Effect of temperature on ammonia emissions from gasoline and ethanol flexi fuel cars

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Ammonia (NH_3) is a toxic compound that is involved in the formation of secondary aerosols. The formed aerosols not only impoverish the urban air quality but, when transported to remote areas, their deposition leads to hypertrophication of waters and acidification of soils with negative effects on nitrogen-containing ecosystems (Bouwman et al., 2002; Erisman et al., 2003). The particulate matter that is formed, namely ammonium nitrate and ammonium sulfate, is also associated adverse health effects.

Vehicleswith internal combustion engine are considered to be an important source of NH_3 in the urban environment and may be comparable to natural source emissions in certain urban areas (Livingston et al., 2009). Traffic-related NH_3 is considered to be mainly produced in the Three-Way-Catalyst of gasoline light duty vehicles. Therefore, it is crucial to quantify the NH_3 emissions from vehicles exhaust in order to develop effective air quality control strategies. In the Three-Way-Catalyst NH_3 is formed 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):

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

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

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

Three Euro 5 light duty vehicles, two gasoline and one ethanol flexi fuel cars, were tested at the European Commission Joint Research Centre, Ispra, Italy, in the Vehicle Emission Laboratory (VELA) and over the New European Driving Cycle (NECD) (Table 1) aiming to foreground that NH_3 emissions are far from being negligible for Euro 5 cars. For this purpose NH_3, among other gases, was monitored at 1Hz acquisition frequency by a High Resolution Fourier Transform Infrared spectrometer (HR-FTIR – MKS Multigas analyzer 2030 HS, Wilmington, MA, USA). In order to avoid the absorption of NH_3 in condensed water and/or the CVS' stainless steel walls, the raw exhaust was sampled directly from the vehicles' tailpipe using a PTFE (politetrafluoroetilene) heated line at 190 °C and a pumping system. The tests were performed using the test cell at 22 and -7 degrees Celsius as suggested by the legislation. Three examples, one for each vehicle, of the time resolved results that are obtained when using this procedure are shown in Figures 1-3. The obtained results are summarized in Table 2.

Vehicle	Displacement (cm^3)	Power (kW)	Odometer (km)	Fuel	Fuel system	Weight (kg)
GLDV1	1390	90	38951	E5	GDI	1363
GLDV2	1997	135	6738	E5	GDI	1820
FLDV1	1596	132	24334	E85 E75HVP	DI	1481

Table 1. Vehicles features. The acronims GLDV stand for Gasoline Light Duty Vehicle and FLDV stands for Flexifuel Light Duty Vehicle. Fuel E85 and E75 correspond to summer and winter ethanol fuels, where 85 and 75 are the percetaje of ethanol contained in the fuel.

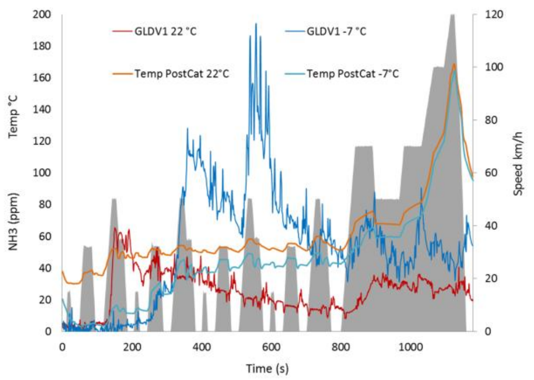

Figure 1.

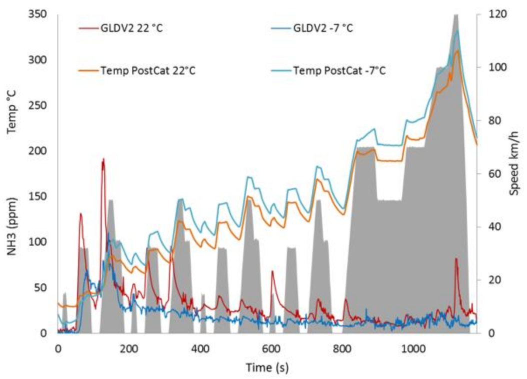

Figure 2.

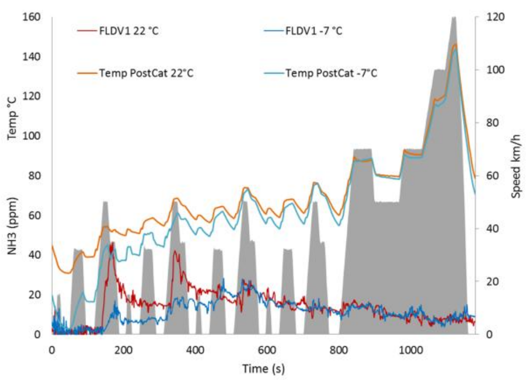

Figure 3.

Figure 1-3. Time-resolved mixing ratio of NH_3 at the tailpipe of: 1. GLDV1, 2. GLDV2 and 3. FLDV1 over the NEDC (grey area) at 22 °C (red line) and -7 °C (blue line). Orange and light blue represent the time-resolved temperature after the catalyst.

Vehicle	Cycle	22 °C	-7 °C
GLDV1	**NEDC**	**11 ± 2**	**32 ± 1**
	UDC	14 ± 2	34 ± 1
	EUDC	10 ±2	31 ± 1
GLDV2	**NEDC**	**27 ± 2**	**20 ± 4**
	UDC	39 ± 2	41 ± 4
	EUDC	17 ± 2	8 ± 4
FLDV1	**NEDC**	**5.0 ± 0.3**	**6 ± 1**
	UDC	8.0 ± 0.1	9 ± 1
	EUDC	3.1 ± 0.1	5 ± 1

Table 2. Ammonia emission factors (mg/km) at 22 and -7 °C over the entire NEDC and the two phases of the cycle, i.e. urban driving cycle (UDC, that goes from 0 to 780 seconds) and extra urban driving cycle (EUDC, from 780 to 1180 seconds).

From these preliminary results (Table 2) we could draw three main conclusions: first, while for each vehicle the reproducibility of the experiments is very good, the NH_3 emission varies substantially from one vehicle to the other. This shows a dependency on the technology of the different vehicles and/or the fuel that is used. In fact, for the flexi fuel car, fueled with 85 or 75% ethanol, the NH_3 emissions are considerably lower compared to the gasoline cars at both 22 and -7 °C. Second, the engine power seems to play an important role on the emission levels, when comparing vehicles that use the same kind of fuel. Finally, the HR-FTIR is been proven to an appropriate technique to monitor NH_3 emissions at the vehicles raw exhaust.

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Livingston C., Rieger P., Winer A. 2009. Ammonia emissions from a representative in-use fleet of light and medium-duty vehicles in the California South Coast Air Basin. Atmospheric Environment 43, 3326-3333.

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1. INTRODUCTION AND MOTIVATION OF THIS STUDY

Ammonia (NH_3) is a toxic compound that involved in the formation of secondary aerosols. The formed aerosols not only impoverish the urban air quality but, when transported to remote areas, their deposition leads to hypertrophication of waters and acidification of soils with negative effects on nitrogen-containing ecosystems [1].

Vehicles are considered to be an important source of NH_3 in the urban environment and may be comparable to natural source emissions in certain urban areas [2]. Up to now, traffic-related NH_3 is considered to be mainly produced in the Three-Way-Catalyst of gasoline light duty vehicles. Therefore, it is crucial to quantify the NH_3 emissions from vehicles exhaust in order to develop effective air quality control strategies.

2. INSTRUMENTATION AND METHODS

- NH_3 emission factors were obtained for three Euro 5 cars, two of which gasoline (GLDV1 and GLDV2) and one ethanol flexi fuel (FLDV1), in the Vehicle Emission Laboratory (VELA) and over the New European Driving Cycle (NEDC). See Table 1.
- NH_3, among other gaseous compounds, was monitored at the raw exhaust using a High Resolution Fourier Transform Infrared spectrometer (1 Hz, HR-FTIR – MKS Multigas analyzer 2030, Wilmington, MA,USA).
- The raw exhaust was sampled with a heated PTFE line (190 °C) and a pumping system to avoid the absorption of NH_3.
- Tests were performed at 22 and -7 °C.

Figure 1

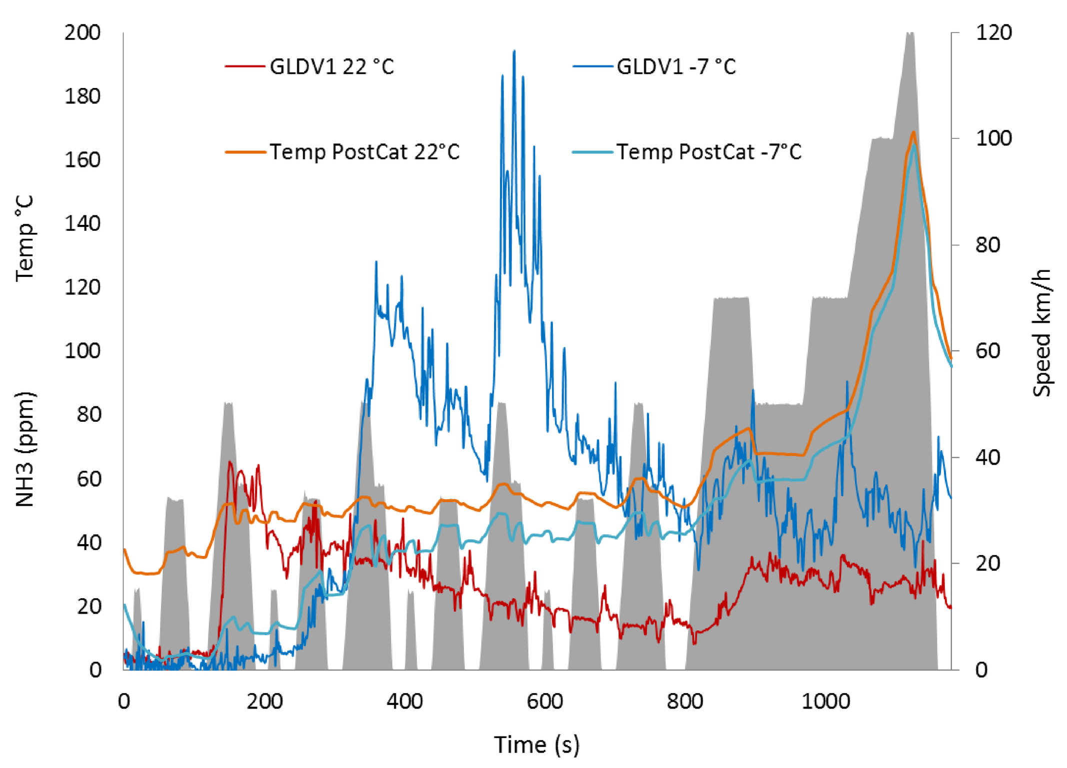

Figure 2

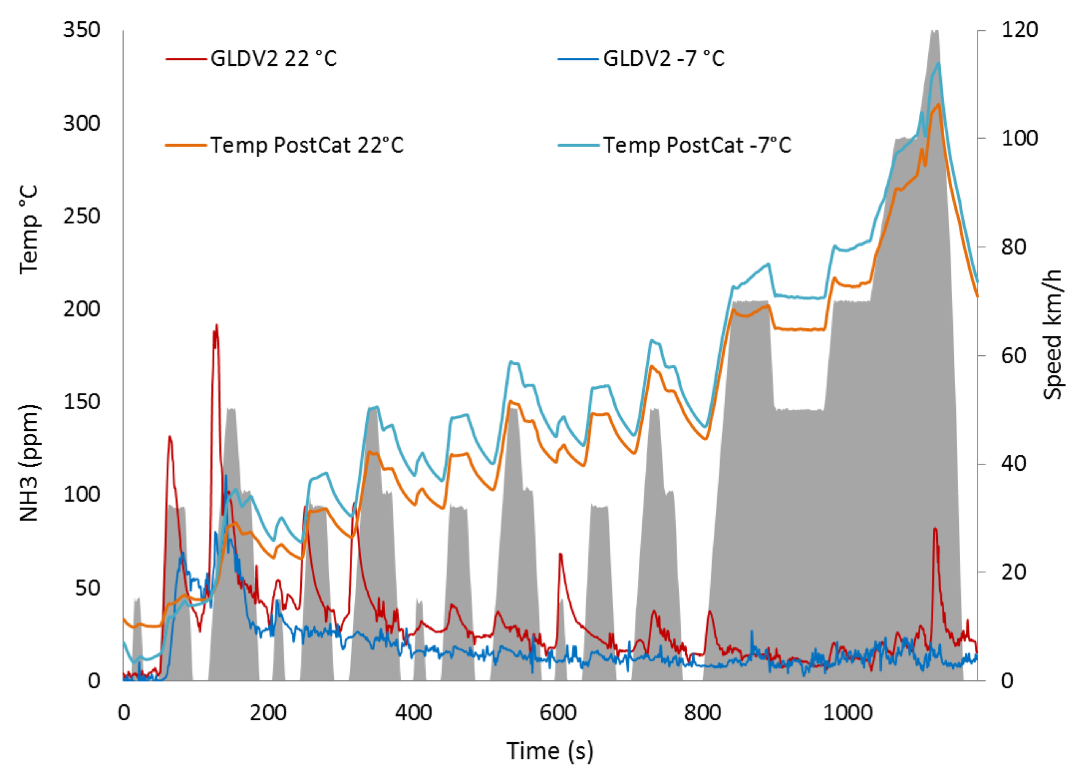

Figure 3

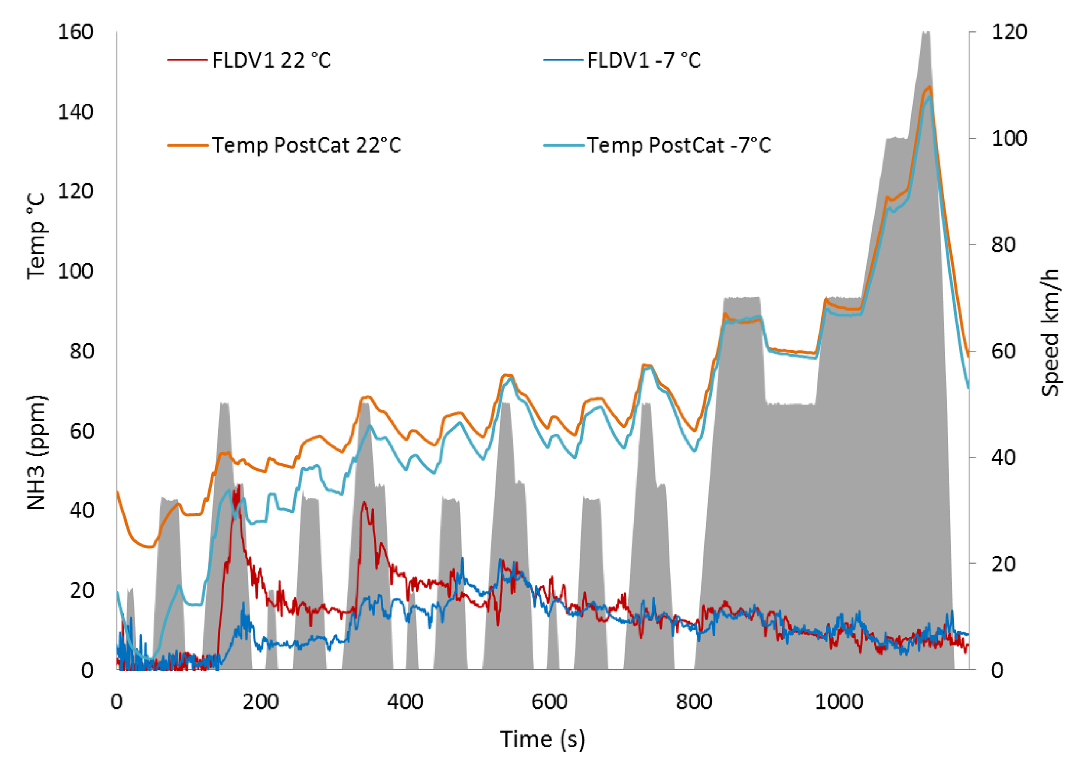

Figure 1-3. Time-resolved mixing ratio of NH_3 at the tailpipe of: 1. GLDV1, 2. GLDV2 and 3. FLDV1 over the NEDC (grey area) at 22 °C (red line) and -7°C (blue line). Orange and light blue represent the time-resolved temperature after the catalyst.

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	UDC	8	9
	EUDC	3	5

Table 2. NH_3 emission rates (mg/km) at 22 and -7 degrees Celsius over the NEDC and contribution of each phase of the cycle, i.e. urban driving cycle (UDC) and extra-urban driving cycle (EUDC). Errors correspond to 2σ.

3. CONCLUSIONS

- NH_3 emissions vary substantially and depend on the vehicle technology and/or fuel.
- NH_3 emissions are lower for the flexi fuel car at 22 and -7 °C.
- HR-FTIR is an appropriate technique to monitor NH_3 emissions at the vehicles raw exhaust.
- The NH_3 emission rates of GLDV2 and FLDV1 do not seam to be influenced by the ambient temperature. However, GLDV1 NH_3 emission rate varies and it is higher at lower temperature.

4. REFERENCES

[1] Erisman, J.W., Grennfelt, P., Sutton, M., 2003. The European perspective on nitrogen emission and deposition. Environment International 29, 311–325.
[2] Livingston C., Rieger P., Winer A. 2009. Ammonia emissions from a representative in-use fleet of light and medium-duty vehicles in the California South Coast Air Basin. Atmospheric Environment 43, 3326-3333.0

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