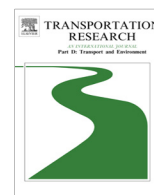Contents lists available at ScienceDirect

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Isocyanic acid and ammonia in vehicle emissions

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ABSTRACT

Vehicles are considered to be an important source of ammonia (NH_3) and isocyanic acid (HNCO). HNCO and NH_3 have been shown to be toxic compounds. Moreover, NH_3 is also a precursor in the formation of atmospheric secondary aerosols. For that reason, real-time vehicular emissions from a series of Euro 5 and Euro 6 light-duty vehicles, including spark ignition (gasoline and flex-fuel), compression ignition (diesel) and a plug-in electric hybrid, were investigated at 23 and $-7\,°C$ over the new World harmonized Light-duty vehicle Test Cycle (WLTC) in the Vehicle Emission Laboratory at the European Commission Joint Research Centre Ispra, Italy. The median HNCO emissions obtained for the studied fleet over the WLTC were $1.4\,\text{mg km}^{-1}$ at $23\,°C$ and $6\,\text{mg km}^{-1}$ at $-7\,°C$. The fleet median NH_3 emission factors were $10\,\text{mg km}^{-1}$ and $21\,\text{mg km}^{-1}$ at 23 and $-7\,°C$, respectively. The obtained results show that even though three-way catalyst (TWC), selective catalytic reduction (SCR), and NOx storage catalyst (NSC) are effective systems to reduce NOx vehicular emissions, they also lead to considerable emissions of the byproducts NH_3 and/or HNCO. It is also shown that diesel light-duty vehicles equipped with SCR can present NH_3 emission factors as high as gasoline light-duty vehicles at both, 23 and $-7\,°C$ over the WLTC. Therefore, with the introduction in the market of this DeNOx technology, vehicular NH_3 emissions will increase further.

1. Introduction

Vehicular emissions significantly influence the atmospheric composition and have a strong impact on climate change (Uherek et al., 2010), environment and human health (Pope et al., 2002). Light-duty vehicles (LDVs) are considered to be an important source of ammonia (NH_3) and isocyanic acid (HNCO), being in some cases the main source in urban areas (Chitjian et al., 2000; Battye et al., 2003; Whitehead et al., 2007; Kean et al., 2009; Ianniello et al., 2010; Meng et al., 2011; Nowak et al., 2012; Reche et al., 2012; Wentzell et al., 2013; Yao et al., 2013; Woodward-Massey et al., 2014; Reche et al., 2015).

Ammonia is classified under the European dangerous substances directive (67/548/EEC) as toxic, corrosive and dangerous for the environment. The U.S. Occupational Safety and Health Administration has set for ammonia an eight-hour exposure limit at 25 ppm and a short-term (15 min) exposure level at 35 ppm (Agency for Toxic Substances and Disease Registry, 2004). Ammonia is also a precursor in the formation of atmospheric secondary aerosols (Behera and Sharma, 2010). Its reaction with nitric and sulfuric acid leads to the formation of ammonium nitrate and ammonium sulfate. The particulate matter that is formed (ammonium nitrate and ammonium sulfate) is associated with adverse health effects (Pope et al., 2002). Furthermore, when transported to remote areas, their deposition leads to hypertrophication of waters and acidification of soils with negative effects on nitrogen-containing ecosystems (Sutton et al., 2000; Bouwman et al., 2002; Erisman et al., 2003). Recent studies have shown that LDVs are also one of the main sources of isocyanic acid (Wentzell et al., 2013; Brady et al., 2014; Woodward-Massey et al., 2014). Isocyanic acid has been shown to be a highly toxic gaseous acid and a potential health concern due to its dissociation at physiological pH (Roberts et al., 2011). Isocyanic acid and its aqueous anion ($CNO-$) isocyanate have been linked to several negative health effects such as atherosclerosis, cataracts, and rheumatoid arthritis through carbamylation reactions (Stark et al., 1960; Lee and Manning, 1973; Wang et al., 2007; Roberts et al., 2011). Carbamylation is a chemical process whereby amine, hydroxyl, and sulfhydryl groups in human proteins add across the $N-C$ bond of the CNO group impairing protein function in the body (Stark et al., 1960; Lee and Manning, 1973; Wang et al., 2007). Roberts et al. (2011) estimated that inhalation of concentrations as low as 1 ppbv may be sufficient to commence carbamylation reactions in the human body. Recently, Wentzell et al. (2013) reported mean ambient HNCO mixing ratios of 85 pptv, with spikes as high as 990 pptv, in Toronto, Canada, suggesting that, there are circumstances where HNCO concentrations could be large enough to have a detrimental effect on human health. Despite its toxicity, HNCO-specific exposure or air quality standards do not exist. Consequently, ammonia and HNCO vehicular emissions should be thoroughly studied due to the close proximity between the sources, i.e., vehicles, and the population.

Vehicular emissions of total hydrocarbons (THC), CO and NOx from LDV are legislated by the directive (EC) No 692/2008 (European Commission, 2008). In order to decrease their emissions, the automotive industry have introduced a series of different after-treatment systems over the last years, e.g., three-way catalyst (TWC), selective catalytic reduction (SCR), lean-NOx trap (LNT) and NOx storage catalyst (NSC). The introduction of the TWC was a major step towards the vehicular emissions control. Molecular nitrogen is the aimed reaction product during the reduction of NOx over the TWC, but ammonia and HNCO have been found to be byproducts during this process (see reactions 1–4). In the TWC, ammonia is formed via steam reforming from hydrocarbons (Whittington et al., 1995) and/or via reaction of nitrogen monoxide (NO) with molecular hydrogen (H_2) (through reaction 2a or 2b) produced from a water-gas shift reaction between CO and water (reaction 1) (Bradow et al., 1977; Barbier and Duprez, 1994). High catalyst temperatures (<360 °C) are usually associated to NH_3 emissions (reactions 1 and 2). HNCO, on the other hand, is formed when NO, CO, and either H_2 or NH_3 react over precious metal catalysts (e.g., platinum, palladium, or rhodium), typically used in modern TWC, at relatively low temperatures (∼250 °C; reaction 3) (Dümpelmann et al., 1995; Chambers et al., 2001; Cant et al., 2003, 2004, 2005). The HNCO is formed by reaction of NCO groups with adsorbed H_2 (Chambers et al., 2001). As the catalyst temperature increases H_2 is consumed and the majority of the surface bounded H_2 is formed following NH_3 dissociation. These studies suggested that despite the relatively high yields of HNCO from nitrogen on the catalyst surfaces present in a modern TWC, a rapid and complete hydrolysis of HNCO, leading to NH_3 formation, takes place on the oxide wash-coat of the TWC (reaction 4). In that case, light-duty gasoline vehicles (LDGVs) should emit negligible concentrations of HNCO. However, Brady et al. (2014), reported emission factors for HNCO from a fleet LDGVs and Wentzell et al. (2013), observed HNCO emissions factors from a single light-duty diesel engine operating under four different steady-state driving modes. These are, to our knowledge, the only studies that report HNCO vehicular emissions.

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{1}$$

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

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

$$2NO + 5CO + H_2O \rightarrow 2HNCO + 3CO_2 \tag{3}$$

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

SCR, LNT and NSC after-treatment systems have recently been incorporated to LDVs as DeNOx systems. The SCR is an after-treatment system whose goal is to reduce NOx emissions by reacting the NO and NO_2 with NH_3 (formed by the reduction of the urea injected into the system) on a catalyst surface (see reactions 5–7). The over-doping of urea, and low temperatures in the system and/or the catalyst degradation may lead to ammonia emissions. Furthermore, previous studies have shown that HNCO is a byproduct in urea based SCR systems (Koebel et al., 2000; Heeb et al., 2011).

$$CO(NH_2)_2 \rightarrow NH_3 + HNCO \tag{5}$$

$$HNCO + H_2O \rightarrow NH_3 + CO_2 \tag{6}$$

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \tag{7a}$$

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \tag{7b}$$

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

LNT and NSC are systems that have as final goal to reduce NOx into N_2 in diesel and gasoline vehicles. This reaction takes place on a catalytic converter during the phases when the engine runs on a rich air/fuel mixture (air/fuel ratio < 1) that provides the CO and hydrocarbons needed for the reduction of nitrogen oxides. These are the same conditions that lead to NH_3 and HNCO formation over a catalyst surface.

The present study provides real-time vehicular emissions and emission factors of HNCO and NH_3 from various Euro 5 and Euro 6 spark and compression ignition vehicles, as well as a plug-in electric hybrid vehicle. Tests were performed at 23 and $-7\,°C$ using the new World harmonized Light-duty vehicle Test Cycle (WLTC), which was designed to be representative of real world driving conditions. Measurements of HNCO and NH_3 were done with a high resolution Fourier Transform Infrared spectrometer at 1 Hz directly at the raw exhaust.

2. Experimental section

Vehicle testing was performed in the Vehicle Emission Laboratory (VELA) at 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 simulates ambient conditions (temperature range: -10 to $35\,°C$; RH: 50%). Duplicated tests were performed on a chassis dynamometer (inertia range: (454–4500) kg), designed for two and four-wheel drive LDV (two 1.22 m roller benches – Maha GmbH, Germany). The emissions were fed to a Constant Volume Sampler (CVS, Horiba, Japan) using a critical Venturi nozzle to regulate the flow (CVS flow range: 3–30 $m^3\,min^{-1}$). A series of thermocouples monitored the temperature of the oil, cooling water, exhaust, and ambient conditions. A lambda (λ) sensor was connected to the tailpipe to follow the air to fuel ratio.

2.1. Test vehicles

A fleet of ten light duty vehicles were tested (see technical details in Table 1). The fleet comprised Euro 5 or Euro 6 vehicles ((EC) No 692/2008). Three gasoline LDVs, four diesel LDVs, two flex-fuel LDVs and one plug-in electric hybrid LDV, were tested. Notice that flex-fuel vehicles (FFVs) are spark ignition vehicles that can operate with standard gasoline (hereinafter E5, gasoline containing up to 5% vol ethanol) or any ethanol blend. In Europe, FFVs can run on blends of ethanol and gasoline containing 5% ethanol and up to 85% during the summer (also known as E85) or 75% during winter (E75, winter blend). The selected fleet covers a wide range of engine power, displacement, millage and after-treatment systems. Tests were performed over the worldwide harmonized light-duty driving test cycle (WLTC) at $23\,°C$ and also at $-7\,°C$ for most vehicles.

The WLTC (UNECE, Global Technical Regulation, 2016) is a cold-start driving cycle, i.e., the vehicle and its components (oil, coolant, catalyst, etc.) must be at 23 or $-7\,°C$, ±1 °C. For that reason, vehicles were stored inside the climatic cell under the WLTC typical conditions (known as the soaking time) for at least 12 h before being tested. The WLTC, consisting of four phases with different speed distributions (see Fig. 1), 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 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

Table 1
Fleet general features.

Vehicles	Combustion type	EU emission standard	After-treatment	Engine displacement (cm^3)	Engine power (kW)	Odometer (km)
GV1	S.I.	Euro 6	TWC,NSC	1991	155	11,211
GV2	S.I.	Euro 5	TWC	1390	132	38,541
GV3	S.I.	Euro 6	TWC	1242	51	10,523
DV1	C.I.	Euro 6	SCR	2987	140	32,178
DV2	C.I.	Euro 5	DOC	1560	84	16,871
DV3	C.I.	Euro 6	SCR	1997	110	14,365
DV4	C.I.	Euro 6	LNT	1422	55	6229
FV1	FF S.I.	Euro 5	TWC	1596	132	25,098
FV2	FF S.I.	Euro 5	TWC	1600	112	9143
PHV1	H. plug-in S.I.	Euro 6	TWC	2996	330	14,012

S.I. (Spark ignition); C.I. (Compression ignition); FF (Flex-fuel); H. plug-in (Hybrid plug-in); Three-Way Catalyst (TWC); NOx Storage Catalyst (NSC); Selective Catalytic Reduction (SCR); Diesel Oxidation Catalyst (DOC); Lean-NOx Trap (LNT).
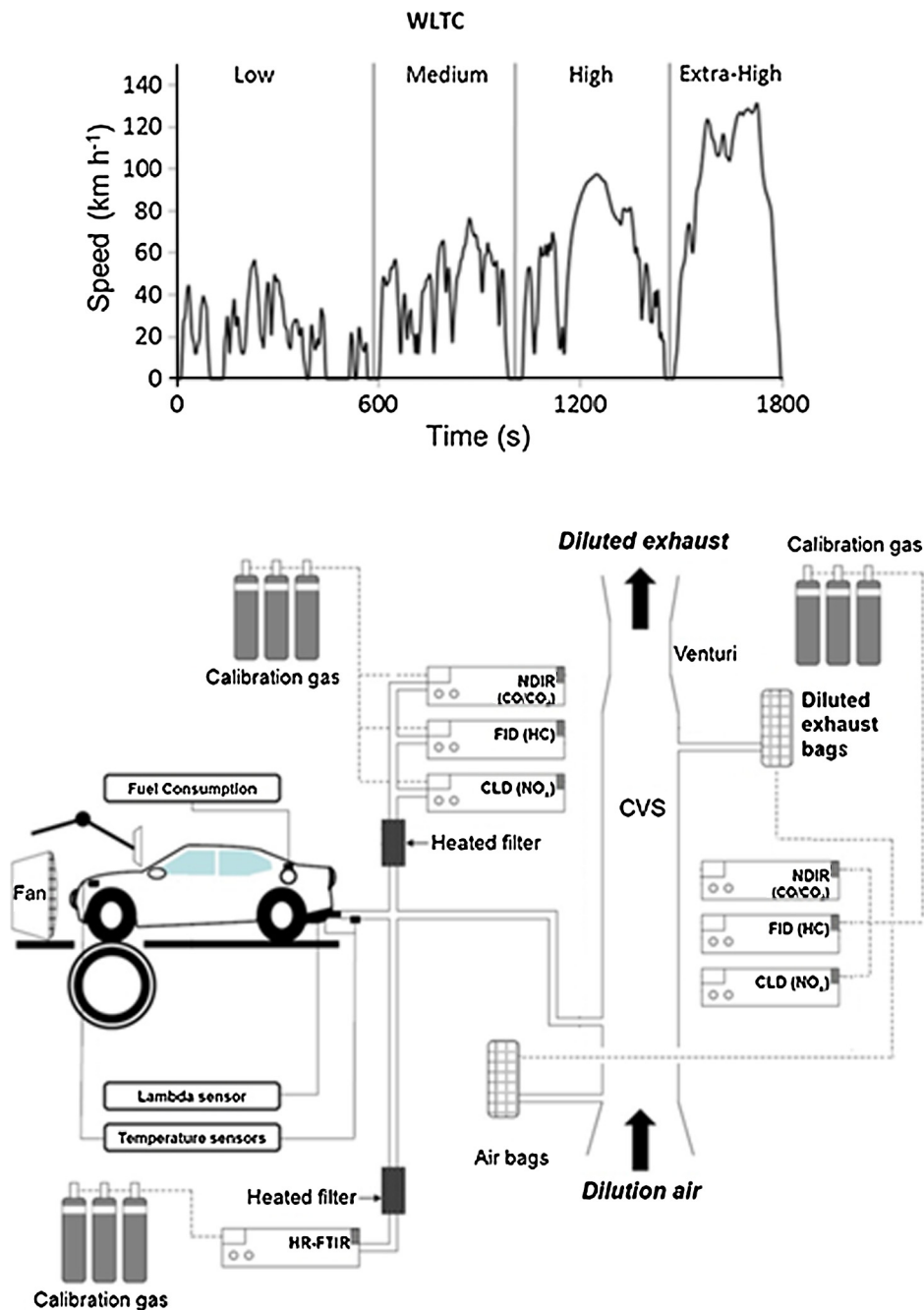
Fig. 1. WLTC (top) and schematic diagram of the experimental setup (bottom).

study pertains to class 3 (power/mass > 34 kW/ton and maximum speed > 120 km/h), which is the highest power and speed class. Fig. 1 illustrates the version WLTC 5.3 of the speed profile applicable for this class of vehicles.

2.2. Analytical instrumentation

The regulated 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 detector (FID; for THC). Gaseous compounds contained in the raw exhaust 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 (Clairotte et al., 2012) therefore, only a brief description is given here. The device consist 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).

The raw exhaust was sampled directly from the tailpipe of the vehicles with a heated PTFE (polytetrafluoroethylene) line and a pumping system (flow: ca. 10 L min^{-1}, T: 191 °C) in order to avoid condensation and/or adsorption of hydrophilic compounds (e.g., ethanol, ammonia). The residence time of the undiluted exhaust gas in the heated line before the FTIR measurement cell was less than 2 s. The ambient pressure during the measurement was 1013 hPa (±20), and the temperature of the gas cell of the FTIR was set to 191 °C. Another set of analysers, i.e., non-dispersive infrared (for CO/CO_2) and chemiluminescence detector (for NOx) were also connected to the tailpipe allowing a time-resolved (at 1 Hz) measurement of these compounds from the raw exhaust. CO, CO_2 and NOx measurements from the previously described analysers were used to synchronize the FTIR signal.

The raw exhaust flow was determined by subtracting the flow of dilution air introduced into the tunnel, measured with a Venturi system, to the total flow of the dilution tunnel, measured by a sonic Venturi (Horiba). Mass flows were derived from the exhaust gas flow rates (m^3 s^{-1}) and from the measured concentration (ppmv). 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 and discussion

3.1. Regulated compounds

The emission factors (mg km^{-1}) of the regulated gases and CO_2 (g km^{-1}) obtained for ten light-duty vehicles tested over the WLTC at 23 or −7 °C are summarized in Tables 2 and 3, respectively. The plug-in hybrid vehicle (PHV1) and spark ignition vehicles (GV1, GV2, FV1 and FV2) presented emissions below Euro 5 and Euro 6 emissions limits, with the exception of GV3 whose CO emissions were about 9 times higher the Euro 6 standard. The diesel vehicles tested, presented NOx emissions 2.6–4.4 times higher than their corresponding NOx Euro 5 or Euro 6 limits. The high NOx emissions may be due to the aggressiveness of the WLTC, which is more representative of real-driving stile, with respect to the New European Driving Cycle (NEDC), which was the cycle used for the type approval of these vehicles but it may also be due to the lack of effectiveness of the after-treatment they were equipped with. Even though DV1 and DV3 were equipped with SCR as DeNOx after-treatment and DV4 was equipped with a LNT, NOx emissions were about 4 times higher than the maximum allowed by the Euro 6 standards when the vehicles were tested over the WLTC at 23 °C. Similar behavior was recently reported by Franco et al. (2014) for a series of Euro 6 diesel vehicles tested on-road (Franco, 2014).

Higher emissions were observed when vehicles were tested at −7 °C. The temperature effect was observed to be more pronounced on the spark ignition vehicles, particularly for PHV1 and also GV1 and GV3. Cold-start operation of spark ignition vehicles is associated with rich combustion to avoid misfires due to condensation effects on the cylinder. The enrichment of the air/fuel mixture during cold-start operation results in incomplete fuel combustion, leading to higher CO and hydrocarbon emissions during this period (Dardiotis et al., 2013). This effect is more pronounced at lower temperatures. Moreover, since TWC require a certain temperature (typically above 300 °C) to work at full efficiency, emissions are significantly higher until the catalyst reaches the optimal working conditions (Weilenmann et al., 2009). At lower ambient temperatures, the engine and catalyst take longer to warmup, which results in higher emissions. Alvarez et al. suggested that the influence of low ambient temperatures on regulated emissions from hybrid vehicles is similar to that on spark ignition vehicles (Alvarez and Weilenmann, 2012). Moreover, at low temperatures, internal combustion engine and after-treatment performance

Table 2
Average emission factors (mg km^{-1}) for the regulated gases and CO_2 (g km^{-1}) over the WLTC at 23 °C. In brackets maximum semi-dispersion of the two tests.

Vehicles	THC	NMHC	CO	NOx	THC + NOx	CO_2
FV1 E5	89(±18)	83(±18)	394(±0)	62(±9)		152(±1)
GV1	12(±1)	8(±1)	267(±9)	16(±1)		160(±0)
GV2	33(±11)	28(±11)	306(±32)	21(±4)		137(±0)
GV3	42(±1)	38(±1)	8681(±200)	17(±1)		215(±1)
DV1	6(±0)	2(±0)	222(±5)	225(±14)	231(±15)	328(±0)
DV2	9(±4)	7(±4)	292(±27)	470(±35)	479(±31)	125(±1)
DV3	3.0(±0.1)	1.8(±0.1)	69(±2)	352(±1)	355(±1)	160.2(±0.1)
DV4	12.4(±0.2)	2.1(±0.7)	34.9(±0.6)	306(±15)	318(±15)	146.3(±0.1)
FV1 E85/E75	37(±5)	26(±5)	401(±31)	28(±5)		141(±2)
FV2 E85	38(±1)	23(±1)	365(±54)	22(±6)		136(±1)
PHV1	67(±2)	61(±2)	185(±4)	48(±3)		76(±1)

Euro 5–6 spark ignition emission limits mg km^{-1}: THC = 100; NMHC = 68; CO = 1000; NOx = 60.
Euro 5 compression ignition emission limits mg km^{-1}. THC + NOx = 230; CO = 500; NOx = 180; Euro 6 compression ignition emission limits mg km^{-1}. THC + NOx = 170; CO = 500; NOx = 80.

Table 3

Average emission factors (mg km^{-1}) for the regulated gases and CO_2 (g km^{-1}) over the WLTC at −7 °C. In brackets maximum semi-dispersion of the two tests. GV2, DV2 and FV2 were not tested at −7 °C.

Vehicles	THC	NMHC	CO	NOx	THC + NOx	CO_2
FV1 E5	136(±1)	123(±1)	932(±59)	76(±13)		169(±0)
GV1	134(±2)	120(±1)	1107(±52)	79(±15)		163(±1)
GV2	–	–	–	–		–
GV3	216(±1)	201(±1)	15,237(±50)	13(±2)		231(±1)
DV1	7(±0)	4(±0)	281(±4)	771(±11)	778(±14)	372(±2)
DV2	–	–	–	–	–	–
DV3	4(±1)	3(±1)	180(±60)	862(±14)	866(±16)	200(±9)
DV4	17.5(±0.8)	4(±2)	45.6(±0.6)	487(±15)	504(±15)	175(±3)
FV1 E85/E75	163(±6)	123(±5)	1183(±242)	27(±1)		169(±2)
FV2 E85	–	–	–	–		–
PHV1	216(±0)	201(±0)	15,237(±0)	13(±0)		231(±0)

Euro 5–6 spark ignition emission limits mg km^{-1}: THC = 100; NMHC = 68; CO = 1000; NOx = 60.
Euro 5 compression ignition emission limits mg km^{-1}. THC + NOx = 230; CO = 500; NOx = 180; Euro 6 compression ignition emission limits mg km^{-1}. THC + NOx = 170; CO = 500; NOx = 80.

may be affected by the presence of an electrical motor and an energy storage system that supply the needed energy during the low regime of the vehicle, delaying and/or modifying the vehicle cold-start. In fact, PHV1 run on pure electric mode for most part of the WLTC at 23 °C, whereas at −7 °C, they used the internal combustion engine as much as the electric motor, resulting in much higher emissions (see Fig. 2). The large differences showed by GV1, equipped with NSC system, may be related to the NSC, which remained deactivated during the warming-up period (see below). For diesel vehicles the major effect was observed on NOx emissions, which resulted to be 1.6–3.4 times higher at −7 °C than at 23 °C.

As of today, CO_2 emissions have not been regulated by EU legislation for type approval emission tests. However, car manufacturers will have to ensure that their entire light duty vehicle fleet does not emit more than an average 95 g km^{-1} by 2020 (European Parliament and of the Council of the European Union, 2014). Vehicles emitted from 76 g km^{-1} (PHV1) and up to 328 g km^{-1} (DV1) of CO_2. With the exception of GV1, which presented similar CO_2 emissions at both temperatures, and PHV1 whose CO_2 emissions were 3 times higher at −7 °C than at 23 °C, tested vehicles emitted about 10–20% more CO_2 when tested at −7 °C.
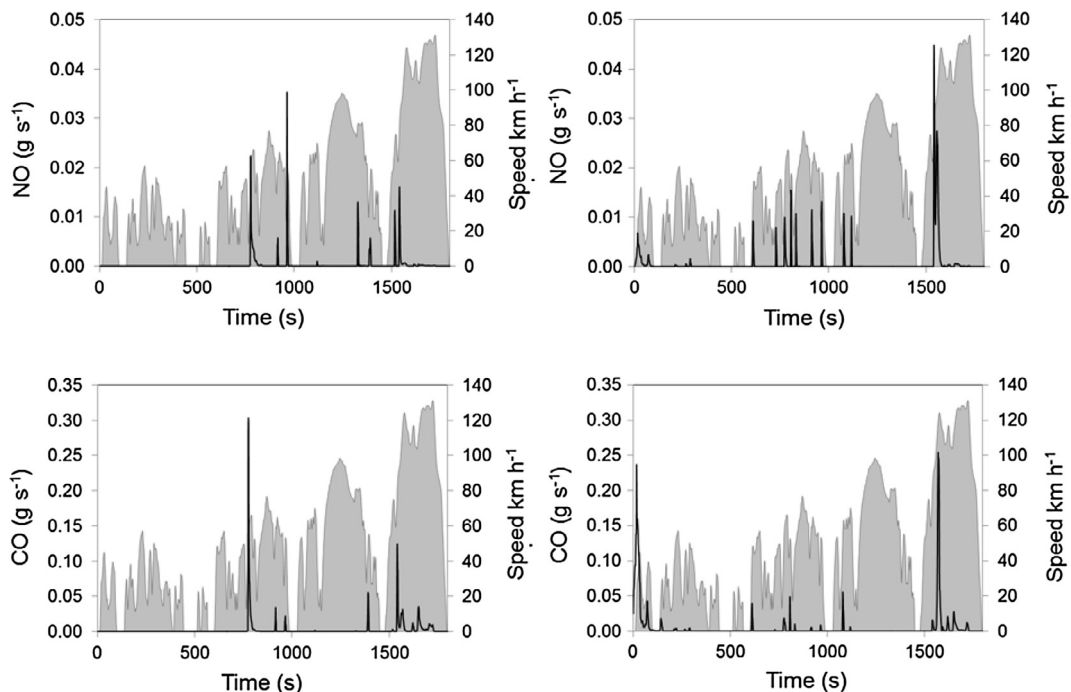

Fig. 2. PHV1 emission rates (g s^{-1}) of NO(top) and CO (bottom) over the WLTC (grey) at 23 °C (left) and −7 °C (right).

3.2 NH$_3$ and HNCO formation and emissions

Fig. 3 illustrates NH$_3$ and HNCO emission factors obtained over the WLTC at 23 and −7 °C. Table 4 summarizes average NH$_3$ and HNCO emission factors relative to the WLTC, as well as emissions factors relative to the first phase of the cycle, which represents the urban share of the cycle, lasting 3.1 km.

The average NH$_3$ and HNCO emission factors varied, respectively, from 7 to 40.5 mg km^{-1} and 0.1–21.8 mg km^{-1} at 23 °C, and from 3.0–54.6 mg km^{-1} and 0.4–39.8 mg km^{-1} at −7 °C. Same as for the regulated compounds, emissions of NH$_3$ and HNCO were higher at −7 °C. GV1 resulted in the highest NH$_3$ emissions and GV3 the highest HNCO emissions, at the two studied temperatures (see Table 4). DV1 and DV3, both equipped with SCR, presented the lowest HNCO emissions (DV1 0.1 and 0.4 mg km^{-1}; DV2 0.4 and 0.1 mg km^{-1}) at 23 and −7 °C, respectively. The other vehicles resulted in HNCO emission factors going from 0.4 to 2.4 mg km^{-1} at 23 °C and from 0.9–9 mg km^{-1} at −7 °C (see Table 4). Therefore, contrary to the assumption of negligible HNCO emissions from LDVs (Dümpelmann et al., 1995; Chambers et al., 2001; Cant et al., 2004, 2005), substantial HNCO emissions can be produced by gasoline, diesel and also hybrid LDVs (Brady et al. (2014) and Wentzell et al. (2013)). Cant et al. investigated the emissions from gasoline LDVs measuring the formation HNCO via reaction of NO, CO, and either molecular hydrogen (H$_2$) or NH$_3$ over metal catalysts using FTIR (Cant et al., 2004, 2005). In those studies, they set a 20 ppmv upper limit on the concentration of HNCO emitted from LDGVs, as it was the detection limit for the FTIR used. In the present study we have measured a 0.3 ppmv and 5 ppmv limit of detection for NH$_3$ and HNCO, respectively, equivalent of 3σ standard deviation of the measured background.

The fleet median emissions of NH$_3$ during the phase 1 of the cycle were 12 mg km^{-1} and 23 mg km^{-1} at 23 and −7 °C, respectively. In the case of HNCO, the fleet median emissions during the phase 1 were 7 mg km^{-1} and 27 mg km^{-1} at 23 and −7 °C, respectively, about 5 higher than the WLTC median.

As explained in the Introduction section, NH$_3$ and HNCO, can be formed over the TWC, NSC, LTN and diesel oxidation catalyst (DOC), through a series of reactions that involve NO, CO and H$_2$. In these systems, NH$_3$ can also be formed by the hydrolysis of HNCO (see reaction 4), and HNCO could be formed by reaction of NH$_3$ with NO and CO at higher temperatures regimes (Cant et al., 2004). Catalyst temperature is the key parameter that drives the reaction towards the formation of either NH$_3$ or HNCO (see reactions 1–3). Thus, opposite to what observed by Brady et al. (Brady et al., 2014) but in agreement with what suggested by Dümpelmann et al. (1995), HNCO is mainly formed, and emitted, at the beginning of the cycle, when the catalyst is still cold. Emissions increased until catalyst light-off at which point the formation of HNCO stops as a result of limited availability of the precursors, CO and NO, over the catalyst (Dümpelmann et al., 1995). HNCO emissions are accompanied by
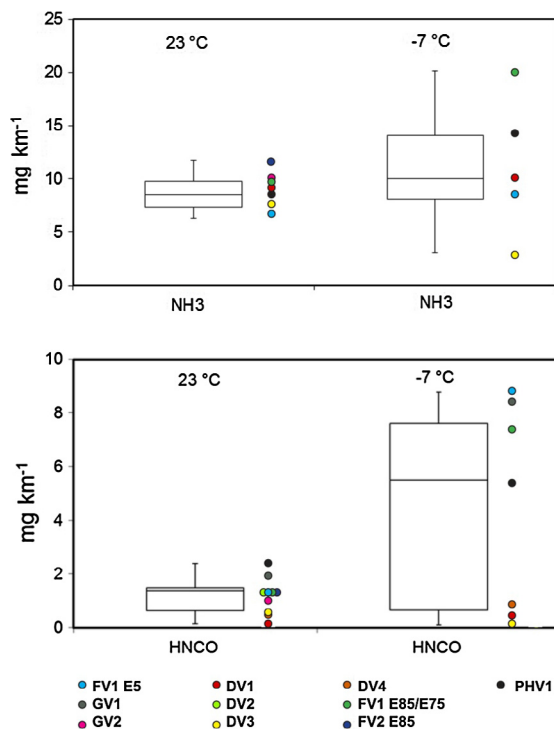

Fig. 3. EFs plotted as box-and-whiskers (median line; 25th and 75th percentile, box; max and min EFs, whiskers) of NH$_3$ (top) and HNCO (bottom) at 23 and − 7 °C. Coloured dots shown next to the box-and-whiskers are the average EFs from each vehicle. Outliers, GV1 and GV3 for NH$_3$ and GV3 for HNCO, were excluded.

Table 4

Ammonia (NH_3) and Isocyanic acid (HNCO) average emission factors (mg km^{-1}) over the WLTC (bold) at 23 and −7 °C. n.d. not detected. In brackets maximum semi-dispersion of the two tests. GV2, DV2 and FV2 were not tested at −7 °C.

	NH_3				HNCO			
	23 °C		−7 °C		23 °C		−7 °C	
	WLTC	Urban	WLTC	Urban	WLTC	Urban	WLTC	Urban
FV1 E5	**6.3**(±0.2)	19(±4)	**8**(±6)	39(±13)	**1.4**(±0)	10.1(±0)	**9**(±6)	40(±11)
GV1	**40.5**(±0)	8.8(±0)	**50**(±1)	165(±39)	**1.9**(±0)	7.2(±0)	**8.5**(±0.8)	48(±3)
GV2	**10.0**(±0)	16(±2)	**–**	–	**1.0**(±0.1)	7(±1)	**–**	–
GV3	**34.1**(±0)	8.8(±0.8)	**55** (±5)	21 (±2)	**22**(±2)	15(±2)	**40**(±4)	57 (±6)
DV1	**8.5**(±0.4)	17(±1)	**10**(±1)	24(±8)	**0.1**(±0)	0.2(±0.2)	**0.4**(±0)	2.5(±0.3)
DV2	**n.d.**	n.d.	**–**	–	**1.4**(±0.6)	8(±3)	**–**	–
DV3	**7**(±2)	4(±2)	**3.0**(±0.6)	3.6(±0.1)	**0.5**(±0.1)	1.6(±0.5)	**0.1**(±0)	0.5(±0.1)
DV4	**n.d.**	n.d.	**n.d.**	n.d.	**0.4**(±0.0)	0.7(±0.0)	**0.9**(±0.2)	1.3(±0.7)
FV1 E85/E75	**9.5**(±0.6)	26(±1)	**20**(±2)	36(±4)	**1.4**(±0.1)	9.9(±0.1)	**7**(±1)	46(±7)
FV2 E85	**12**(±2)	18(±4)	**–**	–	**1.4**(±0.3)	7.8(±0.1)	**–**	–
PHV1	**7.8**(±0)	n.d.	**14.1**(±0.5)	1.2(±0.5)	**2.4**(±0)	n.d	**5.5**(±0.5)	13(±1)

simultaneous CO emissions, consistent with the vehicles entering into fuel rich regime, as a result of a sharp acceleration (see Fig. S1 of the supplementary material).

In the case of TWC NH_3 formation is triggered at catalyst light-off, and last for the whole experiment (see Fig. 4). Once catalyst light-off the formation of NH_3 is favored over the formation of HNCO due to the high temperature of the catalyst (see Fig. S2). NH_3 formation over the catalyst is enhanced at low air/fuel ratios where conditions are reductive and higher concentrations of CO and H_2 are present (see reaction 1 and 2) (Whittington et al., 1995; Czerwinski et al., 2010). These are the typical conditions during the acceleration and are the main reason why NH_3 emissions peak during the acceleration events (see Fig. 4). A good example is found with GV3 were high HNCO and NH_3 emissions were observed resulting from frequent and long-lasting rich combustion strategy ($\lambda < 1$) used in this vehicle (see Fig. S1 in the supplementary material).

No NH_3 emissions were observed for DV2 (diesel, equipped with DOC). This may be due to a catalyst not reaching the temperature needed for NH_3 to be formed, and/or low emission of hydrocarbons, which are essential for H_2 production and therefore the NH_3 formation. Brady et al. suggested that the higher CO emissions from gasoline vehicles, compared to diesel vehicles, should lead to higher HNCO emissions when driving under similar conditions, assuming the converters are of a comparable size and oxide wash-coat composition. We can observe that DV2, which resulted in a similar CO emission factor, also presented a similar HNCO emission factor, ∼1.4, to the gasoline vehicles.

At 23 °C, GV1 showed emission profiles that were substantially different than the other conventional gasoline vehicles, i.e., GV2 and FV1 (Fig. 4), because it uses an after-treatment set up composed by a TWC and NSC, which is more complex than what is commonly used by spark ignition vehicles, i.e., only TWC. The final goal of the NSC system is to reduce NOx into N_2. This reaction takes place on a catalytic converter during the phases when the engine runs on a rich air/fuel mixture that provides the CO and hydrocarbons needed for the reduction of nitrogen oxides. These are the same conditions that lead to NH_3 formation over the TWC surface. GV1 showed the highest NH_3 emission factors of the studied fleet at the two studied temperatures, up to 3.2 and 6.3 times higher than the other vehicles at 23 and −7 °C, respectively. At 23 °C, the highest NH_3 concentrations were measured during the regeneration of the NSC system. At −7 °C, the NH_3, CO and NO emission profiles were similar to those usually observed for the gasoline and the flexi-fuel vehicles, i.e., cold-start emissions of CO, followed by a diminution of the CO emissions and rise up of the NH_3 emissions due to catalyst light-off. Once the system warmed up the emission profiles were similar to those at 23 °C (see Figs. 4 and S3 supplementary material). This suggests that the NSC remained deactivated at such low temperatures and until the vehicle reached optimal working temperature.

DV4, diesel vehicle equipped with LNT, was expected to present a similar emission pattern to that shown by GV1, gasoline equipped with NSC, as the principle of the two after-treatment is alike (see above). However, contrary to GV1, NOx were emitted along the whole cycle, and no regeneration, accompanied with CO and NH_3 emissions, was observed (see Fig. S4 in the supplementary material). These, together with the very high NOx emissions observed, suggest a malfunctioning of the LNT system present in the DV4. For that reason, hereinafter, DV4 will be considered as it was a conventional compression ignition vehicle.

Due to the working principle of its after-treatment system (SCR), DV1 and DV3 also presented different emission profiles than the other studied vehicles (see Fig. 5). In order to reduce NOx emissions, the system (SCR) injects aqueous urea solution into the exhaust NH_3 is obtained by the reduction of the urea on the catalyst surface. The over-doping of urea, low temperatures in the system and/or the catalyst degradation may lead to NH_3 and/or HNCO emissions. Constant emissions of NH_3 were registered during the tests, which in the case of DV3 increased in the phase 3 (i.e., high phase), and resulted in emission factors equal to 8.5 and 10 mg km^{-1} for DV1 (at 23 and −7 °C, respectively) and 7 and 3 mg km^{-1} for DV3 (at 23 and −7 °C, respectively). The NH_3 emissions factors resulting from these two vehicles were lower compared with those from spark ignition vehicles. Still, it has to be noticed that NH_3, together with the catalyst, is used to reduce NOx emissions, and NOx emissions from these vehicles were higher than Euro 6 NOx emissions standards. Hence, further use of urea (thus, NH_3) may be needed in order to reduce the NOx emissions, which at the same time may lead to higher NH_3 emissions.
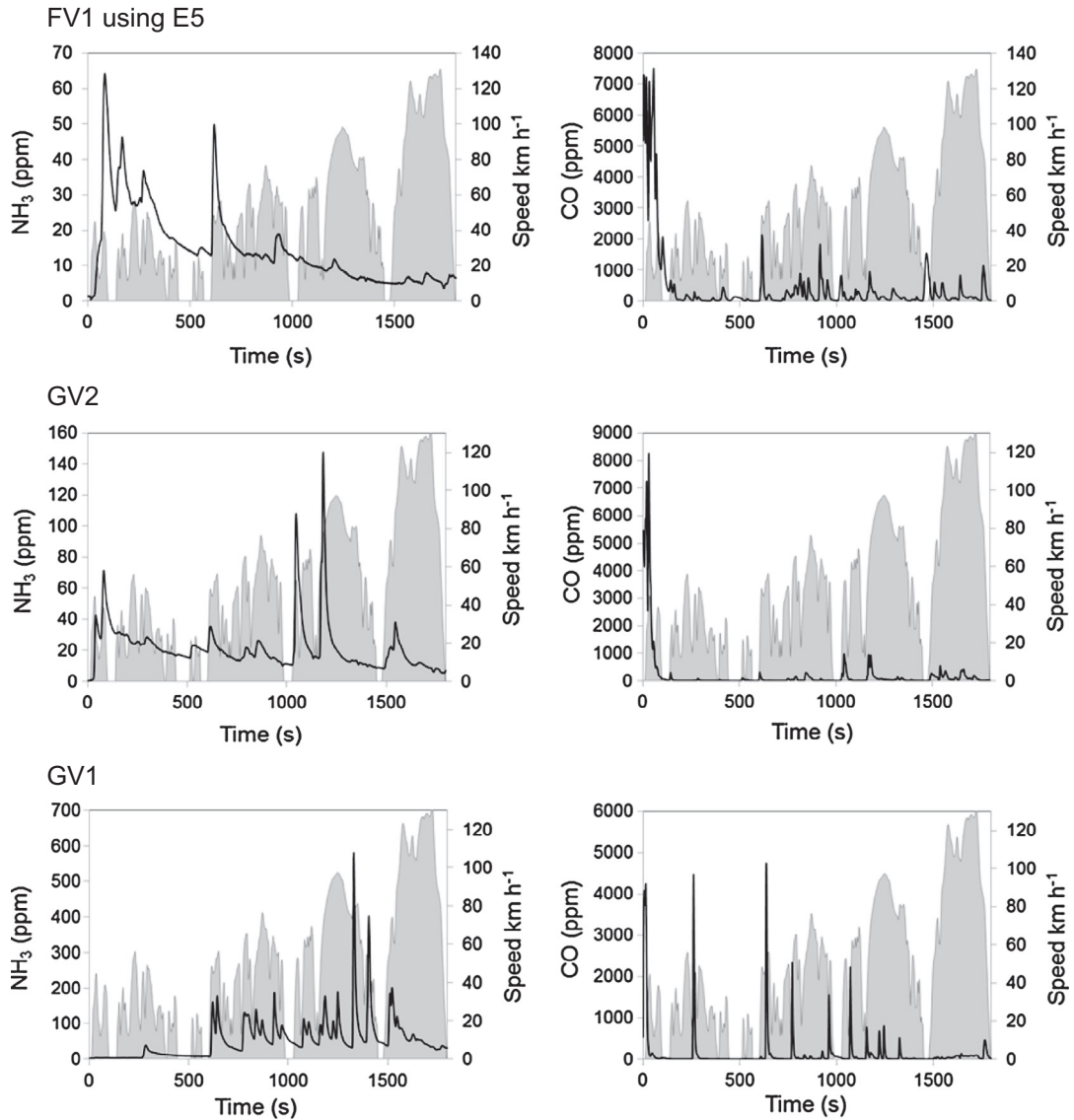
FV1 using E5

GV2

GV1

Fig. 4. Time-resolved concentration (ppm) of NH$_3$ and CO for the vehicles FV1 using E5 blend, GV2 and GV1 over the WLTC (grey) at 23 °C.
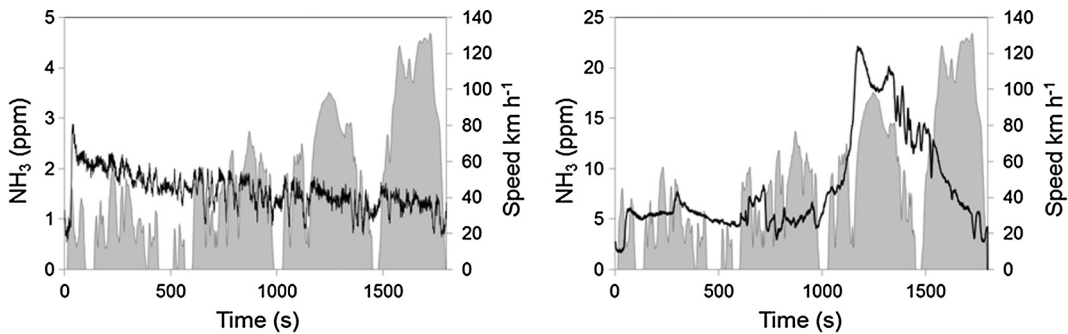

Fig. 5. Time-resolved concentration (ppm) of NH$_3$ from DV1 (left) and DV3 (right) over the WLTC (grey) at 23 °C.

Low HNCO emissions were observed for DV1 and DV3 at both temperatures (the lowest of the studied fleet). These could be related to the high H$_2$O level expected in the catalyst when the urea, as aqueous solution, is injected. The presence of H$_2$O would lead to the hydrolysis of HNCO into NH$_3$ (see reaction 4).

The fleet median NH_3 emission factors were 10 mg km^{-1} at 23 °C and 21 mg km^{-1} at −7 °C. These results do not take into account DV2 and DV4, which are the diesel LDVs without SCR. The obtained emissions factors over the WLTC, which was designed to be representative of real world driving conditions based on real world vehicle trips from several countries, are in-line with results previously reported for Euro 5 vehicles (13 and 23 mg km^{-1} at 22 and −7 °C) tested over the less dynamic NEDC (Suarez-Bertoa et al., 2014). Moeckli et al. reported 15(±4) mg km^{-1} of NH_3 been emitted in the Gobrist tunnel, Switzerland in 1996 (Moeckli et al., 1996). Durbin et al. reported NH_3 emissions ranging between 9 and 13 mg km^{-1} for a series of Super Ultra-Low Emission Vehicles (SULEV), Ultra-Low Emission Vehicles (ULEV) and Low Emission Vehicles (LEV) tested over the Federal Test Procedure (FTP) and emission rates approximately 5 times higher over the more aggressive US06 cycle (Durbin et al., 2004). Huai et al. showed NH_3 emissions to be 5.8 mg km^{-1} for SULEV, 13.5 mg km^{-1} for ULEV and 21.7 mg km^{-1} for LEV (Huai et al., 2003). Heeb et al. reported NH_3 emission factors of 26(±12) and 10(±7) mg km^{-1} from a series of Euro 3 and Euro 4 gasoline vehicles, respectively (Heeb et al., 2006; Heeb et al., 2008). All these studies date several decades back, suggesting that, even though emissions of CO and NOx (NH_3 precursors) have been reduced over the years with more stringent limits, emissions of NH_3, which are not regulated, have remained similar.

The fleet median HNCO emission factors were 1.4 mg km^{-1} at 23 °C and 6 mg km^{-1} at −7 °C, or in mass kg$_{fuel}^{-1}$ units, 30 mg kg$_{fuel}^{-1}$ at 23 °C and 140 mg kg$_{fuel}^{-1}$ at −7 °C. Brady et al. reported an average HNCO emission factor for eight gasoline LDVs of 0.91 ± 0.58 mg kg$_{fuel}^{-1}$, one to two orders of magnitude lower than the average emission factor obtained for the studied gasoline LDVs at 23 °C (93 mg kg$_{fuel}^{-1}$ for all studied gasoline vehicles, 29 mg kg$_{fuel}^{-1}$, if GV3 is not taken into account). Wentzell et al. reported HNCO emissions factors, for a single light-duty diesel-powered engine, ranging between 0.69 and 3.96 mg kg$_{fuel}^{-1}$ (Wentzell et al., 2013), which are one order magnitude lower than what obtained for DV2 (37 mg kg$_{fuel}^{-1}$). Wentzell et al. and Brady et al., measured HNCO concentration, after dilution of the engine/vehicle exhaust, whereas in the present study measurements were done directly at the tailpipe (Wentzell et al., 2013; Brady et al., 2014). These dilutions and delays on the measurements, could have led to hydrolysis of the HNCO into NH_3 or to wall artifacts, such as deposition or adsorption, causing a diminution of the HNCO concentration, resulting in an underestimation of the emissions.

While the maximum allowed concentration of HNCO at the workplace is 20 µg m^{-3} [SUVA, 2011], the median HNCO emissions for the studied fleet corresponded to mean exhaust concentrations of 2200 and 5278 µg m^{-3} at 23 and −7 °C. Therefore, during the cold-start of a vehicle, the maximum allowed concentration of HNCO may be largely exceeded in the proximity of the vehicle or if vehicle ignition takes place in poorly ventilated environment.

4. Conclusions

Vehicles are considered to be one of the main emission sources of ammonia (NH_3) and isocyanic acid (HNCO) in urban areas. For that reason, emissions from a series of Euro 5 and Euro 6 LDVs, including spark ignition (gasoline and flex-fuel), compression ignition (diesel) and a plug-in electric hybrid, were investigated at 23 and −7 °C over the WLTC.

During the tests it was observed that HNCO was mainly formed, and emitted, at the beginning of the cycle, when the catalyst is still cold. NH_3 emissions, on the other hand, were associated to high catalyst temperatures.

The median HNCO emissions for the studied fleet over the WLTC were 1.4 mg km^{-1} (33 mg h^{-1}) at 23 °C and 6 mg km^{-1} (95 mg h^{-1}) at −7 °C. HNCO emissions factors were 5 times larger when only the urban part (phase 1) of the WLTC, which last about 10 min and is 3.1 km long, is considered. DV1 and DV3, both equipped with SCR, presented the lowest HNCO emissions (DV1 0.1 and 0.4 mg km^{-1}; DV2 0.4 and 0.1 mg km^{-1}) at 23 and −7 °C, respectively.

The fleet median NH_3 emission factors (without taking into account DV2 and DV4, which are diesel LDVs lacking of SCR) were 10 mg km^{-1} and 21 mg km^{-1} at 23 and −7 °C, respectively. Up to now, NH_3 emissions inventories only considered gasoline LDVs as possible source, as diesel vehicles did not emit NH_3. However, it has been shown here that a diesel LDV equipped with SCR can present NH_3 emission factors as high as a gasoline LDVs at both, 23 and −7 °C over the WLTC. Therefore, with the introduction in the market of this DeNOx technology, the fleet NH_3 emissions will be further increased. Hence, it should be considered to include NH_3 emissions from diesel vehicles in the inventories. At the same time, vehicles equipped with SCR and LNT systems resulted in NOx emissions 4 times higher than Euro 6 limits.

It has been observed that the NH_3 present in highly urbanized areas can react with nitric acid, resulting from NOx emission and subsequent oxidation, to form ammonium nitrate (NH_4NO_3), which accounts for a large fraction of the $PM_{2.5}$ mass (Kim et al., 2000; Phan et al. 2013). Therefore, staying to the obtained emission factors, very large amount of NH_3 are being emitted into urbanized areas every day, which would lead to particle formation and deterioration of the air quality. Moreover, since NH_3 emissions are not regulated for LDV, the lambda control strategy is focused on comply with the NOx and CO standards. Hence, even though TWC, NSC and SCR are indeed effective systems to reduce the nitrogen oxides, they also produce important amounts of the byproducts NH_3 and/or HNCO.

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.trd.2016.08.039.

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