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NH₃ and CO Emissions from Fifteen Euro 6d and Euro 6d-TEMP Gasoline-Fuelled Vehicles

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Abstract: Ammonia (NH₃) plays a key role in atmospheric chemistry and largely contributes to the PM_{2.5} measured in urban areas around the globe. For that reason, the National Emission Ceilings directive, Gothenburg Protocol under the United Nations Convention on Long-Range Transboundary Air Pollution, and International Panel for Climate Change (IPCC) directive required a reduction of the emissions of NH₃. Nonetheless, the European Environment Agency (EEA) indicated that road transport emissions of NH₃ have increased. Moreover, recent studies reported that, not only vehicle NH₃ emissions are greater than agricultural emissions in areas that gather > 40% of the U.S. population, but urban emissions of NH₃ for passenger cars are underestimated by a factor of 17 in UK. In this study, fifteen gasoline-fuelled vehicles, meeting the most recent European emission standards, Euro 6d or Euro 6d-TEMP, were investigated in laboratory tests over the type-approval worldwide-harmonized light-duty vehicles test cycle (WLTC), at 23 °C and −7 °C, as well as over the motorway cycle Bundesautobahn (BAB). Results show that all the vehicles tested emitted NH₃ over the different duty cycles, and presented emissions level that are comparable to those previously reported for Euro 4–Euro 6b vehicles. Finally, good agreement between the CO and the NH₃ emissions was registered during the acceleration events, and, in general, a fair correlation, with R² > 0.75, was obtained, when comparing the CO and NH₃ emissions of the studied vehicles.

Keywords: transport emissions; ammonia; emissions measurements; fuel enrichment

Citation: Selleri, T.; Melas, A.; Bonnel, P.; Suarez-Bertoa, R. NH₃ and CO Emissions from Fifteen Euro 6d and Euro 6d-TEMP Gasoline-Fuelled Vehicles. *Catalysts* **2022**, *12*, 245. <https://doi.org/10.3390/catal12030245>

Academic Editor: Ioannis V. Yentekakis

Received: 10 January 2022

Accepted: 19 February 2022

Published: 22 February 2022

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1. Introduction

Ammonia (NH₃) plays a key role in the formation of PM_{2.5} in the atmosphere, being a precursor of ammonium nitrate (NH₄NO₃) and ammonium sulphate ((NH₄)₂SO₄) [1,2] and essentially determining the overall available amounts of such substances. NH₃ enhances particle nucleation by several orders of magnitude, increasing the number of potential cloud condensation nuclei that affect climate [3], and it can enhance secondary organic aerosol (SOA) formation [4,5].

NH₃ is considered to be among the most harmful air pollutants, in terms of damage to ecosystems, as the chemically-formed ammonium species leads to eutrophication of waters and contributes to the acidification of soil, lakes, and rivers, causing the loss of animal and plant life and biodiversity [6–9]. In fact, an estimated 7% of the total of the European ecosystem area was at risk of acidification in 2014 and 2016, and the critical loads for eutrophication were still exceeded in over 62% of the European ecosystem area [10]. Moreover, NH₃ contributes to negative short- and long-term impacts on human health. Short-term exposure (over a few hours or days) is linked to acute health effects, whereas long-term exposure (over months or years) is linked to chronic health effects [11].

Recent studies point out that ammonium nitrate and ammonium sulphate are the most abundant atmospheric secondary inorganic aerosols in many regions [12,13] and largely contribute to particulate matter (PM) and, in particular, the PM_{2.5} measured in urban areas around the globe [14–16]. Secondary PM may account for up to 50% of atmospheric PM_{2.5}

mass concentrations in certain European regions [17], with NH_3 contributing through secondary PM formation to 10–20% of the $\text{PM}_{2.5}$ mass in densely populated areas in Europe [6]. $\text{PM}_{2.5}$ is currently one of the major environmental concerns, as it affects human health [18] and impacts the global radiation budget [19,20]. Current estimates indicated that 82% to 97% of the EU-28 urban population was exposed to concentrations exceeding the WHO AQG value for $\text{PM}_{2.5}$ in 2015, resulting in 399,000 ($\pm 35\%$) premature deaths, attributed to $\text{PM}_{2.5}$ exposure.

For these reasons, the National Emission Ceilings directive 2001/81/EC [21], Gothenburg Protocol under the United Nations Convention on Long-Range Transboundary Air Pollution (LRTAP Convention) (UNECE 1999), and IPCC directive [22] required a reduction of the emissions of NH_3 . Over the past two decades, the agriculture and waste management sectors have reduced their NH_3 emissions by 29% and 24%, respectively, while road transport emissions have increased by 378% [23]. Moreover, within the framework of The Clean Air Policy Package for Europe, the EU agreed on a revised National Emissions Ceilings (NEC) directive [24], which set 2020 and 2030 emission reduction commitments for SO_2 , NO_x , non-methane volatile organic compounds (NMVOCs), NH_3 , and $\text{PM}_{2.5}$, aiming at further improving Europe's air quality, so that, by 2030, the number of premature deaths would be reduced by half, compared to 2005. At the moment, NH_3 emissions present the smallest reduction (4% in the EEA-33) of all primary and precursor emissions contributing to ambient air concentrations of PM.

According to the EEA, the agricultural sector is the largest contributor to total NH_3 emissions, accounting for 93% of total NH_3 emissions in the EU-28 in 2015, and road transport accounted for 1% of the EU-28 total emissions. The EEA indicates, in their latest air quality report [25], that overall NH_3 emissions have been reduced by approximately 10% in EU-28 but of only 2% in EEA-33, from 2000 to 2018. However, more recent studies [26,27] have shown that modern vehicles present the highest NH_3 emission ever recorded. Although agricultural is considered the dominant source of NH_3 in the U.S., and also at global scale, Sun et al. [28] and Fenn et al. [29] have recently reported that vehicle NH_3 emissions are greater than agricultural emissions in areas that gather > 40% of the U.S. population. Moreover, it has been recently reported that the inventory estimates of urban emissions of NH_3 for passenger cars are underestimated by a factor of 17 in the UK [29].

NH_3 is present in exhaust from Diesel vehicles, since the introduction of selective catalytic reduction systems (SCR) and lean- NO_x traps (LNT) [26,30–32]. Nonetheless, emissions of this compound have been measured in the exhaust of TWC-equipped gasoline vehicle, long before LNT and SCR systems were introduced in the automotive sector [33–35].

The emissions of NH_3 from spark ignition engines equipped with TWCs have been associated to rich combustion [27,30,31,36–38]. Fuel-rich combustion is used at high engine loads to increase the maximum engine power output, avoiding at the same time excessive exhaust gas temperatures, with effects also on the after-treatment system, and knock. Such a strategy may exist on certain vehicles but should be, in principle, approved by authorities only when engine protection clauses can be invoked, which should happen only under exceptional circumstances [39].

During rich operation, NO_x and H_2 react to form NH_3 over the TWC, which are then emitted. For that reason, NH_3 can be the dominant reactive nitrogen species emitted by spark ignition engines [26,40], including hybrids [41,42]. Moreover, since CO emissions are also associated to rich operation [43], CO and NH_3 emissions from gasoline vehicles have been shown to present a good correlation [30,36,44,45].

The present study investigates the emissions of NH_3 gasoline EU RDE type-approved vehicles, namely Euro 6d and 6d-TEMP, and their correlation to CO emissions. The results obtained will contribute the creation of more accurate emission inventories for these modern vehicles and would allow more reliable modelling of the N (nitrogen) cycle.

2. Experimental

Fifteen gasoline-fuelled vehicles meeting the Euro 6d or Euro 6d-TEMP standard were tested at the Joint Research Centre (JRC) vehicle emissions laboratories (VELA 8 and VELA 2) of the European Commission. All vehicles were tested over the type-approval worldwide-harmonized light-duty vehicles test cycle (WLTC) at 23 °C, and eight of them were also tested at -7 ± 3 °C on the same cycle. WLTC is the reference cycle used at type approval in the laboratory. It consists of four sections, characterised by different duration and increasing average speed, simulating urban to motorway driving. The cycle is a part of the worldwide-harmonized light vehicles test procedures, as presented in the UNECE global technical regulation no 15 (GTR15). Four vehicles were also tested using the ADAC (Allgemeiner Deutscher Automobil-Club e.V.) motorway cycle (also known as BAB 130, where BAB stands for Bundesautobahn, i.e., federal highway). BAB is a motorway cycle, characterised by high-speed driving, at constant speed alternated with short deceleration–acceleration events, to simulate an overtake. Figure 1 illustrates the cycles' speed profiles.

Figure 1. Test cycles speed profiles. Left panel: WLTC, right panel: BAB.

The tested vehicles covered a wide variety of powertrains, including eight conventional internal combustion engines (hereinafter ICE), two conventional or non-plug-in hybrids (hereinafter hybrids), and six plug-in hybrids (hereinafter PHEV). They also covered different fuel injection technologies, including direct injection (DI), port fuel injection (PFI), and a spark-controlled compression ignition (SPCCI). The after-treatment system of all vehicles tested, included a TWC, and most of them also used a GPF to control particulate emissions. Table 1 below summarises the main characteristics of the vehicles tested.

Tests were performed at VELA 8 and VELA 2, two chassis dynamometer climatic test cells with controlled temperature and relative humidity. The characteristics of the climatic test cells are described elsewhere [46,47]. For all the tests conducted, all regulated gaseous emissions (CO, HC, NMHC, and NO_x) were measured from the full dilution tunnel in real-time, using either an AMA i60 bench (AVL, Austria) or MEXA-7400HTR-LE (HORIBA, Japan), in VELA 8 and VELA 2, respectively.

NH₃ emissions were measured using three FTIR spectrometers. Two FTIRs SESAM i60 from AVL were used in the tests performed in VELA 8 and VELA 2. The systems are equipped with a heated polytetrafluoroethylene sampling line at 191 °C. The FTIR instruments (Nicolet Antaris IGS Analyser—Thermo Electron Scientific Instruments LLC, Madison, WI, USA) were equipped with a multipath gas cell with a 2 m optical path, downstream sampling pump (6.5 L/min sampling rate), and acquisition frequency of 1 Hz, with a working pressure of 860 hPa. Moreover, three vehicles were tested at VELA 2, using a MKS Multigas analyzer 2030-HS (MKS instruments, Wilmington, MA, USA). The device was equipped with a heated polytetrafluoroethylene sampling line at 191 °C, a multipath

gas cell with a 5.11 m optical path, upstream sampling pump (10 L/min sampling rate), and acquisition frequency of 5 Hz. Data were reported at 1 Hz.

Table 1. Characteristics of the vehicles tested; ICE: conventional internal combustion engine, hybrid: hybrid engine, PHEV: plug-in hybrid engine. DI: direct injection, PFI: port fuel injection, SPCCI: spark-controlled compression ignition.

#	Powertrain	Injection	Displacement (cm ³)	ICE Power (kW)	Euro Standard
1	ICE	SPCCI	1998	132	Euro 6d-ISC
2	ICE	DI	1499	100	Euro 6d-TEMP
3	ICE	DI	2498	129	Euro 6d-TEMP-EVAP-ISC
4	ICE	DI	1798	165	Euro 6d-TEMP
5	ICE	PFI	1199	61	Euro 6d-TEMP
6	ICE	PFI	1248	55.2	Euro 6d-TEMP
7	ICE	PFI	1398	64	Euro 6d-TEMP
8	Hybrid	DI	1988	90	Euro 6d-TEMP-EVAP
9	Hybrid	PFI	1798	72	Euro 6d-TEMP
10	PHEV	DI	1499	100	Euro 6d-TEMP-EVAP-ISC
11	PHEV	DI	1598	133	Euro 6d-ISC
12	PHEV	DI	1580	77.2	Euro 6d-TEMP
13	PHEV	DI	1499	100	Euro 6d-TEMP
14	PHEV	DI	1598	133	Euro 6d-ISC
15	PHEV	PFI	2360	99	Euro 6d-TEMP

The exhaust flow rate 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 critical flow Venturi. Mass emissions were derived from the exhaust gas flow rates (m³/s) and measured concentration (ppmV). The emission factors (mass per distance units) presented for the different vehicles at 23 °C, over the WLTC, correspond to the average of at least two tests performed at the same temperature and cycle for each vehicle.

The emissions presented for the PHEVs correspond to those obtained from charge-sustaining tests. This means that the vehicles were tested with the battery at their minimum state of charge. This approach was followed to be able to compare the different powertrains, pure ICE, hybrid, and PHEV, under more similar operative conditions.

3. Results and Discussion

The fifteen Euro 6d and Euro 6d-TEMP gasoline-fuelled vehicles emitted NH₃ when tested over the different driving cycles. As Figure 2 illustrates, these emissions vary from 1 to 9 mg/km for most vehicles tested at 23 °C, over the WLTC, with two vehicles presenting higher emissions, 16 and 53 mg/km, respectively. These two vehicles were both pure ICE GDI vehicles. Four of the tested vehicles presented low NH₃ emissions, 1–2 mg/km. They have different powertrains: three were PFI, and one was SPCCI.

Figure 2. Bar plots of average NH₃ and CO emissions emitted by fifteen vehicles on the WLTC, at 23 °C and at −7 °C. Error bars correspond to standard deviation.

NH₃ is formed in the TWC by the reaction of NO and H₂, according to reactions 3 and 4, presented below. H₂ is formed due to steam reforming of hydrocarbons (reaction 1) and/or the water gas shift of reaction 2 [34,35]. The air-to-fuel ratio significantly impacts the NH₃ formation, which increases as the conditions become richer. Hence, the formation of NH₃ needs the presence of H₂ and NO, under rich conditions.

CO emissions vary from 29 up to 1063 mg/km. Interestingly, the highest CO and NH₃ emissions are from the same vehicle. Two vehicles presented low CO emissions, below 100 mg/km; one was hybrid, and the other was PHEV. For reference the regulatory limit on the WLTC cycle, at 23 °C, in Europe, is 1000 mg/km.

The NH₃ emissions measured were comparable to those reported from Euro 4, 5, and 6b gasoline vehicles, tested under similar conditions [27,30,31,38,41,48]. This is in contrast with a recent remote sensing study, which suggests that absolute NH₃ emissions gradually decrease with increasing Euro class. It has been shown that for gasoline vehicles equipped with TWC, emissions of NH₃ increase along with the mileage [26,49,50]. Hence, the decreasing NH₃ emission trend with increasing Euro class reported by Farren et al. [50] could well be associated to an expected lower mileage of newer vehicles, i.e., those meeting Euro 6 standards, compared to previous ones.

Vehicles meeting Euro 6d and 6d-TEMP standards have entered the market very recently (2018). As consequence, the vehicles tested in this study have very low mileage (see Table 1). According to the aging effect, shown by previous studies, one could assume that, as these vehicles' catalyst age, their NH₃ emissions will likely increase.

Ageing of these catalytic systems has been linked, among other factors, to high temperatures to which automobile catalyst are exposed during driving (up to 1000 °C), leading to loss of activity and oxygen storage performance and, thus, the formation of NH₃ mainly at high operating temperatures [51].

Besides the air-to-fuel ratio, the operation temperature plays an important role in the formation of NH₃, as well [51]. For that reason, eight vehicles were also tested at −7 °C, over the WLTC. The results showed that for all vehicles NH₃ emissions increased

as the temperature decreased, as also shown in Figure 2. Higher emissions at sub-zero temperatures (i.e., -7°C) have also been linked, by several studies, to rich combustion, mainly during cold-start operation [30,31,37,41]. The use of rich mixture during cold-start at cold temperatures has been associated with improved combustion performances and/or overcoming the poor mixing of the inlet charge, as a result of the cylinder walls being cold [52,53]. This was also true for those vehicles that presented low NH_3 emissions at 23°C . At this temperature, the emissions varied from 9 to 27 mg/km . This is also in line with what has been shown for Euro 5 and Euro 6 vehicles, including hybrids and plug-in hybrid vehicles [42].

Figure 3 shows average CO and NH_3 emissions on the WLTC at 23°C and -7°C , as a function of the different engine technologies. It can be easily seen that pure ICE vehicles (left panel) tend to have a similar behaviour at the different temperatures, with an increase of approximately 25% of CO emissions at colder temperatures (CO increases from 395 up to 502 mg/km). NH_3 also increased from 13 to 18 mg/km at -7°C . Interestingly, the situation was significantly different for plug-in hybrids vehicles. These showed a better behaviour at 23°C (251 mg/km of CO and 5 mg/km of NH_3), with, however, an almost 4 times increase in emissions at -7°C (820 mg/km of CO and 20 mg/km of NH_3). Conventional hybrids were generally well-behaved, although only two vehicles for this category were tested.

Figure 3. Bar plots of average NH_3 and CO on the WLTC at 23°C and at -7°C for the different engine technologies.

Several studies have suggested that, due to the use of fuel enrichment, NH_3 emissions correlate well with CO emissions [27,30,31,36–38]. Gasoline vehicles present high CO emissions during rich operation, when fuel is in excess, with respect to air. These conditions also favour the formation of H_2 via reforming of hydrocarbons after the light-off of the catalyst. As summarised by reactions 3 and 4, the presence of H_2 and NO lead to the formation of NH_3 . Therefore, rich operation leads to both the emission of CO and conditions for the formation and emission of NH_3 . Hence, these emissions appear simultaneously during the vehicle operation, as shown with an example in Figure 4. This, in turn, results in the correlation of the emissions of these two pollutants.

Figure 5 shows that, for all the NH_3 and CO emissions (mass units) gathered in this study, the correlation was fair ($R^2 = 0.75$). For this analysis, only emissions recorded after the light-off temperature for NH_3 production on the catalyst are taken into consideration. This means that the CO peak, usually recorded in the initial phases of cold-start, is not considered, since, in this period, no NH_3 is produced, due to the low temperature, and the two phenomena are independent. The correlation improved to $R^2 > 0.85$ when the vehicles were subdivided by their powertrains in pure ICE and hybrids + PHEVs (see Figure 5, central and bottom panels). Although Figure 5 illustrates that higher emissions of CO are accompanied by higher emissions of NH_3 , attention shall be paid to the fact that the

correlations might be influenced by a few experimental points high concentration values, representing vehicles with high CO and NH₃ emissions. The analysis herein reported has been repeated, excluding these high emitters and obtaining correlation coefficients of 0.7, 0.68, and 0.73 for the top, central, and bottom panels, respectively. Beside the points at high CO and/or NH₃ concentration, it is evident from the scatter plot of Figure 5 that few vehicles do not follow the correlation with satisfactory agreement. This is an interesting point that will require additional investigation and may relate to different engine mapping or combustions strategies, as well as with catalysts with different precious metal ratios.

Figure 4. Example of CO (red line) and NH₃ (light blue line) emission profiles over a WLTC. Speed profile reported in grey.

Notice that, in both cases, the linear regression was performed without forcing the intercept to zero. Although this might have a slight impact on the R^2 , it was done to easily highlight the deviation at zero, with respect to an ideal behaviour.

CO emissions varied largely for the vehicles tested. In this case, the emissions factors ranged from 29 to 1061 mg/km, under the same conditions. As in the case of the NH₃, the emissions of CO also increased for all the vehicles, when they were tested at sub-zero temperatures.

The emissions of CO were an order of magnitude higher during the BAB cycle, compared to the WLTC for the four vehicles tested over this cycle. A summary of the emission factors, in the different cycles and for the vehicles considered, can be found in Table 2 below.

The BAB is a hot cycle that presents highly dynamic, high-speed, and high-load operations. For that reason, we have used it to investigate the possibility of enrichment events. Figure 6 shows that high peaks of CO are measured during the BAB's accelerations events, where fuel enrichment is expected to be triggered. Figure 6 also shows the good agreement between the CO and major NH₃ emission peaks (i.e., >10 ppm) in these acceleration events during motorway driving. This is in line with previous studies, which suggested that NH₃ emissions increased during strong acceleration events, as well as during dynamic cycles [44,54,55]. These studies associated the high NH₃ emissions over more dynamic cycles, once again, to rich operation [44,54,55].

Figure 5. NH₃ vs. CO concentrations correlation. Top panel: all measured emissions per vehicle for all tested vehicles. Central panel: all measured emissions from pure ICE vehicles. Bottom panel: all measured emissions from hybrids and PHEVs.

Table 2. Summary of emission factors for the vehicles tested (averaged values, if test is more than one).

#	WLTC CO (mg/km)	WLTC NH ₃ (mg/km)	BAB CO (mg/km)	BAB NH ₃ (mg/km)	WLTC @ −7 °C CO (mg/km)	WLTC @ −7 °C NH ₃ (mg/km)	BAB @ −7 °C CO (mg/km)	BAB @ −7 °C NH ₃ (mg/km)
1	126	2	2424	9	474	9	-	-
2	243	16	-	-	530	27	-	-
3	1063	53	-	-	-	-	-	-
4	240	7	-	-	-	-	-	-
5	178	2	-	-	-	-	-	-
6	274	9	-	-	-	-	-	-
7	532	6	-	-	-	-	-	-
8	126	6	-	-	-	-	-	-
9	29	1	-	-	-	-	-	-
10	358	9	4170	20	746	21	-	-
11	332	4	2417	8	740	15	1141	6
12	34	5	-	-	772	26	-	-
13	319	8	-	-	-	-	-	-
14	274	3	5591	11	850	24	-	-
15	188	1	-	-	1040	16	-	-

Figure 6. Examples of emission profile of NH₃ (light blue lines) and CO (red line lines) during a BAB. Left panel: vehicle #1; right panel: vehicle #10. Speed profile reported in grey.

Following these considerations, the emissions obtained, during what can be considered the urban phases of the WLTC (low and medium phases, see Figure 1), where driving is not aggressive and at relatively low speeds, were compared to those measured during a portion of the BAB covering the same distance (approx. 8 km). The four vehicles presented 4 to 8 times higher emissions during the BAB operation (16–63 mg/km) than during the “urban” operation (3–11 mg/km), which, in turn, were higher than those measured during the whole WLTC.

4. Conclusions

Fifteen gasoline-fuelled vehicles, meeting the Euro 6d or 6d-TEMP standard, were tested over the type-approval WLTC, at 23 °C, eight of which were also tested at -7 ± 3 °C, on the same cycle, and four were also tested using the ADAC highway cycle (BAB 130).

All the vehicles tested emitted NH_3 over the different driving cycles. The NH_3 emissions increased when the vehicles were tested at -7°C . The NH_3 emissions measured from these Euro 6d or 6d-TEMP vehicles were comparable to those reported from the Euro 4, 5, and 6b gasoline vehicles, tested under similar conditions.

The emissions of NH_3 and CO, subdivided by their powertrains, in pure ICE and hybrids+PHEVs, resulted in a fair correlation with $R^2 > 0.75$. Moreover, excellent agreement between the CO and the NH_3 emission peaks was registered during the acceleration events of the BAB cycle.

Higher emissions at sub-zero temperatures have been associated to rich combustion during cold-start operation, and the correlation of NH_3 and CO emissions have been shown to be linked to fuel enrichment. Therefore, the combined presence of emissions of NH_3 and CO during a test can be used as an indicator to recognise fuel enrichment events.

Author Contributions: Conceptualisation, T.S., R.S.-B., P.B.; Formal analysis, T.S., R.S.-B., A.M.; Writing—original main draft preparation, R.S.-B.; Writing—additional writing, reviewing and editing, T.S., R.S.-B., A.M., P.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: Authors would like to acknowledge the support and collaboration of A. Bonamin, M. Carriero, P. Le Lijour, M. Sculati, M. Otura-Garcia, M. Centurelli, C. Ferrarese, L. Bigozzi, C. Bonato, and A. Migneco.

Conflicts of Interest: The authors declare no conflict of interest.

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