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Ammonia exhaust emissions from spark ignition vehicles over the New European Driving Cycle

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HIGHLIGHTS

- All studied vehicles emitted NH_3 when tested over the NEDC at 22 and −7 °C.
- NH_3 emissions from Euro 5–6 vehicles are similar to those reported a decade ago.
- Vehicular emissions of NH_3 and CO presented good correlation.
- Emission of NH_3 depends on ambient temperature and NO_x emission control.

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ABSTRACT

A study aiming to measure ammonia emissions from light duty vehicles has been performed in the Vehicle Emission Laboratory at the European Commission Joint Research Centre, Ispra, Italy. Ammonia, known for being toxic and dangerous for the environment, also contributes to the formation of particulate matter that has been related with adverse health and environmental effects.

Nine modern light duty vehicles tested over the New European Driving Cycle showed that ammonia emissions are considerable for gasoline and ethanol flexi-fuel vehicles and also for one diesel vehicle equipped with a selective catalytic reduction system, ranging from 4 mg/km to 70 mg/km. Real-time ammonia emission profiles were monitored at the tailpipe by a High Resolution Fourier Transform Infrared spectrometer during tests at 22 and/or −7 °C. Ammonia emissions are thoroughly discussed and compared to those of its precursors, CO and NO, and other regulated compounds.

1. Introduction

The World Health Organisation's International Agency for Research on Cancer (IARC) has recently announced that air pollution as a whole, as well as particle matter that makes up part of air pollution, causes cancer (IARC.fr).

Ammonia (NH_3) is a toxic compound and a precursor in the formation of atmospheric secondary aerosols (Behera and Sharma, 2010). The particulate matter that is formed, namely ammonium nitrate and ammonium sulphate, is also associated with other adverse health effects (Pope et al., 2002). Kim et al. showed that ammonium can account for as much as 14–17% of the total mass of $PM_{2.5}$ in the South Coast Air Basin (Kim et al., 2000). It has also been reported that for some European cities 40% of the total $PM_{2.5}$ is formed by secondary inorganic compounds, namely ammonium, nitrate, and sulphate (Sillanpää et al., 2006). The formed aerosols not only impoverish the urban air quality but they also have an impact on climate due to their capability to scatter solar radiation back to space (Forster et al., 2007; Brasseur et al., 1999) and because they can act as cloud condensation nuclei, modifying cloud properties, producing an increase of droplet number concentration and a decrease of droplet sizes as well (Twomey, 1991). 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., 2008; Bouwman et al., 2002; Erisman et al., 2003). Exceedances of the critical levels for NH_3 were recorded at roadside locations in the UK (Gadsdon and Power, 2009; Cape et al., 2004).

Although gas phase NH_3 is generally associated with rural environments, it has been observed that in certain urban areas the NH_3 levels are comparable to what is typically observed in the rural areas (Livingston et al., 2009). Vehicles with internal combustion engine are considered to be the main source of NH_3 in the urban

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environment (Livingston et al., 2009; Battye et al., 2003) and vehicle-related NH_3 is considered to be mainly produced in the widely used Three-Way Catalyst (TWC) of gasoline light duty vehicles (LDV). In the TWC NH_3 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 (1) (Bradow and Stump, 1977; Barbier and Duprez, 1994):

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (1)$$

$$2NO + 2CO + 3H_2 \rightarrow 2NH_3 + 2CO_2 \quad (2a)$$

$$2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O \quad (2b)$$

Therefore, it is crucial to quantify the NH_3 emissions from vehicles exhaust in order to evaluate their impact on the air quality and develop effective control strategies. The National Emission Ceilings Directive 2001/81/EC (NECD), the Gothenburg Protocol under the United Nations Convention on Long-Range Transboundary Air Pollution (LRTAP Convention) (UNECE 1999) and the IPPC Directive (2008/1/EC) aimed at reducing the emissions of several compounds, including NH_3. Over the past two decades sectors like agriculture and waste management have reduced their NH_3 emissions by 29 and 24%, respectively. Road transport emissions however, have increased by 378% (Ammonia (NH_3) emissions (APE 003) – Assessment published Dec 2012) (Technical report No 6/2013). Furthermore, while CO and NO_x emissions from LDV are controlled by the European legislation, NH_3 emissions have not been regulated yet. According to the National Emission Inventory (NEI) done by the US Environmental Protection Agency (EPA) in 2011, NH_3 emission from mobile on-road gasoline LDVs have decreased by 4% since 2005 (Reis et al., 2009; EPA, 2011a,b inventory). However, they still are the third largest NH_3 emission source of the US, after agriculture and fires, and although they account for 3% of the total NH_3 emissions, previous studies have pointed out that vehicular contribution can reach about 18% in the California South Coast Air Basin, and more than 70% in Charlotte and Fresno during winter (Chitjian et al., 2000; Battye et al., 2003).

A number of studies have shown that vehicular NH_3 emissions may vary considerable, depend on the vehicle and that they are also related to different features such as: driving style (Livingston et al., 2009), vehicle specific power (Huai et al., 2003, 2005) and catalyst aging (Durbin et al., 2002). In the literature we can find NH_3 emissions reported from highway tunnels (Fraser and Cass, 1998; Kean et al., 2000; Emmenegger et al., 2004), air quality urban environments (Perrino et al., 2002; Moya et al., 2004), chassis dynamometers (Durbin et al., 2002; Huai et al., 2003, 2005; Heeb et al., 2006, 2008), remote sensing (Baum et al., 2001) and chassis vehicle (Herndon et al., 2005).

The use of the DeNO$_x$ selective catalytic reduction system (SCR) in heavy duty diesel vehicles rose up the concern of NH_3 being injected into the atmosphere. The SCR is an after-treatment system whose goal is to reduce NO_x 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. The over-doping of urea, low temperatures in the system and/or the catalyst degradation may lead to NH_3 emissions. Eventually, that concern led to the introduction of an ammonia emission limit for heavy duty vehicles (HDV) in the Euro VI standards ((EC) No 582/2011). However, the NH_3 produced, and emitted, by other in-use technologies have been neglected. Furthermore, new diesel LDV have started using SCR technologies to meet the upcoming Euro 6 standards, but no limits on NH_3 emissions has been enforced for this vehicle category yet.

The present study aims to better quantify the NH_3 emissions from spark ignition Euro 5 and Euro 6 vehicles at 22 and −7 °C by measuring it directly at the raw exhaust with a High Resolution Fourier Transform Infrared spectrometer (FTIR) at 1 Hz. We monitored NH_3 (and several other compounds) at real-time over the New European Driving Cycle (NEDC), which is currently used for type approval of LDV in Europe. One light duty diesel vehicle equipped with and SRC was also study to set a bar for the comparison of the NH_3 exhaust emitted by spark and compressed ignition vehicles.

2. Experimental section

The study was conducted 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 the typical ambient conditions in Europe (temperature range: −10–35 °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). A series of thermocouples monitored the temperature of the oil, cooling water, exhaust, and ambient conditions. A lambda sensor was connected to the tailpipe to follow the air to fuel ratio.

2.1. Test vehicles and fuels

One flexi-fuel LDV (Car 1), seven gasoline LDVs (Car 2–8), and one diesel LDV (Car 9) were tested (see technical details in Table 1). Car 2 and Car 7 were equipped with a multiport injection system, the other vehicles were equipped with a direct injection engine. Gasoline and flexi-fuel vehicles were equipped with a TWC. Most vehicles used a turbo charged air intake system. Car 2 and Car 4 used the naturally aspired air intake system. Car 8 was equipped with a NO_x storage converter (NSC). Car 9 was equipped with a SCR system, a diesel oxidation catalyst (DOC) and a diesel particle filter (DPF) system. Car 1–7 complied with Euro 5 spark ignition EU emission standards, Car 8 with Euro 6 spark ignition emission limits and Car 9 with Euro 6 compression ignition emission limits ((EC) No 692/2008). The selected fleet features a wide range of engine power, displacement, mileage and weight, typical of the European fleet. The New European Driving Cycle (NEDC) was used. The NEDC is a cold-start driving cycle (i.e., performed with a cold engine at the beginning of the test cycle). It includes a first urban phase of 780 s (UDC) followed by an extra-urban phase of 400 s (EUDC). The tests were conducted at test cell temperature of 22 and −7 °C, and at 50 ± 2% RH. The temperature refers not only to the cell temperature but also to the vehicle's oil temperature, ±1 °C, at the beginning of each test (see Fig. 1). Vehicles were kept inside the climatic cell under the NEDC typical conditions (known as soaking time) for at least 12 h. A certified reference fuel E5 (5% of maximum ethanol content) was used in the spark ignition vehicles. The flexi-fuel vehicle was also fuelled with summer E85 and winter E75 blends (85 and 75% ethanol content, respectively) when tested at 22 and −7 °C, respectively. A certified reference fuel B5 was used for the diesel vehicle. A detailed description of the fuels characteristics is available in the Table 1 of the supplementary information (SI).

2.2. Analytical instrumentation

The vehicle's regulated emissions were measured in conformity with directive 70/220/EEC and its following amendments, with an

Table 1
Fleet general features.

Denomination	Car 1	Car 2	Car 3	Car 4	Car 5	Car 6	Car 7	Car 8	Car 9
Combustion type	Flex-fuel gasoline-EtOH	Gasoline	Gasoline	Gasoline	Gasoline	Gasoline	Gasoline	Gasoline	Diesel
EU emission standard	Euro 5a	Euro 5a	Euro 5a	Euro 5a	Euro 5a	Euro 5a	Euro 5	Euro 6	Euro 6
After-treatment	TWC	TWC	TWC	TWC	TWC	TWC	TWC	TWC, NSC	SCR, DPF, DOC
Fuel	E5, E85 and E75	E5	E5	E5	E5	E5	E5	E5	B5
Fuel system	DI	MPI	GDI	GDI	GDI	GDI	MPI	GDI	CDI
Engine displacement (cm^3)	1596	1242	1798	1598	1390	1997	875	1991	2987
Air intake system	Turbo	N.A.	Turbo	N.A.	Turbo	Twin Turbo	Turbo	Turbo	Turbo Diesel
Engine power (kW)	132	51	118	81	90	135	62.5	155	140
Odometer (km)	24,334	6100	58,005	27,722	38,951	6738	1376	11,211	32,678
Vehicle weight (kg)	1481	1090	1925	1182	1363	1820	830	1605	2430
Ambient testing temperature (°C)	−7, 22	22	22	22	−7, 22	−7, 22	−7, 22	−7, 22	22

DI (Direct Injection); MPI (multiport Injection); GDI (Gasoline Direct Injection); CDI (Common rail diesel injection).
N.A. (Naturally aspirated); Turbo (Turbo charged); Twin Turbo (Twin Power Turbocharged).

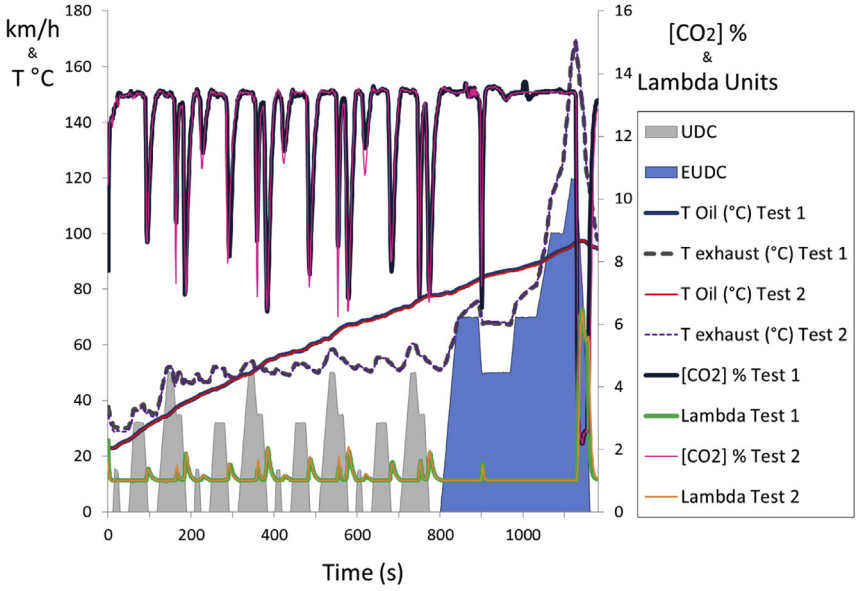

Fig. 1. Example of some setup capabilities (Oil temperature, exhaust temperature, air/fuel ratio (lambda), CO_2 emissions) and repeatability for the two tests performed for Car 5 (Test 1 and Test 2) over the NEDC (UDC + EUDC) at 22 °C. Temperature (°C) and cycle speed (km/h) should be read on the left *Y* axis, while CO_2 concentration ([CO_2]%) and air/fuel ratio on the right axis.

integrated setup (Horiba, Japan) that analyse diluted gas from the CVS (see above) using the following techniques: non-dispersive infrared (for CO/CO_2), a chemiluminiscence (for NO_x) and a heated (191 °C) flame ionization detector (FID for total hydrocarbons (THC)). NH_3, among other unregulated compounds, was 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 is described in more 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). For the test cell configuration, see Fig. 2.

Previous studies of NH_3 emissions from vehicles have shown certain limitations when measurements were performed at the dilution tunnel. These limitations are due to adsorptive losses and long-lasting memory effects of NH_3 (Durbin et al., 2002; Mohn et al., 2004; Heeb et al., 2006, 2008). Therefore, raw exhaust measurements have been considered to be more suitable for real-time measurement of NH_3 emissions. The raw exhaust was sampled directly from the tailpipe of the vehicles with a heated PTFE (politetrafluoroetilene) 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., 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 ambient pressure during the measurement was 1013 hPa (±20), and the temperature of the gas cell of the FTIR was set to 191 °C. The calibration of the instrument was based on a factory developed multivariate model. Another set of analysers: non-dispersive infrared (for CO/CO_2) and chemiluminiscence detector (for NO_x) were also connected to the tail-pipe allowing a time-resolved (at 1 Hz) measurement of these compounds from the raw exhaust. CO, CO_2 and NO_x measurements from the previously described analysers were used to synchronize the FTIR time-resolved 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) and from the measured

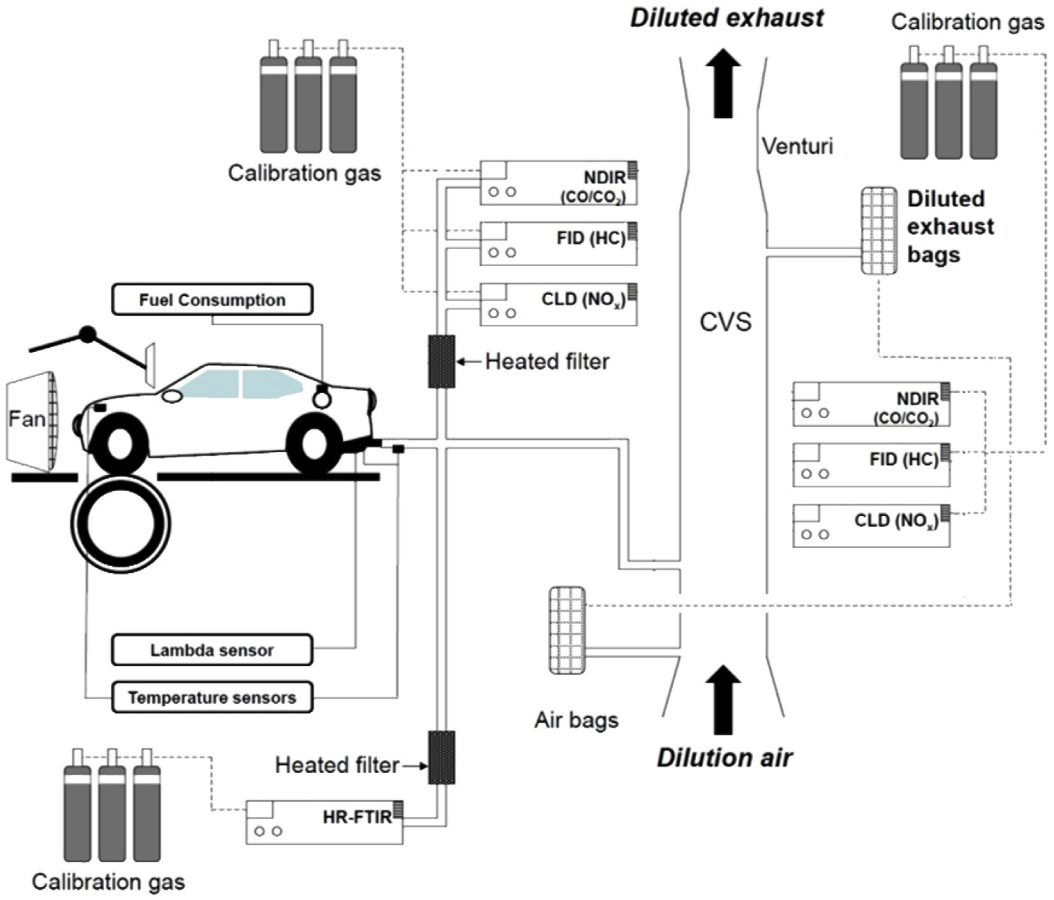

Fig. 2. Schematic diagram of the experimental setup.

concentration (ppmV). Emission factors (mg/km) were calculated from the integrated mass flow and the total driving distance of the NEDC, about 11 km.

3. Results and discussion

3.1. Regulated compounds

The emission factors of the regulated gases and CO_2 for the nine vehicles studied over the NEDC at 22 and −7 °C and obtained using the analytical instrumentation and setup described above (see *Analytical instrumentation*), are summarized in Table 2.

For the flexi-fuel vehicle (Car 1) we present the emission factors for three different fuels blends, i.e. certified reference fuel E5 used at both 22 and −7 °C, the summer blend E85 used at 22 °C and the winter blend E75 used for the tests performed at −7 °C. Car 1 presented THC and NMHC emissions above Euro 5 limits at 22 °C. Cars 2–8 complied with Euro 5 emission standards at 22 °C. Car 9 showed THC + NO_x and NO_x emissions higher than Euro 6 emission limits.

For spark ignition vehicles, the low temperature emission test, known as type VI test, is limited to the urban part of the cycle (UDC) and only regulates CO (15 g/km) and THC (1.8 g/km) emissions (Directive 98/69/EC). Vehicles studied at −7 °C (Car 1 and Car 5–Car 8) comply with Type VI Euro 5 emission standards for that temperature (see Table 2 in the SI). The emissions of the regulated compounds and CO_2 were found to be higher during the UDC phase than during the EUDC phase or over the entire NEDC, for all the studied vehicles at both temperatures (see Table 2 and Fig. 2 in the SI).

The CO_2 emission factor obtained for flexi-fuel, Car 1, when tested using the E5 blend, was 3% lower at −7 °C than at 22 °C. In the other cases, the vehicles (Car 1 E85/E75, Car 5 to Car 8) emitted from 14% to 22% more CO_2 at −7 °C than at 22 °C. The CO_2 emission factors from the flexi-fuel vehicle at 22 °C were lower for the high ethanol content blend (E85) than for the standard gasoline (E5). The opposite behaviour was observed when the test was performed, with same vehicle, at −7 °C, i.e., higher CO_2 emission factor for high ethanol content (E75).

3.2. NH_3 formation and emission

Table 2 shows average NH_3 emission factors, in terms of mg/km for all the studied vehicles at 22 and −7 °C. The table also shows the average NH_3 mixing ratios (ppm) during the test and the maximum mixing ratio (ppm) measured for each vehicle. Fig. 3 illustrates the emission profiles presented by all the tested vehicles at 22 and −7 °C. An example of the repeatability achieved can be seen for CO_2 emissions (commonly used as vehicle testing quality check), oil temperature, exhaust temperature and/or lambda in Fig. 1. The good repeatability obtained supports the fitness of the testing procedures. A similar behaviour was observed for all the tested vehicles, with some small differences at −7 °C. Most regulated gases and NH_3 emissions showed repeatability within 20% or better. For each individual vehicle, the NH_3, NO and CO emissions profiles of the two performed tests were alike, following always the same pattern.

Table 2
Average, maximum and minimum emission factors (mg/km) for the regulated gases and CO_2 (g/km), measured in conformity with directive 70/220/EEC and its following amendments, and NH_3 emission factors (mg/km) over the NEDC at 22 and −7 °C. Average (Av [NH_3]) and maximum ammonia (Max [NH_3]) concentration (in ppmV units) measured during the tests.

Vehicles	Car 1 E85/E75		Car 1 E5		Car 2	Car 3	Car 4	Car 5		Car 6		Car 7		Car 8		Car 9[a]
Temp °C	22	-7	22	-7	22	22	22	22	-7	22	-7	22	-7	22	-7	22
THC	102	**359**	141	**206**	28	58	49	40	**362**	33	**165**	69	**245**	32	**327**	20
Max	158	**368**	161	**225**	30	62	52	46	**365**	44	**170**	75	**245**	33	**348**	20
Min	72	**349**	121	**187**	26	53	47	33	**362**	25	**160**	62	**244**	32	**307**	20
NMHC	89	**320**	136	**189**	26	42	41	34	**334**	27	**152**	62	**218**	22	**299**	14
Max	144	**329**	156	**206**	28	46	43	39	**335**	39	**157**	68	**220**	22	**318**	14
Min	59	**311**	116	**172**	26	38	39	28	**334**	20	**147**	55	**217**	22	**281**	14
CO	413	**893**	363	**932**	402	445	470	466	**1420**	882	**1218**	741	**1978**	395	**2145**	439
Max	465	**909**	363	**1133**	432	487	581	614	**1590**	917	**1243**	764	**2022**	397	**2279**	447
Min	386	**877**	362	**732**	372	403	358	350	**1256**	831	**1194**	718	**1933**	393	**2012**	430
NOx	6	**23**	10	**25**	21	18	4	27	**217**	15	**79**	35	**66**	14	**96**	211
Max	7	**23**	11	**26**	25	19	5	27	**225**	16	**86**	39	**68**	17	**105**	229
Min	5	**22**	10	**24**	17	16	4	26	**207**	15	**71**	31	**64**	12	**88**	193
CO_2	149	**182**	169	**164**	137	174	166	149	**170**	250	**298**	121	**141**	176	**203**	315
Max	151	**188**	169	**164**	138	174	166	150	**171**	252	**301**	121	**141**	176	**211**	316
Min	147	**176**	168	**163**	136	173	166	147	**170**	248	**296**	120	**141**	175	**194**	313
NH_3	5	**6**	4	**5**	4	7	9	11	**30**	27	**21**	35	**53**	62	**70**	12
Max	5	**6**	4	**7**	4	8	11	12	**34**	28	**22**	-	**55**	68	**74**	18
Min	4	**6**	4	**4**	4	7	9	10	**25**	26	**19**	-	**52**	58	**66**	6
Av [NH3]	11	**11**	7	**10**	6	14	24	26	**62**	23	**21**	66	**100**	108	**107**	6
Max [NH_3]	47	**27**	14	**34**	16	35	203	96	**216**	192	**149**	433	**748**	547	**528**	20

Emission factors obtained at −7 °C are represented in bold figures.

Euro 5-6 spark ignition emission limits: 22 °C (mg/km): THC= 100; NMHC= 68; CO= 1000; NOx= 60

[a] Euro 6 compression ignition emission limits mg/km. THC+NOx= 170; CO= 500; NOx= 80

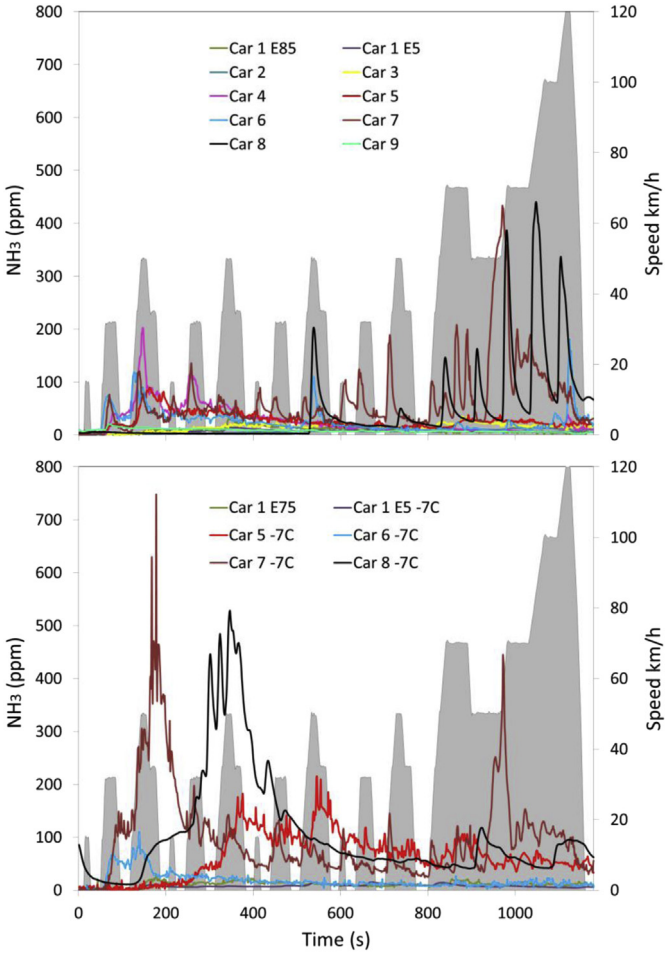

Fig. 3. Fleet NH_3 emission profiles (ppm) over the NEDC at 22 °C (top chart), and at −7 °C (bottom chart).

The average NH_3 emission factors of the Euro 5 vehicles varied from 4 to 35 mg/km at 22 °C and 5 to 53 mg/km at −7 °C. The highest emissions, at the two studied temperatures, were always observed for Car 7 and the lowest for Car 2 and the flexi-fuel vehicle (Car 1) when run with E5. NH_3 emission factors from the studied vehicles were higher when the tests were performed at −7 °C than those obtained at 22 °C, with the exception of Car 6. The greatest increase was observed for Car 5 (136%). Car 1 tested with E85 blend, showed the lowest increase (20%). NH_3 emission factor of Car 6 decreased from 27 mg/km at 22 °C to 21 mg/km at −7 °C (22%). While Car 2, Car 3 at 22 °C and Car 5 at −7 °C presented similar NH_3 emission factors during the two phases of the NEDC (i.e. UDC and EUDC), most of the Euro 5 vehicles (with the exception of Car 7 at 22 °C) mainly emitted during the UDC phase (see Table 2 and Figs. 1a–p and 2 of the SI).

The Euro VI emission standards for HDV include a 10 ppm limit for the average emitted NH_3, which, up to now, is the only NH_3 vehicular emission limit enforced in Europe. This limit was set to deal with the possible NH_3 slip from the use of urea in SCR systems. The average and maximum mixing ratios (ppm) of NH_3 obtained from the studied fleet are shown in Table 2. The average NH_3 mixing ratios obtained for the Euro 5 vehicles ranged from 6 ppm (Car 2) and up to 66 ppm (Car 7) at 22 °C and from 10 ppm (Car 1) and up to 100 ppm (Car 7) at −7 °C. The maximum concentration measured for the Euro 5 vehicles ranged from 14 to 433 ppm at 22 °C and from 27 to 748 ppm at −7 °C.

Fig. 4 shows the average mass (mg/km) of NO, NH_3, and CO emitted by each vehicle over the NEDC 22 °C and −7 °C. Fig. 5a–f illustrate some examples of emission rates (g/s) and concentrations (ppm) of NH_3 and its precursors, NO and CO, at 1 Hz, over the NEDC (Examples for each vehicle can be found in the Supplementary material). Some general features of the vehicular NH_3 emissions can be highlighted from the presented data. For instance, the onset of the NH_3 emissions for all vehicles typically occurred right after the catalyst light-off (Figs. 3, 5 and 10 and SI Fig. 1a–p). However,

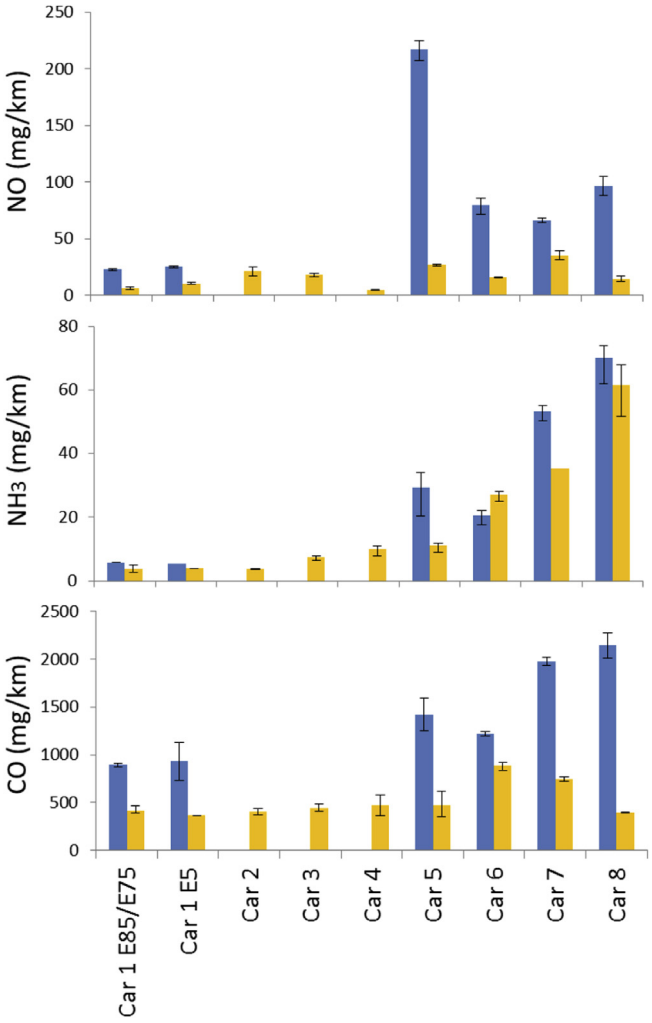

Fig. 4. Average emission factors (mg/km) of NO, NH_3, and CO from each spark ignition vehicle over the NEDC at 22 °C (yellow) and −7 °C (blue). Error bars indicate maximum and minimum measured values. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

once catalyst light-off, NH_3 emission profiles will follow different repeatable patterns. While catalyst light-off of Cars 1, 3, 4, 6 and 7 is observed after around 60–100 s at the studied temperature, Car 5 catalyst light-off at −7 °C take place 100 s later than it did at 22 °C. This vehicle shows the strongest variation on NH_3 and NO emission factors when comparing 22 with −7 °C (see Fig. 1h and i SI). The results also show that the emissions of NH_3 peaked during acceleration events.

The Euro 6 vehicle, Car 8, shows a completely different pattern at 22 °C (Fig. 6a) because it uses a different after treatment setup. The after treatment that Car 8 was equipped with (TWC + NSC) was more complex than the one used by the other gasoline vehicles (only TWC). Therefore, it will be discussed separately.

The time resolved NH_3 emission profiles obtained using the different fuel blends at the same temperature (E5 vs E85 at 22 °C and E5 vs E75 at −7 °C) for Car 1 are very similar (see Table 2). The results also show that the emissions of the precursors (CO and NO_x) and NH_3 are similar for the different blends used, indicating that different oxygen content in the fuel has a lower impact on these three compounds emissions (CO, NO_x and NH_3) than the after treatment technology used in the vehicle. For this particular vehicle it is shown that a rich oxygen fuel (E85) gives similar emission factors of NH_3 and NO_x to those of a standard fuel (E5).

Fig. 7a–c are an example of the cumulative mass of NH_3, NO and CO along the cycle. While the NH_3 precursors, namely CO and NO, are mainly emitted at the very beginning of the test (known as cold start emission, and more pronounced during the tests at −7 °C), before the catalyst light-off, NH_3 emissions begin right after catalyst light-off and go on for the rest of the test cycle. This shows that the TWC (see reactions 1, 2b) is an effective system to reduce the nitrogen oxides but it misses the target product N_2, forming instead a large amount of the byproduct NH_3 (among other nitrogen containing molecules that are not discussed here).

Car 8, equipped with a TWC and a NSC system, complied with Euro 6 spark ignition emission limits at 22 °C and −7 °C. The vehicle showed the highest NH_3 emission factors of the studied fleet at the two studied temperatures. Car 8 emitted on average 62 mg/km of NH_3 at 22 °C and 70 mg/km when tests were performed at −7 °C. This vehicle showed also the highest average concentration (108 ppm). Notice that NH_3 emission factor from Car 8 at 22 °C nearly doubles the highest emission factor obtained for Euro 5 vehicles (Car 7) and is one order of magnitude higher than the lowest observed value (Car 2). At 22 °C, the highest NH_3 concentrations were measured during the regeneration of the NSC system. The regeneration is mainly observed during the EUDC phase of the cycle. The obtained results indicate that, although the technology used in Car 8 is effective to comply with Euro 6 standards, it increase dramatically the emissions of NH_3.

The final goal of the NSC system is to reduce NO_x 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 very same conditions that lead to NH_3 formation over a catalyst surface.

Compare with tests performed at 22 °C, Car's 8 NH_3 emission factor increased only by 13% when the tests were performed at −7 °C. This was the lowest increase observed in the fleet. Still, the 13% accounts for 100 mg, which, in terms of total mass, is more than what Cars 1–4 emitted at any studied condition. 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 and NO, followed by a diminution of the CO emissions and rise up of the NH_3 emissions due to catalyst light-off. Then, NH_3 continues to be emitted along the cycle (see Fig. 6b and Supplementary material). This behaviour suggests that the NSC after treatment system does not work properly at such low temperatures. As a consequence the after treatment system of Car 8 remains limited to the only action of the TWC, meaning that the presence of the NSC, at this temperature, is useless. There are some other indications of the deactivation of the NSC system at −7 °C, for instance: i) CO and NH_3 emissions are in very good correlation with the rest of the fleet only at −7 °C (see Fig. 8). ii) at this temperature it can be observed that there is a relationship between NH_3 emissions and the air/fuel ratio, while at 22 °C there is no sign of this effect (see below).

Fig. 9 shows average NH_3 emission factors reported in relatively recent chassis dyno based studies (Durbin et al., 2002; Livingston et al., 2009; Clairotte et al., 2013) together with Cars 1–8 emission factors at 22 °C. From Durbin et al. (2002) and Livingston et al. (2009) we present NH_3 emission factors from Ultra Low Emission Vehicles (ULEV) tested over the Federal Test Procedure (FTP) driving cycle for certification of new vehicles in the USA (FTP 72/75 (1978)). For these type of cars and over this test cycle, Durbin and Livingston et al. reported average NH_3 emission factors equal to 15 and 14 mg/km, respectively. Clairotte et al. reported 7 and 4 mg/km of NH_3 emitted from a Euro 5a flexi-fuel vehicle tested over the

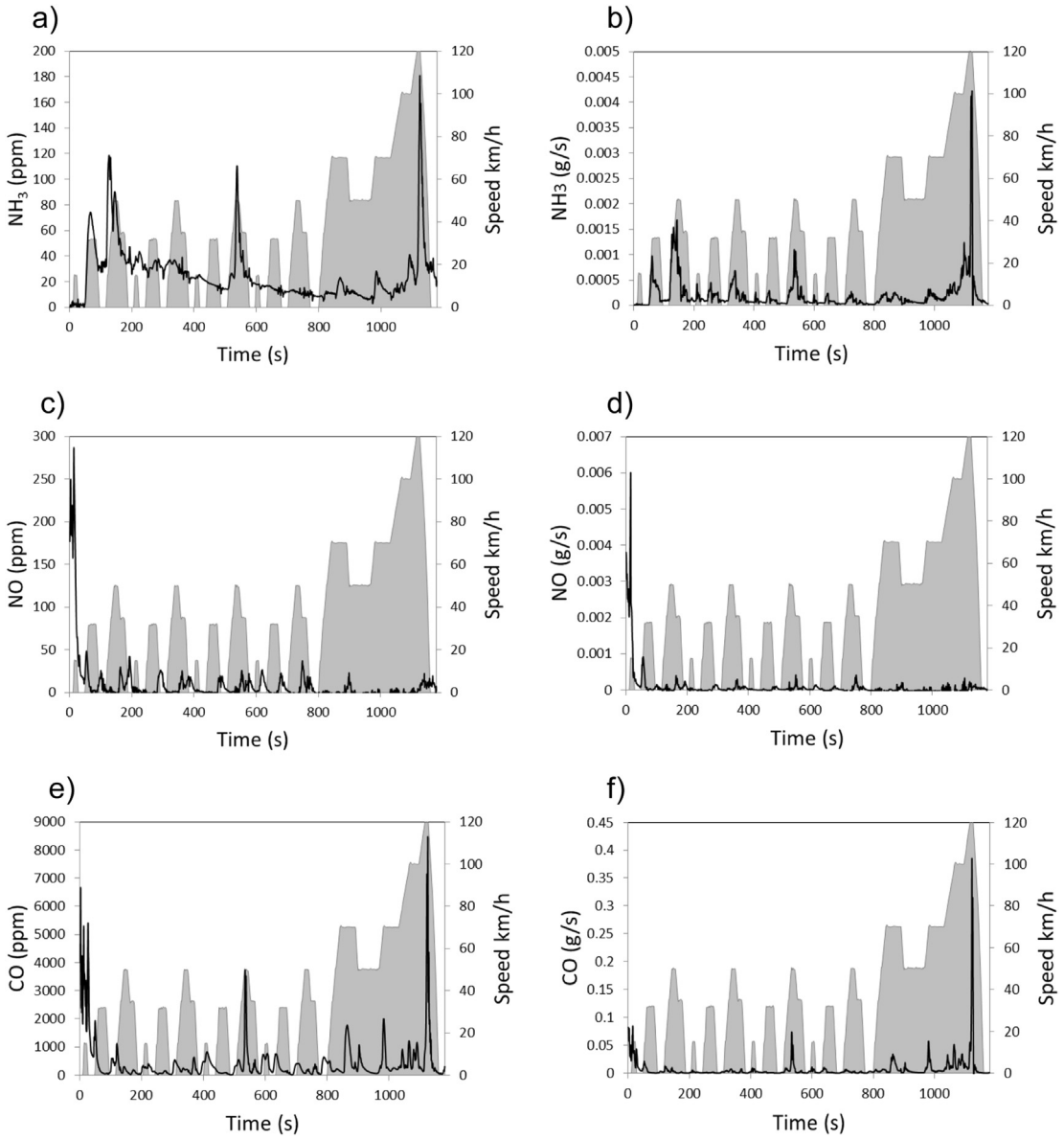

Fig. 5. Example (Car 6 at 22 °C) of time-resolved concentration (ppm) (a, c and e) and exhaust mass flow (g/s) (b, d and f) of NH_3, NO and CO. Time resolution 1 s over the NEDC (grey shadow).

NEDC and fuelled with E5 and E85 blends, respectively. For the flexi-fuel vehicle (Car 1) and gasoline Cars 2 and 3 we obtained NH_3 emission factors (4–7 mg/km) similar to those reported by Clairotte et al. for the Euro 5a flexi-fuel. Car 4 and Car 5 have similar NH_3 emission factors (10 and 11 mg/km) to those previously reported for presented the ULEVs, while NH_3 emission factors from Cars 6–8 are much higher (27, 35 and 62 mg/km).

It has been proposed that CO emissions from gasoline vehicles are indicative of NH_3 formation over the catalyst (Kean et al., 2009; Livingston et al., 2009). Therefore, the correlation between the CO and NH_3 emission factors was analysed and it proved to be excellent at both 22 and −7 °C (see Fig. 8). The correlation is slightly better for the results obtained at −7 °C than those obtained at 22 °C. The CO and NH_3 emission factors from Durbin et al. (2002) and Clairotte et al. (2013) at 22 °C were also introduced in the correlation analysis showing a very good agreement with the results obtained in the present study (see Fig. 8).

One diesel LDV (Car 9), equipped with an SRC system, was also studied at 22 °C for the sake of comparison (see Tables 1 and 2). For this vehicle NH_3 emission factor (12 mg/km) was observed to be within the ranged measured for the Euro 5 gasoline vehicles. The maximum mixing ratio measured was 20 ppm and the average concentration for the cycle 6 ppm. This diesel vehicle shows an average concentration similar to that obtained for Car 1 and Car 2. However, its NH_3 emission factor is three times higher than those of Car 1 and Car 2.

3.3. Linking NH_3 emissions with air/fuel ratio (λ)

The relationship between NH_3 emissions and the air/fuel ratio, lambda (λ), was studied for the gasoline and flexi-fuel vehicles. Fig. 10 illustrates an example of time resolved NH_3 and NO emission profiles together with the lambda factor (λ) along the test. Comparison of signals suggest that there is a connection between air/

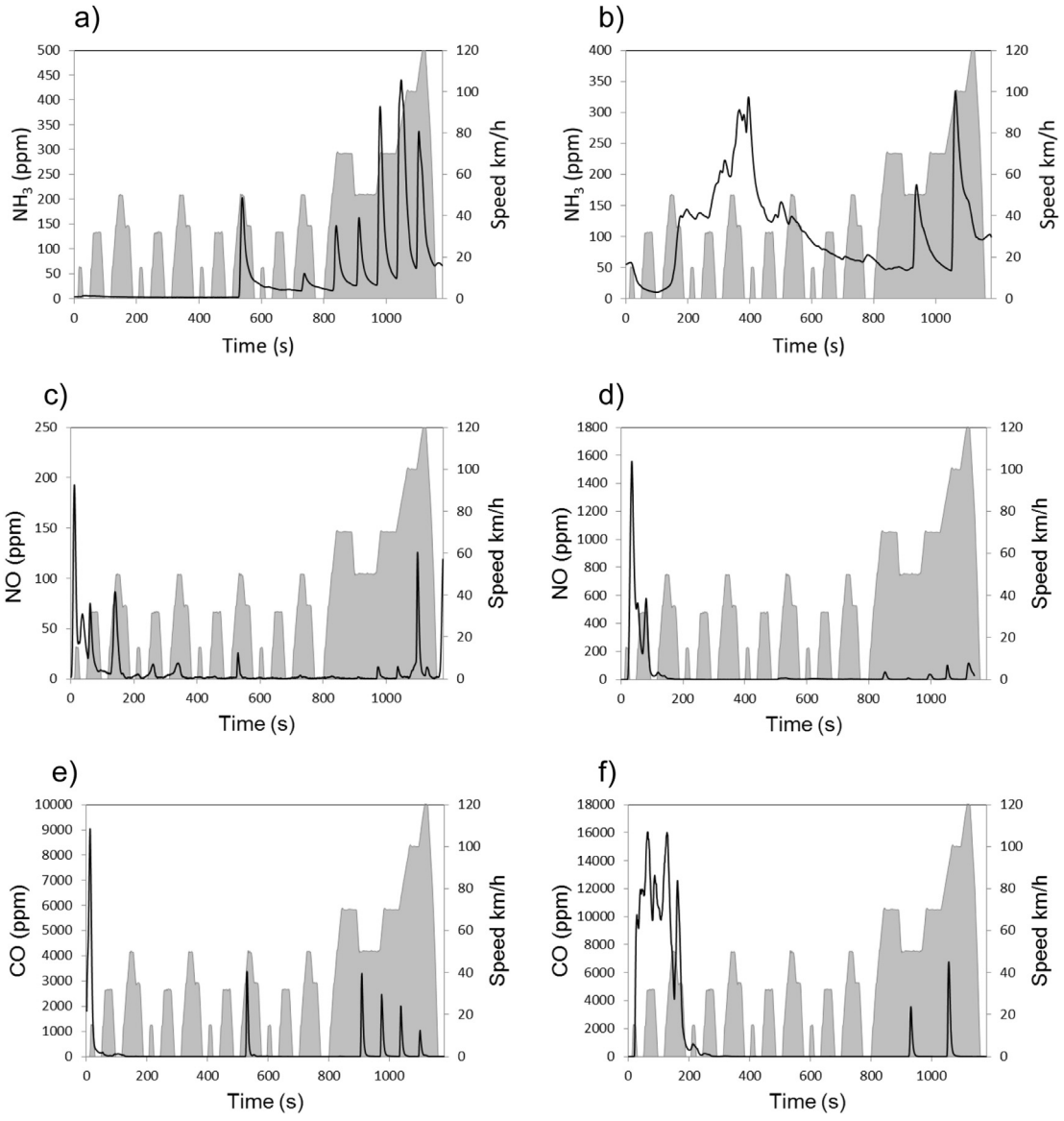

Fig. 6. Car 8 emission profiles over the NEDC at: 22 °C (a) NH_3, (c) NO and (e) CO and at −7 °C (b) NH_3, (d) NO and (f) CO.

fuel ratio and NO or NH_3 emissions. The highest NO emissions (after catalyst light-off) were generally observed during the lean combustion ($\lambda > 1$) and the NH_3 concentration tended to rise at rich combustion ($\lambda < 1$). The same trends were already reported in previous studies (Huai et al., 2003; Heeb et al., 2006). However, Baum et al. (2001) stated that high NH_3 emissions can be found even at lean air/fuel ratios (Baum et al., 2001).

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 (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 Figs. 3, 5 and 10). After the catalyst light-off CO emission profiles match with those of NH_3 (see Fig. 1a–p in SI). Hence, not only the total emitted mass of these two compounds are well correlated as explained before, but after the catalyst light-off they also tend to follow the same emission profile.

As previously observed by Heeb et al. (2006) deceleration events induce short episode of lean combustion ($\lambda > 1$) with excess of oxygen. Therefore, the catalyst is partially oxidized disfavouring the formation of NH_3. Under this conditions NO emission peaks appeared (see Fig. 10).

Since NH_3 emissions are not regulated for LDV, the lambda control depends on the strategy of each car manufacturer and the strategy is focused on comply with the NO_x and CO standards.

It is important to notice that NH_3 emissions depend on driving mode and that NH_3 is mainly formed during acceleration events. Hence, the studied vehicles could present higher NH_3 emissions if the vehicles were driven more aggressively (Huai et al., 2003; Shores et al., 2000; Durbin et al., 2002; Livingston et al., 2009).

4. Conclusions

NH_3 is classified under the dangerous substances directive (67/548/EEC) as: toxic, corrosive and dangerous for the environment. It is responsible for the formation of atmospheric secondary inorganic aerosols that are known for its adverse health and environmental effects. Although, NH_3 is usually associated with the

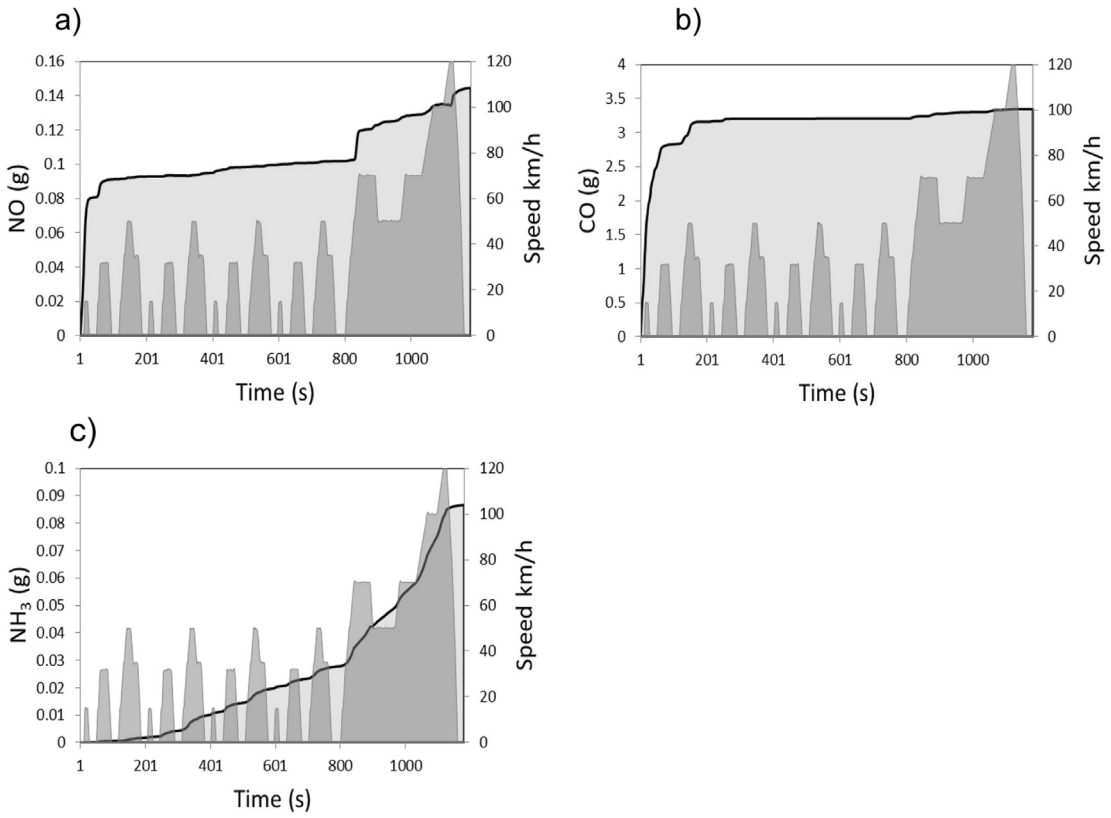

Fig. 7. Car 3 cumulative mass (g) emissions of: (a) NO, (b) CO and (c) NH_3 at 22 °C over the NEDC.

agriculture and the rural environment, it is also observed in urban areas and roadside locations due to vehicular exhaust emissions. Several factors contribute to the formation of NH_3 in vehicle exhaust. NH_3 emissions vary considerable and depend on the vehicle and its emission control technology. While the vehicular emissions of NO_x and CO have substantially decreased over the past years, the NH_3 emissions for Euro 5–6 vehicles reported here (4–62 mg/km) are comparable with those reported during the last decade (Durbin et al., 2002; Huai et al., 2003, 2005; Heeb et al., 2006, 2008; Livingston et al., 2009). Moreover, the vehicle that represented the newest technology and that complied with Euro 6 standards showed the highest NH_3 emission factors at the two studied temperatures (62 and 70 mg/km at 22 and −7 °C, respectively). The presented results show that all tested vehicles, with no exception, emit ammonia. When and how much NH_3 is going to be emitted will depend on the vehicle engine and after-treatment

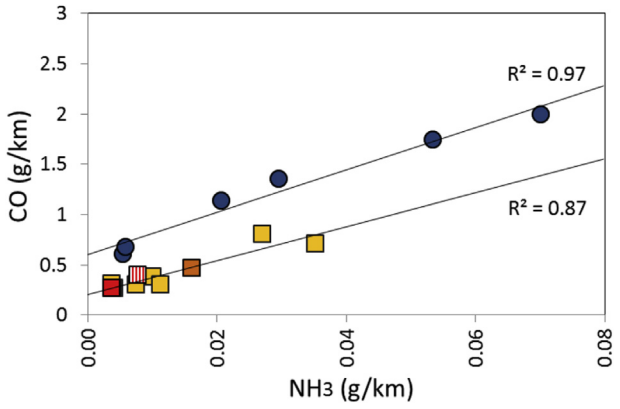

Fig. 8. Correlation chart of CO *vs* NH_3. Emission factors (g/km) of CO and NH_3 emitted by the studied vehicles over the NEDC at 22 °C (yellow squares) and −7 °C (blue). Also shown, data from recent dynamometer studies performed at 22 °C using: ULEVs over the FTP (orange square; Durbin et al., 2002) and a Euro 5a flexi-fuel vehicle (Clairotte et al., 2013) tested with E5 (red strips square) and E85 (red square) fuel blends over the NEDC. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

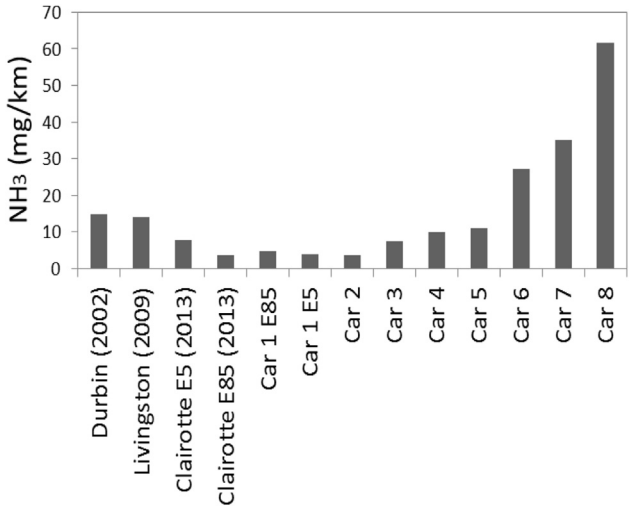

Fig. 9. Comparison of Cars 1–8 NH_3 emission factors (mg/km) at 22 °C over the NEDC with recent dynamometer studies using ULEV over the FTP (Durbin et al., 2002; Livingston et al., 2009) and a Euro 5a flexi-fuel vehicle tested with E5 and E85 fuel blends (Clairotte et al., 2013) over the NEDC.

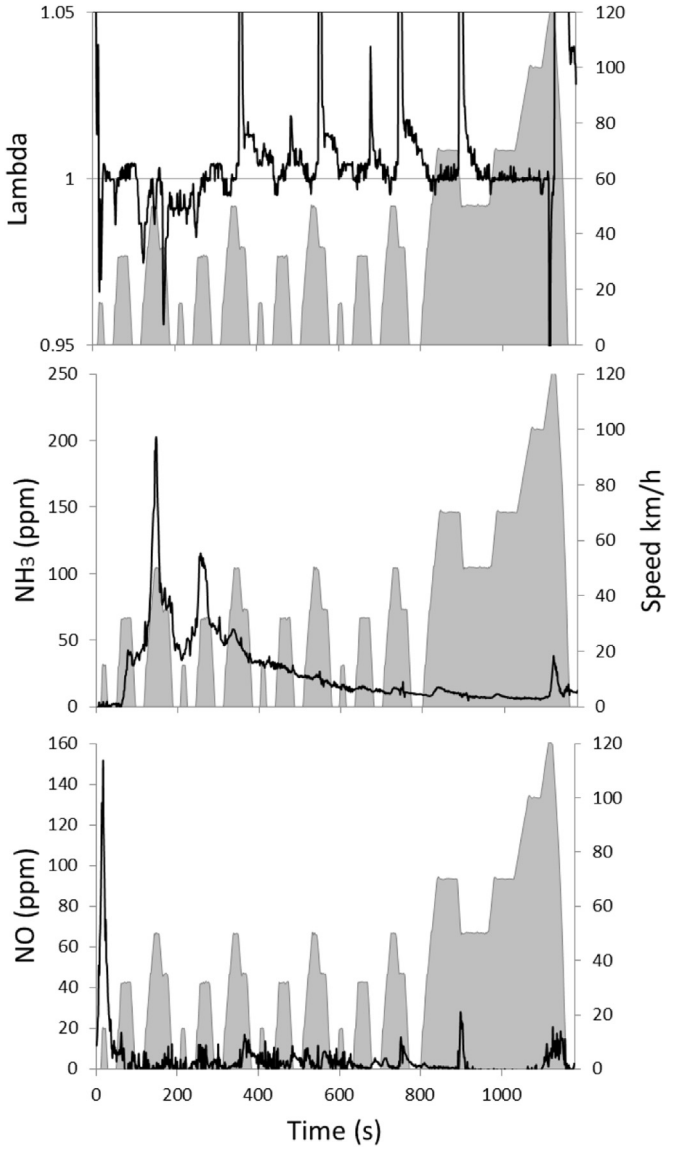

Fig. 10. NH_3 and NO emission profiles for Car 4 at 22 °C over the NEDC and their connection with the air/fuel ratio (lambda).

technology, the ambient temperature, the driving style and the car manufacturer strategy for NO_x emission control.

In the light of the presented results, it is clear the need for the introduction of an NH_3 emission limit for light duty spark and compression ignition vehicles. However, further work should be done before proposing a specific target ammonia limit.

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 data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2014.07.050.

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