-1}. FFV and HV emitted 1 mg km^{-1} of N$_2$O at 23 °C and also at −7 °C.

3.4. Solid particle number emissions

SPN EFs from gasoline vehicles at 23 °C ranged from 2 × 10^{11} # km^{-1} (GV5, PFI) to 24 × 10^{11} # km^{-1} (GV1, GDI). At cold temperature, SPN EFs from gasoline vehicles ranged from 12 × 10^{11} # km^{-1} (GV5, PFI) to 65 × 10^{11} # km^{-1} (FFV-E5, PFI). FFV tested on E85/E75 blends resulted in 2 × 10^{11} # km^{-1} at 23 °C and 12 × 10^{11} # km^{-1} at −7 °C. HV's SPN emissions were 6 × 10^{11} # km^{-1} at 23 °C and 24 × 10^{11} # km^{-1} at −7 °C. While GDI's SPN emissions increased 1.6–2.8 times (HV, GDI, increase 3.9 times) from 23 to −7 °C, PFI increased 2.8–5.8 times.

SPN emissions from most of the diesel vehicles studied were substantially lower than those from spark ignition vehicles. At 23 °C, SPN EFs from diesel vehicles varied from 5 × 10^9 # km^{-1} (DV1) to 2 × 10^{11} # km^{-1} (DV5). Whereas at −7 °C SPN EFs ranged from 7 × 10^9 # km^{-1} (DV2) to 8 × 10^{10} # km^{-1} (DV4).

DV5 (LNT-equipped) presented the highest emissions of the

diesel vehicles at 23 °C ($2.4 \pm 0.5 \times 10^{11}$ # km^{-1}). These emissions could arise as consequence of the regeneration of the LNT system, which is done by the combustion of a certain amount of fuel on the catalytic converter that is located down-stream of the DPF. On the other hand, at −7 °C SPN emissions are lower, indicating a partial deactivation of the LNT.

4. Discussion

4.1. THC and CO emissions

THC and CO exhaust emissions result from the incomplete combustion of fuel. These emissions have been progressively reduced over the last decades thanks to the introduction of catalytic converters and tighter emission regulations (EEA 2014). Spark ignition vehicles are typically equipped with TWC which can simultaneously oxidise CO and THC to CO_2 and water while reducing NOx to molecular nitrogen (N_2). On the other hand, diesel vehicles are equipped with DOC that converts CO and THC to CO_2 and water. All diesel vehicles studied were equipped with DOC and all spark ignition vehicles were equipped with TWC.

THC and CO emissions measured in this study were higher for the spark ignition vehicles than for the diesel vehicles at the two studied temperatures. THC EFs from diesel vehicles were around one order of magnitude lower than those reported for gasoline vehicles at the two studied temperatures (see Section 3.1.1). This is a consequence of the lower combustion efficiency of the spark ignition vehicles compared to the compression ignition vehicles. CO emissions from diesel vehicles were also substantially lower than those observed for gasoline (see Table 3), which is in line to what reported for pre-Euro 6 vehicles (Moeckli et al., 1996; Phan et al., 2013). Being THC and CO the only pollutants that were regulated at −7 °C, and since diesel vehicles present much lower THC and CO EFs than spark ignition vehicles, diesel vehicles were excluded of the Type 6 test.

Large differences on the THC and CO emissions between tests performed at 23 °C and those performed at −7 °C were observed for the spark ignition vehicles. Higher CO and THC emissions at cold ambient temperatures from spark ignition vehicles have been linked to: use of rich air-fuel mixtures at cold starts, incomplete combustion near the cold cylinder walls during warm up, lower catalytic efficiency and longer periods to reach light-off temperature (Heck et al., 2002). This has led to the assumption that emissions during the extra-urban driving cycle (EUDC), where the TWC should be already working at optimum conditions, are negligible compared to emissions during the UDC (Weilenmann et al., 2005). For that reason, low temperature vehicle testing of spark ignition vehicles in EU was limited to the UDC (lasting 780 s and covering ~4 km, Fig. 1). Therefore, only cold start emissions are accounted for at the moment. However, the results obtained in this study show (Fig. 2) that a large fraction of CO emissions can take place during the high phase (phase 3) and extra-high phase (phase 4) of the WLTC (Fig. 2).

It could be expected that after certain time running at −7 °C (after catalyst light-off and with the engine running hot), the vehicles would reach, or approach, the performance observed at 23 °C. In that case, the emissions of the tested vehicle should be similar at the two temperatures, at least towards the end of the test. However, it was observed that in most cases the emissions measured during Phase 3 and Phase 4 were several times higher at −7 °C than at 23 °C (see Table S1 of the supplementary material). This indicates that the tested vehicles do not reach the convergence performance point between 23 and -7 °C. Hence, temperature not only affects the cold start emissions but also emissions during the entire test. Therefore, cold temperature testing should be

performed during the entire cycle for the proper assessment of emissions.

Dardiotis et al. (Dardiotis et al., 2013) reported emissions below Euro 5 standards for a series of Euro 5 gasoline vehicles tested at −7 and 22 °C over the NEDC. It was suggested that these low emissions were influenced by the improvements made on the vehicles to comply with more stringent Euro 5 standards during EU Type 1 test (Dardiotis et al., 2013). In that study, THC emissions were found to be 3.9 times higher −7 °C than at 22 °C. The emissions at −7 °C were 1.6 times higher than those measured from our Euro 6 vehicles tested over the WLTC. However, CO emissions were comparable to what reported here for Euro 6 type approved vehicles. The absence of improvement in this case is not a surprise as emission limits for gaseous pollutants from spark ignition vehicles have not changed from Euro 5 to Euro 6.

Recent studies have pointed out that THC emissions from modern gasoline and diesel vehicles lead to secondary carbonaceous aerosol formation (Gordon et al., 2014; Platt et al., 2017; Suarez-Bertoa et al., 2015c). These studies show that, for spark ignition vehicles, higher primary organic aerosol emissions and SOA formation take place at cold temperatures (−7 °C) than at temperate temperatures (22 °C). The higher SOA formation is explained to be related to the higher THC emissions at cold temperature. Therefore, unless a tighter limit will be applied to THC emissions at cold temperature, modern vehicles will continue to largely contribute to the total PM budged during the cold season, when PM pollution levels are often higher (Custódio et al., 2016; Wang et al., 2017).

4.2. NOx and NH$_3$ emissions

To better understand NOx and NH$_3$ emissions from modern vehicles one have to look into the catalytic converter systems that are used to reduce NOx emissions. Spark ignition vehicles use TWC and in some cases also NSC (e.g., GV3). Since the introduction of the Euro 6 standards, diesel vehicles use SCR or LNT for this scope. The use of all these catalytic systems to reduce NOx emissions have led to the emissions of other pollutants such as NH$_3$ and N$_2$O. These compounds are formed following different reaction pathways depending on the catalytic system and precursors present on it.

NH$_3$ is formed in the TWC via steam reforming from hydrocarbons (Whittington et al., 1995) and/or via reaction of NO with molecular hydrogen (H$_2$) (through reaction 2a or 2b) produced from a water-gas shift reaction between CO and water (1) (Bradow and Stump, 1977; Barbier and Duprez, 1994):
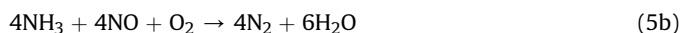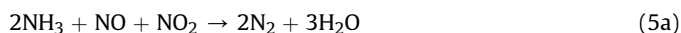
$$CO + H_2O \rightarrow CO_2 + H_2 \tag{1}$$

$$2NO + 2CO + 3H_2 \rightarrow 2NH_3 + 2CO_2 \tag{2a}$$

$$2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O \tag{2b}$$

NSC and LNT systems are used to reduce NOx into N$_2$ from gasoline and diesel vehicles, respectively. NSC and LNT adsorb NOx in the fuel-lean mode and reduces NOx in the fuel-rich mode (regeneration). This process takes place on a catalytic converter while the engine runs on a rich air/fuel mixture, which provides the CO and hydrocarbons needed for the reduction of NOx. It has been shown that NH$_3$ can be emitted as by-product during the so-called regeneration process (Karavalakis et al., 2014). The chemical reactions that take place are the same shown for the TWC (1–2b).

The SCR, on the other hand, reduces NOx emissions by reacting the NO and NO$_2$ with NH$_3$ (formed by the hydrolyzation of the urea injected into the system) on a catalyst surface (see reactions 3–5). NOx in diesel exhaust is usually composed of >90% NO. However,
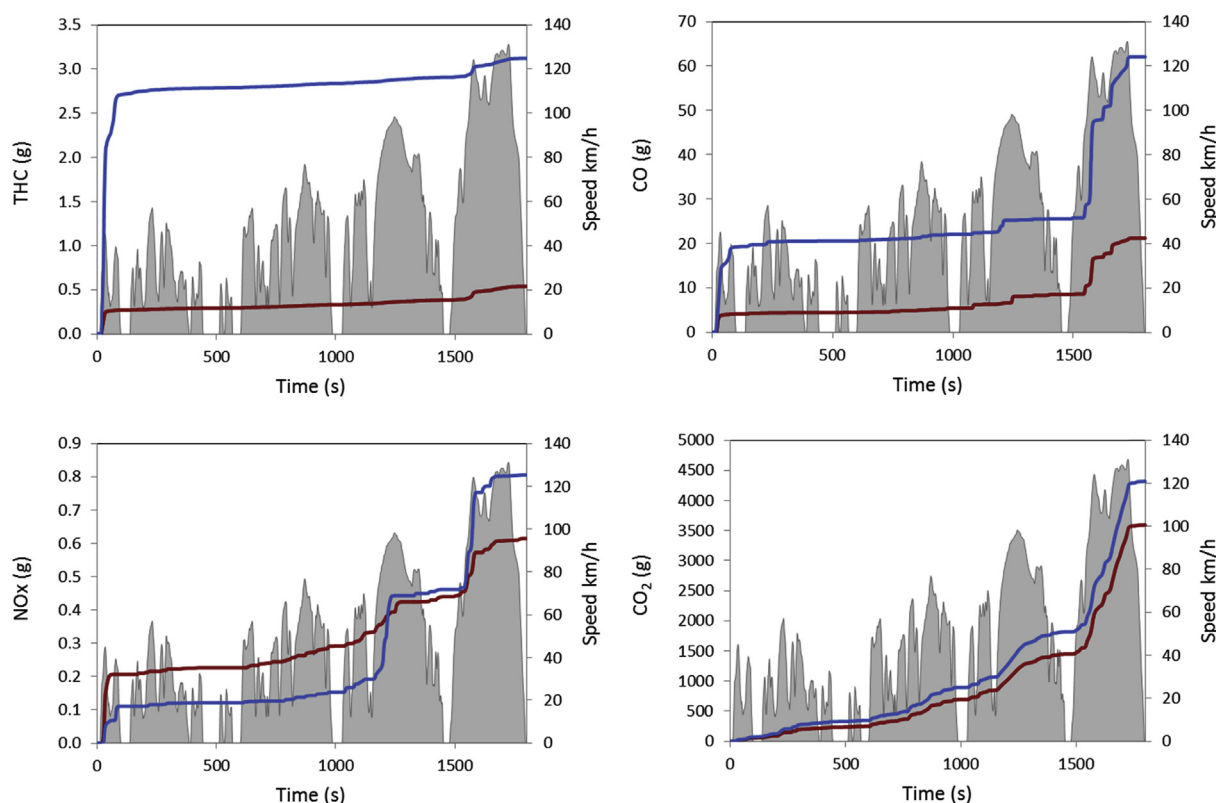
Fig. 2. THC, CO, NOx and CO$_2$ cumulative emissions of GV5 during the WLTC at 23 °C (red) and −7 °C (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

equimolar amounts of NO and NO$_2$ increase the reaction rate with NH$_3$. In order to increase NO$_2$ in the exhaust to increase the reaction rate with NH$_3$, NO is oxidised to NO$_2$ on the DOC (Guan et al., 2014). The over-doping of urea, and low temperatures in the system and/ or the catalyst degradation may lead to NH$_3$ emissions (Guan et al., 2014).

$$CO(NH_2)_2 \rightarrow NH_3 + HNCO \tag{3}$$

$$HNCO + H_2O \rightarrow NH_3 + CO_2 \tag{4}$$

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \tag{5a}$$

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \tag{5b}$$

$$8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O \tag{5c}$$

NOx emissions from the diesel vehicles tested using the WLTC at 23 °C were well above the Euro 6 limits suggesting a poor performance of the catalytic converters (SCR and LNT) or NOx reduction strategy used. High NOx emissions from diesel vehicles, tested using a different methodology than that used during the current type approval, have been recently reported in other studies (O'Driscoll et al., 2016; Suarez-Bertoa et al., 2015a; Suarez-Bertoa and Astorga 2016a; Yang et al., 2015). NOx emissions increased at cold temperature for both spark ignition (2 times) and diesel vehicles (>3 times), which indicates the importance of regulating this pollutant during the cold temperature test procedure. Average NOx emissions from diesel vehicles were ~20 times higher than average NOx emissions from the studied gasoline vehicles.

Cold start NOx emissions from Euro 3 and Euro 4 gasoline vehicles equipped with TWC did not seem to be sensitive to temperature changes (Weilenmann et al., 2005). A change in this trend was reported for Euro 5 vehicles (Dardiotis et al., 2013; Weilenmann et al., 2005), and, in light of our results, it continues for Euro 6 vehicles.

Dardiotis et al. found that NOx emissions from diesel vehicles were quite low after the UDC and suggested that for that reason testing the vehicle over the EUDC could not be needed (Dardiotis et al., 2013). In that study it was stated that this applies in particular to vehicles equipped with an SCR system because this device works satisfactorily only over the EUDC. However, the three SCR-equipped vehicles (DV1-DV3) studied here resulted in extremely high NOx emissions (from 803 ± 15 mg km^{-1} to 1142 ± 3 mg km^{-1}) during the entire test cycle at −7 °C. Furthermore, the absence of NH$_3$ emissions and the lower N$_2$O emissions compared to 23 °C indicates that the SCR system was not working properly, or its efficiency at low temperatures was very low. The absence of data regarding emissions from SCR-equipped diesel vehicles at low temperature does not allow for any further comparison.

Fig. 2 and Fig. 5 illustrate that vehicle emissions pattern at −7 °C are very similar to those obtained at 23 °C (e.g., GV5 and DV5). This could suggest that a refined strategy and control of the after-treatment at 23 °C could be enough to account for the emissions that would take place at −7 °C. However, the after-treatment strategy could change as we change the ambient temperature. In fact, SCR systems stopped working (or worked at lower efficiency) at cold temperature and GV2's NOx emission control worked differently at the two studied temperatures (Figure S1 of the supplementary material). Therefore, the WLTC test should be perform at two different temperatures. Moreover, for a thorough assessment of the vehicles, emissions during the whole extent of the

WLTC should be taken into account for the tests performed at $-7\ ^\circ$C.

NOx emissions from spark ignition vehicles were composed by NO (NO_2 emissions were below our FTIR detection limits). However, the ratio of NOx to NO_2 emissions from diesel vehicles was on average 4, at the two studied temperatures (Table 2 and Table 3). An increase on the NO_2 emissions has also been recently reported for modern diesel fleets (O'Driscoll et al., 2016). The increase of NO_2 emissions and of the ratio of NO_2 in the exhaust may have important effects on the atmospheric chemistry and urban air quality. The EEA has recently reported that following the decrease of the ratio of NO to NOx emissions for diesel vehicles, which leads to less O_3 being consumed in the titration reaction with NO, O_3 concentrations have increased in several traffic stations (EEA, 2014). Furthermore, as indicated in the Introduction section, NO_2 is among the most problematic pollutants in terms of harm to human health in Europe (EEA, 2015). Estimates of the health impacts attributable to long-term exposure to air pollution indicate that NO_2 concentrations in 2013 were responsible for about 68 000 premature deaths in EU-28.

NH_3 emissions from SCR-equipped diesel vehicles ($7-24\ mg\ km^{-1}$) were on the same ranged as gasoline vehicles ($6-46\ mg\ km^{-1}$) at 23 $^\circ$C. SCR systems present in DV1 and DV2, appeared to be deactivated at cold temperature, resulting in very low NH_3 and very high NOx ($>1000\ mg\ km^{-1}$) emissions (see the example of DV2 in Fig. 4). No NH_3 emissions were observed from DV4 (LNT-equipped). However, DV5 (equipped with the latest LNT generation) emitted 2 $mg\ km^{-1}$ of NH_3 at the two studied temperatures.

NH_3 emissions from vehicles equipped with TWC were up to ~6 times higher than those found in the literature for Pre-Euro 6 vehicles (Euro 3, Euro 4, Euro 5, Ultra-Low Emission Vehicles (ULEV) and Low Emission Vehicles (LEV)) (Durbin et al., 2004; Heeb et al., 2006, 2008; Huai et al., 2003; Moeckli et al., 1996; Suarez-Bertoa et al., 2014). NH_3 emissions from gasoline vehicles were up to 5 times higher at cold temperature. HV presented similar NH_3 emissions to the conventional gasoline vehicles. This trend is in good agreement with what reported in a previous study for Euro 5 hybrid vehicles (Suarez-Bertoa and Astorga, 2016b).

The high NH_3 emissions ($6-46\ mg\ km^{-1}$) observed from the spark ignition vehicles seem to result from the emission control strategy that aims at reducing NOx emissions at expenses of emitting NH_3, which is not regulated for light-duty vehicles in most regions of the world. In fact, NH_3 molar emissions from gasoline vehicles exceeded NOx emissions.

NH_3 is becoming the major nitrogen species emitted in modern gasoline fleets (Bishop and Stedman, 2015) and since the introduction of the SCR and LNT systems (Euro 6 vehicles) NH_3 is also present in diesel exhaust (Suarez-Bertoa et al., 2015a). Moreover, NH_3 emissions from SCR-equipped diesel vehicles may increase as a consequence of a higher dosage of urea to meet NOx emission limits under real driving emission test (RDE).

NH_3 and NO_2 act as limiting reagents in the atmospheric formation of ammonium nitrate (NH_4NO_3) (Aksoyoglu et al., 2016; Petetin et al., 2016). Recent studies have shown that particle mass concentrations rapidly increased when vehicles exhaust containing NH_3 is photo-oxidised (Liu et al., 2015), and that NH_3 mass emissions leads to similar secondary inorganic particles ($PM_{2.5}$) mass formation under different NOx environments (Link et al., 2017). Therefore, as previously indicated, the increase of the ratio of NO_2 and of NH_3 emissions from the modern vehicle fleet may have a strong impact on air quality. Furthermore, as for THC emissions, NO_2 and of NH_3 emissions were higher at cold temperature, making vehicle emissions even more critical for air pollution in the cold season.

4.3. GHG emissions

In order to meet the 2020 GHGs reduction targets for transport sector the European Parliament and the Council stablished that average CO_2 emissions from the entire light-duty vehicle fleet of each vehicle manufacturer in EU will have to be lower than 95 g km^{-1} by 2020 (EC 333/2014).

To meet this new regulation, and customers' needs, gasoline direct injection (GDI) technologies were introduced in the vehicle market. GDI generally provides better fuel economy and lower CO_2 emissions because fuel volume and injection timing can be more accurately controlled (Maricq et al., 2012; Myung et al., 2012). GDI vehicles studied here (with the exception of GV3, which was the gasoline vehicle with the higher engine power and displacement) presented lower CO_2 emissions than PFI at the two studied temperatures.

Gasoline and diesel vehicles with similar engine power and engine displacement (DV4 vs GV5 and DV5 vs GV3), presented similar CO_2 emissions at 23 $^\circ$C. DV5 and GV5 presented higher CO_2 emissions than GV3 and DV4 at $-7\ ^\circ$C. In general lines, CO_2 emissions from the tested diesel vehicles experienced a higher increase [9–20%] as temperature decreased than the gasoline vehicles [0–23%]. HV's CO_2 emissions showed the largest difference of all the studied vehicles (30% increase as temperature decreases). Such large difference was related to higher use of the internal combustion engine at low temperature compared to 23 $^\circ$C. GDI and PFI emissions increased respectively by ~9%–16%, as temperature decreased. These results are in good agreement with what reported by Zhu et al. for two vehicles tested using the WLTC.

Since road-load was adjusted for the low temperature tests (see Experimental section), as prescribed by regulation, we are not able to assert to what extent the CO_2 emissions variation were related to the difference in the ambient temperature or to the higher road-load because higher road-loads usually lead to higher CO_2 emissions. These effects are the topic of a future study.

N_2O can be generated as a by-product in various types of after-treatment systems over a broad range of temperatures. It has been demonstrated that TWC, NSC, LNT, DOC and SCR can all potentially contribute to N_2O formation, depending on the catalyst material and exhaust gas conditions as well as the after-treatment operation strategies (Guan et al., 2014).

In a TWC N_2O is formed via a complex series of chemical mechanisms involving NO, molecular nitrogen (N_2) and atomic nitrogen (Wallington and Wiesen, 2014). The result is that some NO is partially reduced and exits the system as N_2O. N_2O is formed in NSC and LNT following similar pathways to those described for the TWC. N_2O is formed in DOC at low temperature as a by-product of NOx reduction by hydrocarbons. The formation of N_2O over DOC is mainly impacted by the type and concentration of hydrocarbons, temperature, and the DOC formulation (Guan et al., 2014). In SCR systems N_2O formation follows two different pathways: i) NH_3 oxidation by NO and ii) oxidation of NH_3 by O_2. (Guan et al., 2014). Hence, N_2O formation is related to the presence of NH_3, which is linked to urea dosage.

N_2O EFs from spark ignition vehicles [$1-14\ mg\ km^{-1}$] at 23 $^\circ$C were in good agreement with what reported by Graham et al. (2009). N_2O EFs from both spark ignition and diesel vehicles increased as temperature decreased (see section 3.3. GHG emissions). N_2O emissions from diesel vehicles were ~4 times higher than those from spark ignition vehicles at the two studied temperatures.
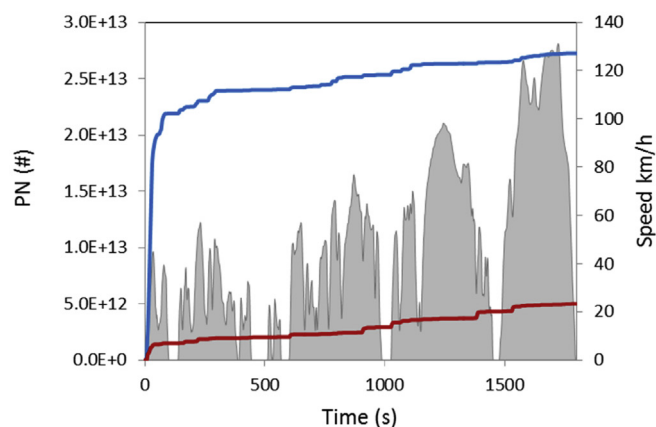
The higher N_2O emissions observed for DV1 − DV4 at $-7\ ^\circ$C compared to those 23 $^\circ$C are linked to the higher NOx concentrations present at cold temperature in the exhaust that are readily to react on the DOC. Similar N_2O emissions, at the two studied

GV1-GDI
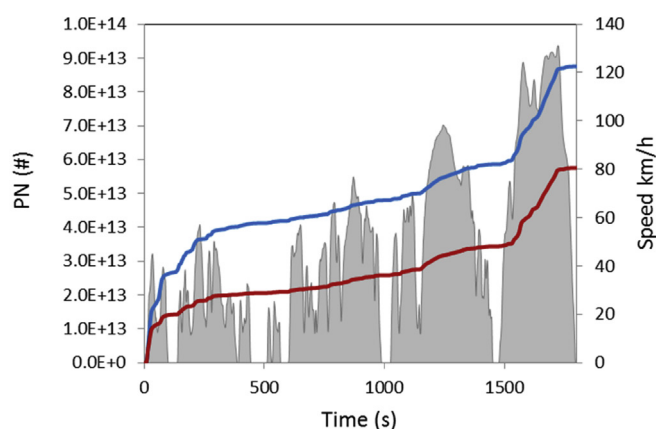
GV5-PFI

Fig. 3. PN cumulative emission profiles for a GDI (GV1; top) and a PFI (GV5; bottom) vehicle at 23 °C (red) and −7 °C (blue) during the WLTC. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

temperatures, were observed for DV5 (equipped with the latest LNT technology). In fact, the emission profiles illustrated in Fig. 5 indicate that the vehicle worked in a similar fashion at the two temperatures.

N_2O emissions are about 5 times higher than those found in the vehicle emission inventories (EEA, 2016). In terms of CO_2 equivalents (N_2O has 298 times the global warming potential of CO_2 over 100 years) those N_2O emissions are ~ 3–5 g CO_2 eq km^{-1}, which is approximately 2% of the average CO_2 emissions of the tested fleet. Considering that EU has set as target a 10% reduction of CO_2 from transport by 2020 and that the inventories underestimate the actual N_2O emissions, 2% is an extremely large figure.

Vehicle's CO_2 emissions are not measured during the cold temperature test (Type 6 test) and N_2O vehicle emissions are not regulated in the EU. Therefore, besides the higher CO_2 and N_2O emissions at cold temperature, these higher GHG emissions are not considered in current transport GHG targets.

### 4.4. Solid particle number emissions

The SPN measurement method, based on the counting of solid particles with a diameter larger than 23 nm, was integrated into the European emissions regulation in 2011 for diesel light-duty vehicles (Euro 5), in 2014 for Gasoline Direct Injection (GDI) light-duty
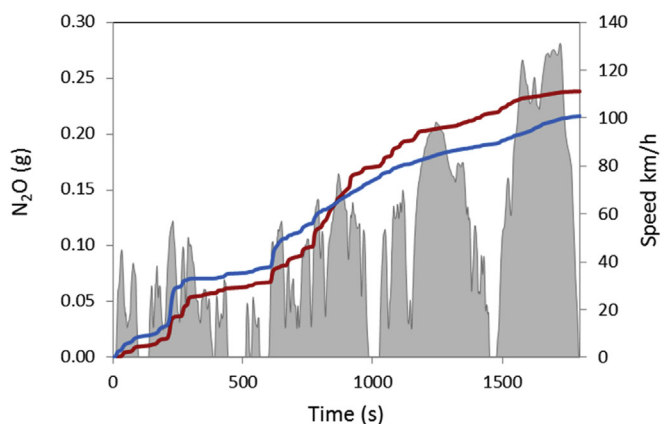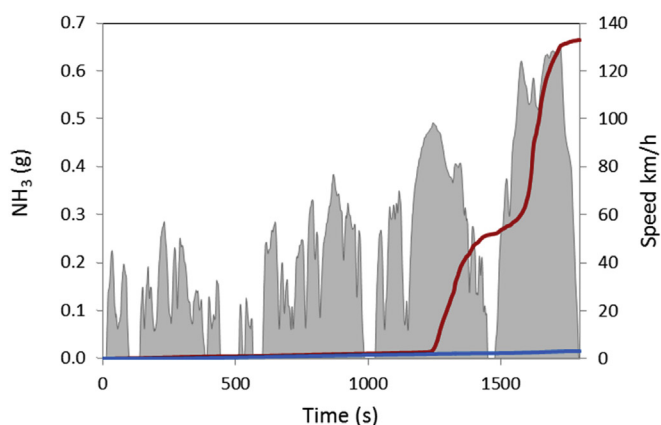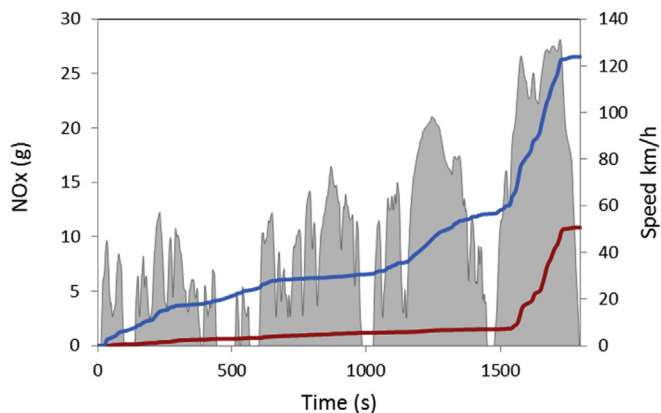
Fig. 4. NOx, N_2O and NH_3 cumulative emissions of DV2 (SCR-equipped) during the WLTC at 23 °C (red) and −7 °C (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

vehicles (Euro 6). A minimum diameter of 23 nm size was selected in order to include the primary soot particles and to avoid the volatile nucleation mode particles (Giechaskiel et al. 2014).

A wide range of SPN EFs resulted from the gasoline fleet tested (2 - 24 × 10^{11} # km^{-1} at 23 °C and 12 - 38 × 10^{11} # km^{-1} at −7 °C). SPN EFs from the Euro 6 GDI vehicles [11 - 24 × 10^{11} # km^{-1}] were higher than Euro 6 SPN standards (6 × 10^{11} # km^{-1}). SPN emissions were low for the tested diesel vehicles, being aprox. 2 orders of magnitude lower than those form gasoline vehicles. This indicates a good performance of the current diesel particle filter (DPF) technologies used in the tested vehicles. The highest SPN emissions were measured from the GDI vehicles (GV1, GV3 and HV). GDI
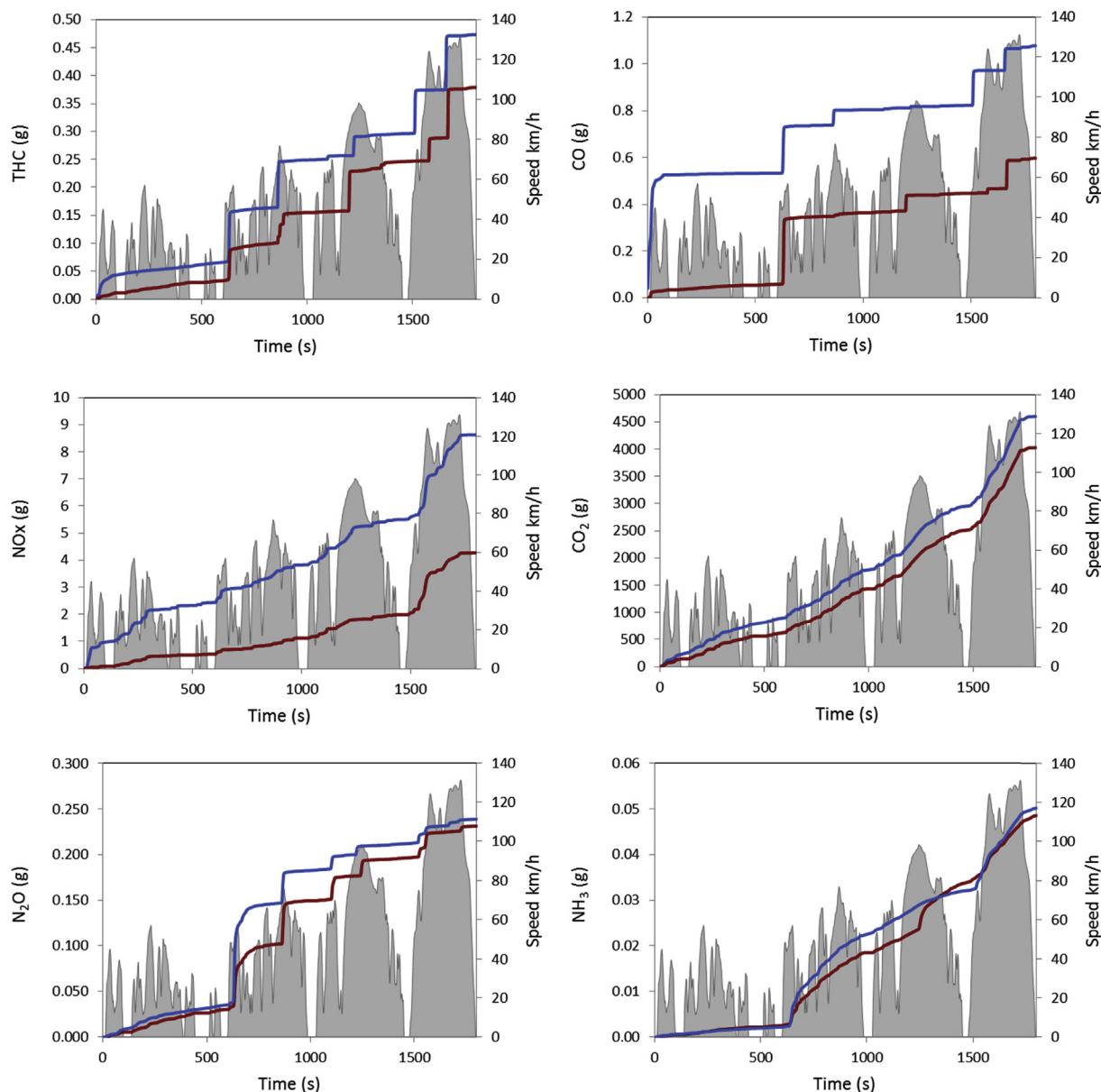
Fig. 5. THC, CO, NOx, CO$_2$, N$_2$O and NH$_3$ cumulative emissions of DV5 (LNT-equipped) during the WLTC at 23 °C (red) and −7 °C (blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

average SPN emissions were 2.8 times higher than PFI at −7 °C and 8.8 times higher at 23 °C. GDI present more particulate emissions than PFI vehicles, due to the limited time available for fuel and air to be thoroughly mixed in the GDI (Überall et al., 2015; Yinhui et al., 2016) compared to the aspired system. The GDIs' SPN emissions increased during the high speed phases accelerations with richer the air/fuel ratios (Fig. 3).

At cold temperature SPN emissions increased for both spark ignition and diesel vehicles. The higher SPN emissions from the diesel vehicles at cold temperature could be: i) semi-volatile material escaping oxidation as the catalytic converters have not yet reached the light-off temperature, ii) blow-out of loose non-volatile particle deposits, as the filter is exposed to highly transient operation with respect to thermal and flow conditions, or iii) related to small filter defects that reduce DPF filtration efficiency at low temperatures (Braisher et al., 2010). In the case of PFI spark ignition vehicles, higher SPN emissions at cold temperature are linked,

similarly to THC emissions, to enrichment of the air-fuel mixture during cold-start engine operation, which compensates for the reduced fuel vaporization and elevated friction of engine components, leading to incomplete fuel combustion. Moreover, at low ambient temperature, catalytic after-treatment systems need longer to reach their light-off temperature. SPN emissions decrease as the engine gets warmer due to better combustion (Fig. 3).

SPN emissions were comparable to those reported in previous studies for gasoline vehicles (Braisher et al., 2010; Chan et al., 2013; Jang et al., 2015; Zhu et al., 2016). Emissions measured at −7 °C were in very good agreement with what recently reported by Zhu et al. for a GDI and a PFI vehicle tested at the same temperature using the WLTC (Zhu et al., 2016).

FFV resulted in higher SPN emissions when tested on E5 than running on ethanol blends (E85/E75) at the two studied temperatures. Lower SPN emissions from flex-fuel vehicles running on ethanol blends are thought to be related to the large percentage of

ethanol (a short-carbon-chain molecule, C2) in the fuel blends (85% and 75%, for E85 and E75, respectively) (Karavalakis et al., 2014). High SPN emissions from FFV when fuelled with E5 could be related to the engine calibration and/or combustion temperature, as these vehicles are expected to run on high concentrations of ethanol blends.

PFI gasoline vehicles used to produce very low particulate emissions in standard testing or driving conditions (i.e., ~23 °C). Therefore, only diesel and GDI gasoline vehicles are required to meet a SPN limit in Europe. However, our results, in good agreement with Zhu et al., indicate that PFI gasoline vehicles can result in very high emissions (GV5 > 1×10^{11} # km^{-1}; FFV > 1×10^{12} # km^{-1}). This highlights the importance of the introduction of SPN emission limit at cold temperatures but also that emission limits should be technology independent.

5. Conclusions

Our experimental results indicate that emissions from both spark ignition (including common gasoline, flex-fuel and hybrid vehicles) and compression ignition vehicles are strongly and negatively affected by low ambient temperatures. Higher emissions of THC, CO, NOx, SPN and NH_3 were observed when vehicles were tested at −7 °C −instead of 23 °C. These pollutants are important sources of the most problematic pollutants in terms of harm to human health in Europe: PM, ground-level O_3 and nitrogen dioxide (NO_2). However, they are not properly addressed for modern vehicles in the current EU vehicle emissions regulation for cold temperature testing (Type 6 test). For that reason, vehicular emissions of THC, CO, NOx, SPN and NH_3 should be addressed in the next revision of the EU legislation of light-duty vehicle emissions at cold temperature for all vehicle technologies.

NO_2 ratio (NO_2/NOx) in diesel exhaust and NH_3 ratio (NH_3/NOx) in gasoline exhaust are higher than those observed for pre-Euro 6 vehicles. These pollutants are involved in fundamental chemical processes in the atmosphere. Thus, this strong variation of their vehicular emissions may have a strong impact on urban air quality.

CO_2 and N_2O (GHGs) emissions were found to be higher (9–30% higher for CO_2 and up to 1.9 times for N_2O) when vehicles were tested at −7 °C than at 23 °C. CO_2 and N_2O emissions are not measured or regulated under the Type 6 test. Therefore, the contribution of the transport sector to the GHG budget may be underestimated, highlighting the importance of a new and representative procedure that enables the authorities to assess the emissions from vehicles at cold ambient temperatures.

It has been observed that a large amount of emissions can take place during the last two phases of the new type approval cycle (i.e., WLTC), and not only during the cold start. This study suggests that vehicles should be tested over the entire WLTC to be able to properly assess their emissions at cold temperature.

Disclaimer

The opinions expressed in this manuscript are those of the authors and should not be considered to represent an official opinion of the European Commission.

Acknowledgments

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2017.10.096.

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