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NH₃ and N₂O Real World Emissions Measurement from a CNG Heavy Duty Vehicle Using On-Board Measurement Systems

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Abstract: The development and utilization of a series of after-treatment devices in modern vehicles has led to an increase in emissions of NH₃ and/or N₂O with respect to the past. N₂O is a long-lived greenhouse gas and an ozone-depleting substance, while NH₃ is a precursor of secondary aerosols in the atmosphere. Certain regions, e.g., the EU and the USA, have introduced limits to the emissions of NH₃ or N₂O for vehicles tested in the laboratory. However, due to the lack of on-board systems that allow for the measurement of these compounds when the regulations were developed, these vehicles' real-world emissions have not been regulated. This work evaluates on-board systems that could allow measuring real-world emissions of NH₃ and N₂O from heavy-duty vehicles. In particular, emissions of NH₃ or N₂O from a Euro VI Step D urban/interurban bus fueled with Compressed Natural Gas were measured using the HORIBA's OBS-ONE-XL, which is based on a specifically developed technique called Infrared Laser Absorption Modulation, and uses a Quantum Cascade Laser as a light source. They were also measured using the PEMS-LAB, which is a more conventional FTIR-based system. Emissions were measured under real-world driving conditions on the road and in a climatic test cell at different ambient temperatures. For most of the conditions tested, the on-board systems correlated well with a laboratory-grade FTIR used as reference. In addition, a good correlation with R² > 0.9 was found for the N₂O concentrations measured by OBS-ONE-XL and PEMS-LAB during on-road testing.

Keywords: transport emissions; ammonia; nitrous oxide; portable emissions measurements

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1. Introduction

The implementation of the vehicle emission regulations in Europe—commonly known as Euro standards—has resulted in a reduction in the emissions of a number of air pollutants from the road transport sector [1–3]. However, despite this positive development, additional efforts are being discussed to counteract the effects of certain trends (such as increases in population and in economic output) currently eroding the beneficial effects of the aforementioned regulations [1]. In order to meet the Euro VI NO_x emission standards, heavy-duty (HD) Diesel vehicles have been equipped with Selective Catalytic Systems (SCRs), and HD compressed natural gas (CNG) vehicles use three-way catalytic converters (TWCs). While reducing the emissions of NO_x, the use of SCRs and TWCs can lead to substantial emissions of other two pollutants, ammonia (NH₃) and nitrous oxide (N₂O). As a result, the concentrations of NH₃ and/or N₂O measured from the exhaust of modern vehicles can be higher than those of NO_x under some operative conditions [4,5].

N₂O is a long-lived greenhouse gas (GHG) with an atmospheric lifetime of 121 years and a 100-year time horizon global warming potential (GWP) of 298 CO₂ equivalent [6].

Moreover, it has been indicated that N_2O released in the atmosphere from anthropogenic sources is the single most important ozone-depleting substance (ODS) [7]. NH_3 , on the other hand, is a pollutant that leads to the formation of ammonium nitrate and ammonium sulfate [8]. It has been widely reported that the deposition of these ammonium salts leads to eutrophication of waters and acidification of soils, negatively affecting nitrogen-containing ecosystems [9–11]. It is important to mention that, according to the last SOER report of EEA [12], anthropogenic-induced alterations to the N-cycle are much more significant than those to the C-cycle, with there being significant concerns for their impact on biodiversity and ecosystems in general. Moreover, ammonium salts are the most abundant atmospheric secondary inorganic aerosols in many regions [13], and they deteriorate urban air quality [14], affect human health [15], and impact the global radiation budget [16].

The HD Euro VI Regulation (EC) No 595/2009 [17] prescribes emission limits of NO_x , CO, PN, PM, NMHC and CH_4 from positive ignition engines (THC in cases of compression ignition engines). It introduced the in-use emission test using portable emissions measurement systems (PEMS) at type approval, and PEMS-based in-service conformity (ISC) verifications. The ISC test is carried out on-road and, since the introduction of the Euro VI Step E, includes the measurement of all the pollutants regulated in the laboratory, the only exception being NH_3 .

The U.S. Environmental Protection Agency (EPA) developed a GHG emissions program, under the Clean Air Act [18], that includes N_2O emission standards of 0.10 g/bhp-h (i.e., 0.133 g/kWh). The measurements are conducted in the laboratory over the Heavy-Duty Engine FTP cycle.

Therefore, although the European Union (EU) and the US EPA have developed standards to limit the emissions of NH_3 or N_2O from HD vehicles, the release of these pollutants during real-world operation is not verified or regulated. The main reason for this was the absence of dedicated portable systems that allow for reliable measurements of these compounds under real-world driving conditions when the regulations were developed. A similar situation is experienced for light-duty vehicles, which face the same technical challenges. In addition, for these vehicles currently, there is no limit for NH_3 emissions.

Previous studies have shown that on-road emissions of NH_3 and N_2O can be reliably measured in HD Diesel vehicles using laboratory grade quantum cascade laser based analysers (QCL-IR) [19,20]. Other studies have investigated the emissions of NH_3 and N_2O from light-duty and light-commercial vehicles using laboratory grade FTIRs [21,22].

The future Euro VII regulation on heavy-duty vehicles appears to move in the direction of including NH_3 and N_2O measurement on-road [23]. Thus, the objective of this study is to evaluate currently available on-board systems that allow for the measurement of real-world emissions of NH_3 and N_2O from HD vehicles. To that aim, a Euro VI Step D CNG bus was tested using two portable instruments: one based on a specifically developed technique known as Infrared Laser Absorption Modulation in tandem with Quantum Cascade Laser as a light source, the HORIBA's OBS-ONE-XL, and an FTIR-based PEMS system, the PEMS-LAB from CERTAM and ADDAIR.

2. Experimental Section

A Euro VI Step D urban/interurban bus fueled with Compressed Natural Gas (hereinafter HD-CNG) was tested on-road and at the heavy-duty Vehicle Emissions Laboratories (hereinafter VELA7) of the Joint Research Centre (JRC) in Ispra, Italy. The vehicle specifications are summarized in Table 1. The measurement setup used on the road and at VELA7 is illustrated in Figure 1.

Table 1. Vehicle specifications.

Production Month/Year	6/2019
Vehicle category	M3 Class I
Emission standard	Euro VI step D
Fuel type	CNG
Mileage (km)	~66,000
Length (m)	12
Vehicle mass empty (kg)/max (kg)	12,085/19,300
Max Speed (km/h)	85
Axle configuration	2 axis/4 wheels/6 tires
Transmissions	Automatic transmission
Displacement (cm ³)	8710
Cylinders	6 in-line
Engine max power (kW)	264 at 2000 rpm
Engine max torque (Nm)	1640
After-treatment	TWC

Figure 1. Measurement setup used during the tests performed on-road (**top**) and at VELA7 (**bottom**).

On the road, the HD-CNG was tested using a route that meets the Euro VI ISC requirements (see Table 2). Figure 2 illustrates the speed profile of the route used. Three tests were performed. During the on-road tests, emissions of NH_3 and N_2O , as well as those of the EU-regulated gaseous pollutants (NO_x , CO, hydrocarbons and CH_4) and CO_2 were measured. The pollutants and CO_2 were measured using a PEMS—AVL MOVE (AVL, Graz, Austria—model 2016). NH_3 and N_2O were measured using the HORIBA's OBS-ONE-XL and the PEMS-LAB from CERTAM and ADDAIR.

Table 2. Route characteristics.

Total Trip Duration	min.	187
Total trip distance	km	122
Trip Work	kWh	110
Average Speed	km/h	39
Average Temperature	K	279
Average Relative Humidity	%	55
Average Altitude	m	249
Urban distance	km	38.50
Rural distance	km	26.37
Motorway distance	km	57.30
Initial coolant temperature	K	289

Figure 2. Speed profile of the on-road tests (**top panel**) and WHVC test (**bottom panel**).

The AVL MOVE system measures from the exhaust gas concentrations of: CO and CO₂ using a non-dispersive infrared sensor; NO and NO₂ using a non-dispersive ultra-violet sensor; and methane and hydrocarbons using a flame ionization detector. Furthermore, this PEMS consisted of: a tailpipe attachment, heated exhaust sampling lines, an exhaust flow meter (EFM), a data logger connected to the vehicle's on-board diagnostics (OBD) port, GPS, and a weather station for ambient temperature and humidity measurements. All relevant emissions data were recorded at a frequency of 10 Hz. Data were reported at 1 Hz after being resampled using a 1 Hz moving average window.

The OBS-ONE-XL is an on-board emissions measurement system that enables the on-board measurement of NH₃ and N₂O from vehicle exhaust gas under real-world driving conditions. The system applies Infrared Laser Absorption Modulation (IRLAM) technology, which is based on infrared absorption spectroscopy, and uses a Quantum Cascade Laser (QCL) as a light source. A QCL can emit light with a very narrow wavelength width in

the mid-IR region where many gas components have strong absorption bands. By using a finely-tuned laser that matches the absorption spectrum of a specific gaseous component, it is possible to measure the targeted species accurately in a complex sample gas mixture. More information can be found in Shibuya et al., 2021 [24].

The OBS-ONE-XL consists of three main units—a sampling probe, analyzer and PC (user interface). The sampling probe used in this setup has a length of 6 m and a polytetrafluoroethylene (PTFE) inner tube with an in-line filter, and is heated at 113 °C in order to ensure fast response time, low adsorption and no condensation. The in-line quartz filter element is specifically designed for the measurement of NH₃ emissions. The heated and filtered sample is passed through a compact gas sampling cell, called the Herriott Cell, with an optical path length of 5 m and an internal volume of 50 cm³, which is operated at 113 °C and 50 kPa. The wavelengths of the QCLs for measuring N₂O and NH₃ are around 7.8 µm and 10.1 µm, respectively. Each QCL modulates the wavelength over a range of about 0.5 cm^{−1}, and acquires an absorption signal with a spectral resolution of about 0.001 cm^{−1}, which corresponds to the laser linewidth. The absorption signal is detected with a non-cooled InAsSb photovoltaic detector. The gas is sampled with a flow rate of approximately 3.3 L min^{−1}. The PC serves as the user interface for the operation of the analyzer, the calculation, and to display the measured concentrations. In this configuration, the device's measurement ranges are 0–1000 ppm for N₂O and 0–1500 ppm for NH₃. The estimated LoD, 3× standard deviation, of the instrument used in this test is 0.06 ppm and 0.09 ppm, respectively. The acquisition frequency is 10 Hz [25].

The PEMS-LAB is an on-board metrology experimental platform conceived to measure gases and particle number from vehicle tailpipe emissions in real driving conditions on road. It includes: a portable FTIR analyzer (p-FTIR); a PEGASOR Particle Sensor PPS-M for solid particulate number (PN) measurement; a dedicated weather station for ambient temperature, pressure and relative humidity measurement; an EFM module. For the purpose of this campaign, the PEMS-LAB's EFM module was not used. A PTFE tube is used to sample raw exhaust directly from the vehicle tailpipe, and it is heated at 220 °C to avoid condensation and/or adsorption of hydrophilic compounds (e.g., NH₃). The sampling rate is 8.5 L min^{−1}. The frequency of acquisition is 1 Hz. The p-FTIR consists of a cell with an internal volume of 200 cm³, a fixed optical path of 2 m, and windows of BaF₂, and uses a mercury cadmium telluride (MCT) thermoelectrically (Peltier) cooled detector. The cell works at 180 °C and atmospheric pressure. A shock resistant interferometer with a spectral range of 900–4200 cm^{−1} and a resolution of 8 cm^{−1} completes the instrument.

At VELA7, the vehicle was tested under the World-Harmonized heavy-duty Vehicle Cycle (WHVC) using four different ambient temperatures: 35 °C, 23 °C, 0 °C and −7 °C. This cycle is a transposition on the chassis dyno of the homologation Type Approval cycle (WHTC—World Harmonized Transient Cycle) that is performed only on the engine at the dyno test bench. The speed profile of the test cycle is reported in Figure 2 above. All the tests were performed with the vehicle carrying 50–60% of its maximum allowed payload at test start. Vehicle coolant temperature matched the ambient temperature (±3 °C) when the test started. It should be noted that due to a technical problem, the PEMS-LAB was not used during the laboratory test performed at 23 °C.

VELA7 is a climatic test cell that comprises a 2-axis roller dynamometer (72" inches) dedicated to heavy-duty vehicle testing. The exhaust gas was connected to the full dilution tunnel, with a 9 m transferline feeding a full dilution tunnel with constant volume sampler (CVS). Criteria pollutants NO_x, CO, HC and CH₄ were measured using AVL AMA i60 analyzers (both the raw exhaust and the dilution tunnel). VELA7 is also equipped with a laboratory grade FTIR spectrometer (Nicolet Antaris IGS Analyzer—Thermo Electron Scientific Instruments LLC, Madison, WI, USA)—SESAM—that allows for the measurement of NH₃ and N₂O. The SESAM was connected along the OBS-ONE-XL and the PEMS-LAB to the vehicle's tailpipe. It uses a heated PTFE sampling line (191 °C). This FTIR was equipped with a multipath gas cell with 2 m of optical path and a downstream sampling pump (6.5 L min^{−1} flowrate), and had the acquisition frequency of 1 Hz with a working

pressure of 860 hPa. The FTIR was made up with a Michelson interferometer (spectral resolution: 0.5 cm^{-1} , spectral range: $600\text{--}3500\text{ cm}^{-1}$) and a liquid-nitrogen-cooled mercury cadmium telluride detector.

To be able to compare the OBS-ONE-XL with another system having an acquisition frequency of 10 Hz (see Section 3), a laboratory-grade QCL-IR (MEXA-ONE-QL-NX) was also used during two dedicated tests performed in the VELA7. The MEXA-ONE-QL-NX measures four nitrogen compounds (NO , NO_2 , N_2O , NH_3) simultaneously by using a QCL light source and Infrared Absorption Spectroscopy (IR spectroscopy) as the measuring principle. The analyzer utilizes a high resolution spectrum and a high vacuum optical cell in order to minimize the interference offered by the co-existing gases. Moreover, the ammonia response has been improved by using a vacuum sample transfer line maintained at a temperature of $113\text{ }^\circ\text{C}$. The system consists of three main components—a Main Control Unit, an analyzer unit and a heated filter (F-01HN). The F-01HN contains a quartz filter element specifically designed to minimize the adsorption of the ammonia molecules present in the exhaust gas. The heated filter is connected to the analyzer unit via a heated line. The sampling of the exhaust is conducted using an insulated stainless steel sampling probe placed in front of the system's pre-filter, and a 10 m heated line connecting the pre-filter and the QCL.

For the chassis dyno tests performed in this study, the concentrations of N_2O and NH_3 measured by the OBS-ONE-XL and the PEMS-LAB were compared to those measured by the laboratory-grade FTIR. The laboratory-grade FTIR (and the QCL-IR in two dedicated tests) was selected as the reference method because FTIR and QCL-IR are two of the techniques prescribed in the EU Regulation 582/2011 [26] and UNECE GTR-15 [27] to measure NH_3 emissions from heavy-duty exhaust and light-duty exhaust, respectively. Furthermore, the UNECE GTR-15 also indicates that N_2O emissions can be measured from light-duty vehicle exhaust using FTIR and QCL-IR, among other techniques (e.g., GC-ECD and NDIR). The regression lines presented in the study were fitted to zero.

3. Results and Discussion

The exhaust emissions of N_2O and NH_3 from the HD-CNG, an interurban bus meeting the Euro VI Step D standard, were measured during real world operation on the road, in real traffic conditions, and at the JRC's VELA7 climatic cell on a dual-chassis dynamometer over the WHVC. In the VELA7, the tests were performed using three instruments: a laboratory grade FTIR (SESAM), an on-board FTIR (PEMS-LAB), and an on-board IRLAM (OBS-ONE-XL), at four different ambient temperatures, $35\text{ }^\circ\text{C}$, $23\text{ }^\circ\text{C}$, $0\text{ }^\circ\text{C}$ and $-7\text{ }^\circ\text{C}$. On the road, emissions of N_2O and NH_3 were measured using the PEMS-LAB and the OBS-ONE-XL over three different tests with ambient temperatures ranging from $4\text{ }^\circ\text{C}$ to $8\text{ }^\circ\text{C}$.

3.1. NH_3 and N_2O Emissions Measurements at Different Ambient Temperatures

The tests performed in the VELA7 already show that the HD-CNG presented N_2O emissions during a short fraction of time during the catalyst light-off. For that reason, Figure 3 shows the first 300 s of the test, in which all N_2O emissions took place. This is in line with what has been previously reported for light-duty positive ignition vehicles equipped with TWC [22]. The concentrations and emission profiles changed slightly between the warm temperatures ($35\text{ }^\circ\text{C}$ and $23\text{ }^\circ\text{C}$) and the cold temperatures ($0\text{ }^\circ\text{C}$ and $-7\text{ }^\circ\text{C}$), and higher N_2O emissions were presented at warmer temperatures compared to the cold ones. Nonetheless, the overall emission pattern, with N_2O emissions taking place only during the catalyst light-off, was not affected by the ambient temperature.

Figure 3. (Left panels) N₂O emission profiles measured using the SESAM (blue), PEMS-LAB (orange) and OBS-ONE-XL (grey) over the first 300 s of WHVC at 35 °C, 23 °C, 0 °C and -7 °C. (Right panels) Correlation of the N₂O concentrations measured by the SESAM plotted against the N₂O concentrations measured by the PEMS-LAB (orange) and against the OBS-ONE-XL (grey). The PEMS-LAB's trend line is represented by a solid black line and the OBS-ONE-XL's trend line is represented by a dashed black line.

All three instruments presented highly comparable N₂O emission profiles under all the studied conditions, with the exception of the PEMS-LAB at -7 °C. The higher noise present for the PEMS-LAB at this very low temperature could be explained by the high concentration of water that can be present in the exhaust of a CNG engine at this cold temperature due to a decrease in the air to fuel ratio or due to water being condensed in the very cold exhaust lines. At high concentrations, the water can be a source of cross-interference due to the lower spectral resolution of the instrument (8 cm^{-1}) compared to the SESAM (0.5 cm^{-1}). In fact, it has been shown that for resolutions lower than 0.5 cm^{-1} , the absorbance bands of water may create interferences, affecting the detection limits of many

compounds [28]. Although to a much lower extent, the interference on the PEMS-LAB measurement can already be noticed during the test performed at 0 °C (see Figure 3).

The R^2 of the N_2O concentrations measured by the PEMS-LAB compared to those measured by the SESAM, was >0.9 for the tests at 35 °C and 0 °C, resulting in a good correlation for the two instruments. A similar result was also obtained for the N_2O concentrations measured by the OBS-ONE-XL, with R^2 ranging from 0.85 to 0.95 for the four temperatures tested. These figures are comparable to the correlation obtained for the N_2O concentrations measured by two laboratory-grade FTIRs [22]. Even though the correlation was good for the range of concentrations measured, it seemed that the correlation of the instruments was better at concentrations up to 50 ppm N_2O . This suggests that some factors, such as response time and time resolution, may have played a role in the obtained results.

The measurement of NH_3 emissions from vehicle exhaust has always been considered challenging as compared to other regulated gases [29,30]. The main reason is that NH_3 can readily adsorb on the setup's surfaces if the sample is not properly handled. For that reason, EU 582/2011 and GTR-15 prescribed the measurement of NH_3 emissions from heavy- and light-duty vehicles to be performed at the tailpipe. This prevents NH_3 from being adsorbed on the CVS walls or other possible cold points of the transferline. Moreover, the sampling lines need to be kept above 100 °C to avoid water condensation, which leads to the loss of hygroscopic compounds such as NH_3 , resulting in wrong estimations of the emissions. Most FTIR systems, such as those used in the present study, operate at 191 °C. On the other hand, in the presence of $HNCO$, a high sample line temperature can decompose the molecule producing NH_3 [31]. Thus, some instruments, such as the OBS-ONE-XL and the MEXA-ONE-QL-NX used in the present study, operate at 113 °C.

Figure 4 shows that the NH_3 emissions of the HD-CNG began at the catalyst light-off. The emissions then continued during high acceleration events. As in the case of N_2O , this is in line with what has been previously reported for light-duty positive ignition vehicles equipped with TWC, including CNG vehicles [32]. The NH_3 emissions increased as the temperature decreased. The duration of the first emission peak during the catalyst light-off was also longer. A similar behavior has been shown for positive ignition light-duty engines equipped with TWC tested at sub-zero temperatures [33,34].

The three instruments presented highly comparable NH_3 emission profiles under all the studied conditions, with the exception of the PEMS-LAB at −7 °C, where the PEMS-LAB may have suffered from the high water content in the exhaust. The SESAM and the PEMS-LAB, both measuring using the same principle, FTIR spectroscopy, and at the same measuring rate, 1 Hz, presented closer emission profiles for the tests at 35 °C and 0 °C than the OBS-ONE-XL. The correlation of the NH_3 concentrations measured by these two instruments was good, resulting in R^2 of 0.87 and 0.96 for the tests at 35 °C and 0 °C, respectively. The R^2 at −7 °C was 0.45, probably due to the water interference.

The OBS-ONE-XL, which measures and reports the concentrations at a 10-Hz frequency, showed higher maximum NH_3 concentrations, with the NH_3 peaks being sharper and better defined. The same pattern was previously reported during an intercomparison study where NH_3 emissions were measured from a TWC-equipped light-duty vehicle with a QCL-IR measuring at a 10-Hz frequency and a FTIR measuring at 1 Hz [35]. It should also be noted that while the SESAM and the PEMS-LAB are used to measure a wide variety of compounds, the OBS-ONE-XL has been developed and optimized for the measurement of N_2O and NH_3 . This optimization includes among other important elements a dedicated quartz filter that reduces adsorption of NH_3 . The effects of this optimization can be seen in the faster response time of the OBS-ONE-XL compared to the other two systems, as well as in the absence of the tailing on the measured peaks after the vehicle accelerations, which can be attributed to NH_3 adsorption. All these elements lead to some differences in the concentrations measured with the two different techniques (IRLAM and FTIR). However, very good correlations were obtained at 0 °C and −7 °C, and a good correlation at 23 °C, where the R^2 values were >0.9 and 0.7, respectively. The largest differences between the OBS-ONE-XL and the FTIR instruments were found at 35 °C, with $R^2 = 0.43$. However, a

second test performed at the same temperature showed a substantially better correlation, $R^2 = 0.72$, between the OBS-ONE-XL and the SESAM (see Figure 5) and a very good correlation ($R^2 = 0.90$) with a laboratory grade QCL-IR (MEXA- ONE-QL-NX) used in the same experiment. The results are in line with, or better than, those obtained when comparing the NH_3 concentrations measured by two laboratory-grade FTIRs [34,36].

Figure 4. (Left panels) NH_3 emission profiles measured using the SESAM (blue), PEMS-LAB (orange) and OBS-ONE-XL (grey) over the WHVC at 35 °C, 23 °C, 0 °C and -7 °C. (Right panels) Correlation of the NH_3 concentrations measured by the SESAM plotted against the NH_3 concentrations measured by the PEMS-LAB (orange) and against the OBS-ONE-XL (grey). The PEMS-LAB's trend line is represented by a solid black line and the OBS-ONE-XL's trend line is represented by a dashed black line.

Figure 5. (Top panel) NH₃ emission profiles measured using the SESAM (blue), the OBS-ONE-XL (grey) and the MEXA-ONE-QL-NX (yellow) over the WHVC at 35 °C. Correlation of the NH₃ concentrations measured by the OBS-ONE-XL plotted against that measured by the SESAM (central panel) and against the MEXA-ONE-QL-NX (bottom panel).

3.2. On-Road Measurement of NH₃ and N₂O Emissions

Figures 6 and 7 illustrate the emissions of N₂O and NH₃ measured on the road using the two on-board systems, the OBS-ONE-XL and the PEMS-LAB. As for the laboratory experiments, the emission profiles recorded by the two instruments were highly comparable, with the N₂O concentrations measured presenting better agreement than the concentrations of NH₃ (see Figure 6). The correlation of the N₂O concentrations measured by the instruments was again very good, with an $R^2 > 0.9$. However, the correlation of the NH₃ concentrations was poor. Although both instruments reported the emission events at the same time (see Figure 7), the OBS-ONE-XL provided better peak resolution for the NH₃ than the PEMS-LAB. This shows that the PEMS-LAB system, using an 8 cm^{−1} spectral resolution and without an optimization for the NH₃ measurement, struggled to provide

reliable readings of NH_3 under the challenging conditions represented by the HD-CNG's exhaust, which has high water content.

Figure 6. (Left panel) N_2O emission profiles measured on-road using the OBS-ONE-XL (grey) and the PEMS-LAB (orange) over the real-driving conditions. The left panel also shows a close up on the first 400 s. (Right panel) Correlation of the N_2O concentrations measured by the OBS-ONE-XL plotted against that measured by the PEMS-LAB.

Figure 7. NH_3 emission profiles measured during an on-road test using the OBS-ONE-XL (grey) and the PEMS-LAB (orange) over the real driving conditions.

The N_2O and NH_3 emissions measured from the HD-CNG on-road and in the laboratory were substantially different from those reported from a Euro VI HD Diesel vehicle equipped with a Diesel Oxidation Catalyst (DOC), a Selective Catalytic Reduction system (SCR) and an Ammonia Slip Catalyst (ASC) [19]. This is because the emissions of N_2O and NH_3 from the two different powertrains are related to different chemical and physical processes. In TWC-equipped vehicles, such as the HD-CNG tested in this study, their emissions are linked to a series of catalytic reactions that take place on the TWC, involving CO, NO, H_2 and H_2O [37,38]. On the other hand, Diesel HDVs' emissions of N_2O and NH_3 are linked to the use of DOC, SCR and/or ASC after-treatment systems and the use of urea aqueous solution to reduce NOx emissions (for more detailed information, see Selleri et al., 2021 [3] and the reference therein).

The N_2O emissions from the HD-CNG were lower than those reported for the HD Diesel vehicle. However, NH_3 emissions were more frequent and had higher concentrations than those reported for the Euro VI HD Diesel.

One of the three on-road tests presented a particular NH_3 emission profile (see Figure 7). During this test, the vehicle was kept on idle for about 600 s to resume the OBD connection of the PEMS system. The NH_3 concentrations measured by the instruments increased, reaching values close to 500 ppm. As Figure 7 illustrates, the emissions measured by the OBS-ONE-XL showed a sort of harmonic oscillation. Although the PEMS-LAB reported higher concentrations, it did not show the quickly oscillating behavior.

In order to clarify whether this behavior might be related to an interference or to a malfunctioning of the specific instrument, a dedicated idle test was performed in the

laboratory using both a QCL-IR (MEXA-ONE-QL-NX) measuring NH_3 at 10 Hz frequency and the FTIR SESAM measuring at 1 Hz. As shown in Figure 8, the NH_3 concentrations increased after approximately 300 s of constant idle. The MEXA-ONE-QL-NX and OBS-ONE-XL, both measuring at 10 Hz, both reproduced the same kind of profile measured during the on-road test, suggesting that the vehicle presents this behavior during idle. The SESAM followed the same overall emission profile; however, its emissions did not show the highly changing concentrations. This is possibly due to its measurement frequency and the cell's volume.

Figure 8. NH_3 emission profiles measured during an idle test using the OBS-ONE-XL (grey), the MEXA-ONE-QL-NX (yellow) and the SESAM (blue) at the VELA7 facilities.

Beside the particular case related to idle operation, NH_3 emissions took place during the TWC light-off and during the acceleration events, with most peaks taking place during the motorway operation. This is in line with what has been reported for on-road operation of CNG light-commercial vehicles (LCV) and other positive ignition engines using TWC [22,33]. However, the concentrations of NH_3 measured on the road from the tested HD-CNG were substantially lower than those reported for the CNG LCV [22]. This could have resulted from the average 10 ppm limit that the HD has to meet in the Euro VI regulatory test performed in the laboratory, while the Euro 6 LCVs did not have an NH_3 limit yet.

4. Conclusions

The measurement of NH_3 and N_2O emissions from a Euro VI Step D urban/interurban CNG bus using two different on-board instruments, the OBS-ONE-XL, which used an IRLAM, and the PEMS-LAB, which used an FTIR, was performed on the road and at the JRC's heavy-duty Vehicle Emissions Laboratories (VELA7) facilities. At VELA7, the tests were performed at four different ambient temperatures, 35 °C, 23 °C, 0 °C and −7 °C.

Both instruments presented good correlations with laboratory-grade FTIR for the measurement of N_2O and NH_3 at all tested conditions. The PEMS-LAB showed limitations in the measurement at sub-zero temperatures, when water concentration in the CNG engine exhaust is high. Interestingly, the SESAM, which uses the same measuring principle, FTIR, did not show this problem. Hence, special attention is needed when the exhaust measured can present high water concentrations. Moreover, FTIRs with a spectral resolution of at least 0.5 cm^{-1} are recommended for these measurements.

On the road, the correlation of the N_2O concentrations measured by the two on-board systems, OBS-ONE-XL and PEMS-LAB, was good, with an $R^2 = 0.95$ obtained. In the case of the NH_3 emissions, the OBS-ONE-XL showed a more accurate performance, with sharper, better defined peaks, and less tailing effects related to NH_3 adsorption on the setup obtained.

The study showed that N_2O and NH_3 concentrations from CNG-HD vehicles can be reliably measured during real world driving operations in a wide range of temperatures and driving conditions. Although further research is needed to assess the performance of the on-board systems when using other types of fuels (Diesel, gasoline, others), the OBS-ONE-XL showed a comparable performance to laboratory-grade instrumentation for

the measurement of N_2O and NH_3 , covering the full temperature range of what has been called normal operation in the Euro VII discussions (from -7°C to 35°C).

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