INVESTIGATION OF THE FORMATION OF NH_3 EMISSIONS AS A FUNCTION OF VEHICLE LOAD AND OPERATING CONDITION

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ABSTRACT

The objective of this study was to examine ammonia (NH_3) exhaust emissions as a function of different vehicle operating conditions and cycles. A total of eight vehicles with low-emission vehicle (LEV) to super-ultra-low-emission vehicle (SULEV) certification were tested over the Federal Test Procedure (FTP75), a US06 cycle, a hot running 505, a New York City Cycle (NYCC), and a specially designed Modal Emissions Cycle (MEC01v7) using both as-received and bench-aged catalysts. Modal NH_3 emissions measurements in the raw exhaust were obtained using a tunable diode laser (TDL). The results show that NH_3 emissions are cycle-dependent, with higher emissions found for more aggressive cycles. Modal emissions data show that NH_3 emissions are primarily generated during acceleration events, although for some vehicles NH_3 emissions are formed in the period immediately after catalyst light-off. Strong correlations were found between tailpipe NH_3 measurements and both vehicle specific power (VSP) and engine-out carbon monoxide (CO) emissions. The correlation with CO is consistent with the role of CO in forming NH_3 emissions via the water-gas shift reaction. Statistically significant but weaker correlations were found between NH_3 emissions and engine-out total hydrocarbons (THC), oxides of nitrogen (NO_x), and air/fuel (A/F) ratio.

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1. Introduction

Understanding the relationship between emissions and mode of vehicle operation is one of the most critical aspects of accurately quantifying vehicle emissions. In recent years, there has been an increased effort to develop more extensive databases of modal vehicle emissions and subsequently utilize these data for model development. The United States Environmental Protection Agency (EPA) has recently begun to develop a new Multi-Scale Motor Vehicle and Equipment Emissions System (MOVES) model that will utilize real-time data for emissions estimates (*1*). In a preliminary modeling "shootout," EPA concluded that approaches using both modal binning as well as vehicle specific power (VSP) were promising for modeling emissions (*1,2*).

While there have been considerable efforts to characterize and understand real-time emissions of regulated pollutants, fewer data are available for emissions of unregulated mobile-source emissions such as ammonia (NH_3). NH_3 is known to contribute to the production of secondary particulate matter (PM), and some recent studies have indicated that NH_3 emission rates from automobiles may be higher than previously estimated, although a wide range of NH_3 emissions estimates have been reported for vehicles (*3-13*). At present, it is estimated that mobile sources are the third-largest source of NH_3 emissions and account for approximately 18% of the inventory in the greater Los Angeles area (*14*).

Studies of the emission rates and formation mechanisms of NH_3 in vehicle exhaust date back to the 1970s (*15-21*). A number of early studies showed that NH_3 formation can be attributed primarily to reactions that occur over the catalyst (*22-27*). Gandhi and Shelef (*25,26*) found that hydrogen produced in the water-gas shift reaction could be a major contributor to NH_3

formation. Studies have also shown that the operating condition of the vehicle plays an important role in the formation of NH_3 in vehicle exhaust. Researchers have found that NH_3 emissions can be more prevalent under conditions where the vehicles are malfunctioning or running rich (*12,20*) or over aggressive driving cycles (*6*). Remote sensing studies, on the other hand, have shown high NH_3 emission levels can also be found even under near stoichiometric conditions (*5*). Clearly, to better understand and eventually to model NH_3 emissions in vehicle exhaust, it is important to understand how a number of factors contribute to NH_3 production, including vehicle technology and operating modes, catalyst technology and age, engine-out emission levels, and the air/fuel ratio.

The objective of the present study was to examine NH_3 emissions as a function of different vehicle operating conditions and modes in real time to better understand the formation of NH_3 emissions in vehicle exhaust. For this study, eight vehicles with low-emission vehicle (LEV) to super-ultra-low-emission vehicle (SULEV) certification were tested over the Federal Test Procedure (FTP75), a US06 cycle, a hot running 505, a New York City Cycle (NYCC), and a specially designed Modal Emissions Cycle (MEC01v7). The modal emissions cycle was designed as part of the development of University of California at Riverside's Bourns College of Engineering-Center for Environmental Research and Technology (CE-CERT) Comprehensive Modal Emissions Model (CMEM) and includes segments where specific modes of operation are utilized (*28*).

An important and unique aspect of this study was the measurement of real-time NH_3 emissions using a tunable diode laser (TDL). This instrument allows *in-situ* measurements of highly time-resolved NH_3 emissions in the raw exhaust. Additional measurements of second-by-second engine-out and tailpipe regulated emissions, and other parameters, were obtained to allow

a correlation of these variables with NH_3 emissions levels. This paper discusses the results of this study and some preliminary insights that might be useful in better understanding NH_3 emissions from vehicles.

2. Experimental Procedures

2.1 Vehicle Recruitment

A total of eight vehicles were tested as part of the study. Table 1 provides a description of the vehicles. The test weights and dynamometer road load coefficients are also included in Table 1 since these terms are utilized to determine VSP. The test matrix was composed of late model vehicles and included 2 SULEV vehicles, 2 ultra-low-emission vehicles (ULEV), and 4 LEV vehicles, as defined by California regulations. These vehicles were recruited from several sources including rental car companies, private owners, and major automobile manufacturers.

2.2 Test Fuel

The test fuel used for this project was a California Phase 2 gasoline doped to 30 ppmw sulfur. This is close to the average fuel sulfur level for in-use California gasoline. The base fuel was a commercial California Phase 2 gasoline obtained from a refiner in northern California. Table 2 provides detailed properties of the test fuel.

2.3 Catalyst and Oxygen Sensor Aging

For this program, each vehicle was tested using the original equipment (OE) as-received catalyst and a bench-aged catalyst. Catalyst aging was conducted at the Southwest Research Institute (SwRI) in San Antonio, TX, for 90 hours aging (120,000 mile equivalent) by using the Rapid

Aging Test-A (RAT-A) protocol (*29*). Catalysts were aged in pairs using a single V8 engine with the RAT-A temperature profile maintained for each catalyst, and using a specially prepared ultra-low 0.2 ppmw sulfur gasoline and a zero-sulfur oil (*30*).

2.4 Protocol for Vehicle Testing

All vehicles were tested over a range of cycles including the FTP75, US06, MEC01v7, NYCC, and hot running 505. Replicate tests were conducted over the FTP75 and US06 on each vehicle/catalyst combination, with a third test conducted on a vehicle/catalyst combination when the duplicates differed by more than the following criteria: total hydrocarbons (THC) 33%, oxides of nitrogen (NO_x) 29%, and carbon monoxide (CO) 70% (*30*). For the other test cycles, only one test was conducted on both the aged and as-received catalyst for each vehicle. The basic characteristics of the 5 test cycles are listed in Table 3. The driving traces are provided in figures discussed below.

The low-speed cycles included the FTP75, hot running 505 and NYCC. The FTP75 is a three-phase cycle designed to represent emissions under cold-start conditions (bag 1), hot stabilized operating conditions over an urban route (bag 2), and hot-start conditions (bag 3). There is a 10-minute soak period between bag 2 and the hot start bag 3. The hot running 505 is the same driving pattern as bags 1 and 3 of the FTP75, but the cycle is run with the vehicle fully warm. This allows the true cold and hot start emission contribution to be determined by comparison between bags 1 and 3. The NYCC test is designed to represent stop-and-go driving conditions in more congested city traffic.

The high-speed cycles included the US06 and MEC01v7. The US06 is a cycle composed of aggressive, high-speed and/or high-acceleration driving behavior, rapid speed fluctuations, and

driving behavior that is not included in the FTP. This cycle is currently being phased into the certification procedures for light-duty vehicles. The MEC01v7 is a cycle that was specially developed by CE-CERT for the development of its CMEM model and iteratively refined to cover major speed, acceleration, and specific power ranges that span the performance envelope of most light-duty vehicles (*28*). It is composed of a series of modal events including different levels of accelerations, deceleration events, a set of constant cruise speeds, speed-fluctuation driving, and constant power driving.

For all tests, standard bag measurements of regulated pollutants were obtained including THC, non-methane hydrocarbons (NMHC), NO_x, and CO. Tests were conducted in CE-CERT's Vehicle Emissions Research Laboratory (VERL) equipped with a Burke E. Porter 48-inch single-roll electric dynamometer. Modal tailpipe and engine-out measurements were also taken for THC, NMHC, NO_x, CO, and carbon dioxide (CO_2). Bag measurements were conducted with a Pierburg AMA-4000 emission bench, while the pre- and post-catalyst emissions were made with a Pierburg AMA-2000 emissions bench.

2.5 NH_3 Tunable Diode Laser Measurements

NH_3 measurements were obtained on a real-time basis for both engine-out and tailpipe using a tunable diode near infrared absorption spectrometer (TDL). The TDL is described in greater detail elsewhere (*30*). Briefly, the TDL system was used because it provides a number of significant advantages for the measurement of low-level NH_3 exhaust emissions. TDL spectroscopy offers the specificity, the sensitivity and response time necessary to investigate low-level concentrations of exhaust gases. Additionally, the TDL has an important advantage in that measurements are made *in-situ* using raw exhaust gases rather than after dilution. The

combination of these advantages allowed the measurement of highly time-resolved engine-out and tailpipe NH_3 emissions with sensitivity levels of better than 0.5 ppmv at two standard deviations, or a minimum detection limit of roughly 0.5 mg/mi.

For these tests, the TDL was configured to provide data once every 2 seconds for both the engine-out and tailpipe emissions. Second-by-second NH_3 concentrations were obtained from the 2-second TDL readings using a linear extrapolation. The concentrations were then converted into mass emissions rates by multiplying by the density and the time-aligned exhaust flow rate. Similar procedures have been used previously in analysis of second-by-second data for regulated pollutants for the development of CMEM (*28*). The exhaust flow rate was determined on a second-by-second basis using the CO_2 tracer method. Temperature and pressure corrections were also applied to the TDL data based on second-by-second measurements made in the sampling cell.

3. Emissions Test Results

3.1 NH_3 Emissions for Different Driving Cycles

Fleet average NH_3 emissions are presented in Figure 1 for each of the 5 cycles for tests conducted on both as-received and aged catalysts. For comparison, fleet average THC, CO, and NO_x are also provided in Figure 1. The individual vehicle results for NH_3 are presented in Figure 2 for each of the test cycle/catalyst combinations. The detailed test results are provided in Table 4. Figure 2 and Table 4 are missing some data that were not obtained for vehicles SU1 and L2 for the as-received catalyst.

The data in Figures 1 and 2 and Table 4 show that NH_3 emissions vary significantly over the range of vehicles and cycles used in this study. Over the low-speed cycles, such as the FTP,

hot running 505 and NYCC, lower NH_3 emissions were generally observed. Over the FTP, NH_3 emissions for 4 of the test vehicles were below 0.005 g/mi, including both of the SULEV vehicles. Of the remaining vehicles, only vehicle L4 had FTP NH_3 emissions above 0.030 g/mi. It should be noted that current EPA NH_3 estimates for light-duty gasoline vehicles are based on earlier studies where emission rates averaged 0.102 g/mi with a range from 0.001 g/mi to 0.516 g/mi (*15*). The lower FTP NH_3 emissions found in this study can be attributed to the more advanced vehicle technologies.

NH_3 emissions for the hot running 505 were comparable to those of the FTP, as expected since the 505 is driven over the same driving trace as those of bag 1 and bag 3 of the FTP. The FTP emissions were slightly higher than those for the 505, which can probably be attributed to different start conditions, as discussed below. The slightly higher NH_3 emissions over the FTP compared with the 505 were found to be statistically significant at greater than a 95% confidence level for a paired t-test.

The NYCC is a low-speed cycle, but the driving conditions are more energy-intensive on a per-mile basis than the FTP or 505, as shown by the higher CO_2 emission rates in Table 4. On a fleet average basis, NH_3 emissions over the NYCC were slightly higher than those for the FTP and the hot running 505. The differences in NH_3 emissions over the FTP and NYCC were not found to be statistically significant, however. For some vehicles with relatively low NH_3 emissions for the FTP cycle, the NH_3 emissions over the NYCC were considerably higher. For other vehicles, however, higher NH_3 emissions were found in the cold-start period leading to higher FTP NH_3 emissions.

NH_3 emissions increased considerably over the more aggressive US06 and MEC01v7 cycles. These cycles had the highest NH_3 emissions for nearly all of the vehicles, including vehicles that had relatively low NH_3 emissions over the FTP, 505 or NYCC. This is consistent with previous studies that have shown that higher NH_3 emissions are found for higher loads or rich operating conditions (*12,20*). One SULEV vehicle (SU1) was an interesting exception, as almost no NH_3 emissions were observed for this vehicle over either the US06 or MEC01v7 cycles. This observation may be attributable to the feedback and control technology used on this vehicle to maintain precise air/fuel ratio (*31*). As discussed earlier, the MEC01v7 is primarily designed to facilitate the development of modal emissions models; hence, results over this cycle cannot be construed as being representative of real-world emissions, except under more aggressive conditions.

NH_3 emissions over the FTP were typically lower than those of the other regulated emissions, including THC, CO, and NO_x. For the FTP, it is important to note that a large fraction of the total cycle emissions for the regulated emissions are formed during the cold-start portion of the test, prior to when the catalyst lights off. Over the hot running 505 and the NYCC, where the catalyst is at full operating temperature, fleet average NH_3 emissions were found to be more comparable to those of THC, but still below those of NO_x and CO. For the more aggressive US06 and MEC01v7 cycles, fleet average NH_3 emissions were actually slightly higher than those of THC and NO_x. Interestingly, the trend in NH_3 emissions was similar to that observed for CO emissions. The similarity in the trends for NH_3 and CO emissions is discussed in further detail below.

On a fleet average basis, NH_3 emissions were slightly higher for the aged catalysts compared with the as-received catalysts for each of the test cycles. The effect of catalyst age was

not consistent between the different vehicles, however, as shown in Figure 2, and the catalyst differences for NH_3 emissions were not statistically significant for any of the cycles. In another similar study, however, differences between the aged and as-received catalyst were found to be statistically significant for both the FTP and the US06, with higher NH_3 emission found for the aged catalysts (*30*).

3.2 Real-Time NH_3 Emissions

To better understand the effects of different driving modes and cycles on NH_3 emissions, it is useful to examine the modal emissions data. The second-by-second NH_3 emissions for a ULEV vehicle with the OE catalyst are shown in Figure 3 for the FTP and NYCC and in Figure 4 for the US06 and MEC01v7 cycle. Similar trends were also found for each of the remaining vehicles, with the exception of SU1, which showed little increase in NH_3 emissions even under aggressive driving conditions. The real-time emissions data show that NH_3 emissions are primarily generated during acceleration events, with higher NH_3 being generated for more aggressive accelerations. Beyond acceleration events, the NH_3 emissions remain relatively low and for the most part are independent of the driving trace. Some NH_3 emissions were also observed during the start period, as discussed below.

The contribution of the acceleration periods was compared with those of other types of operation. For an aggressive cycle, such as MEC01v7, NH_3 emissions generated during accelerations represented greater than 85% of the total NH_3 emissions for the cycle. Decelerations contributed less than 10% and cruise conditions contributed 1~2% of the total NH_3 emissions for the MEC01v7. Similar trends were also found for the US06 cycle with accelerations, decelerations, and cruise conditions representing approximately 75%, 20%, and

5%, respectively, of the total cycle NH_3 emissions. For the lower-speed cycles (FTP75, hot running 505 and NYCC), the acceleration peaks are not as strong and represent only 50% of the total combined cycle NH_3 emissions. Deceleration and cruise conditions represent 40% and 10%, respectively, of the total combined cycle NH_3 emissions.

3.3 NH_3 Emissions at FTP Cold/Hot Start

To better understand the contribution of NH_3 formed during the period immediately following vehicle start-up, comparisons were made between the emissions from the hot running 505 cycle and those from the cold start bag 1 and hot start bag 3 of the FTP (Table 5). Since the driving cycles are identical, the primary difference between the cycles is the start condition. The true cold-start and hot-start emissions can thus be determined by subtracting the hot running 505 emissions from those of bag 1 and bag 3 of the FTP. For most of the test vehicles, higher NH_3 emissions were found during the cold-start period. To better understand this result, a plot of the bag 1, bag 3 and hot running 505 emissions is presented in Figure 5 for one of the test vehicles. This plot shows that in addition to the NH_3 emissions typically formed during the normal driving cycle, there is a tendency for some vehicles to form higher NH_3 emissions immediately after the light-off of the catalyst. A similar trend was not found for the hot-start emissions, however.

3.4 NH_3 Emissions and Vehicle Specific Power

To further investigate the impacts of specific driving events on NH_3 emissions, the relationship between NH_3 emissions and VSP was examined. VSP is defined here as the instantaneous power per unit mass of the vehicle. The equation utilized for VSP is similar to that reported by Jimenez-Palacios (*32*). In the present case, the actual dynamometer road load coefficients are available, so

these were utilized in place of similar terms in the equation used by Jimenez-Palacios (*32*). The VSP equation used in the present study is as follows:

$$VSP\ (kW/Metric\ Ton = m^2/s^3) = v\ [a\cdot(1+\varepsilon_i) + g\cdot grade + 4.448222\cdot(A+B\cdot v'+C\cdot v'^2)/M]$$

Where: v = velocity (m/s)

a = acceleration (m/s^2)

ε_i = "Mass factor", which is the equivalent translational mass of the rotating components (wheels, gears, shafts, etc.) of the powertrain. We utilize a factor of 0.1 for ε_i similar to that used by Jimenez-Palacios (*32*).

g = acceleration of gravity (m/s^2)

grade = vertical rise / horizontal distance (zero in our case)

4.448222 = 1 lb./N

A (lb.), B (lb./mph) and C ($lb./mph^2$) = dynamometer road load coefficients, as presented in Table 1.

v' = velocity (mph).

M = vehicle test weight (kg).

A plot of NH_3 emissions against VSP is provided in Figure 6 for the same vehicle as presented in Figures 3-5. Overall, the NH_3 emissions indicate that VSP is an important factor that should be considered in the modeling of NH_3 emissions. The results show that positive power episodes represent nearly all of the NH_3 emissions for this test. Plots of NH_3 emissions vs. VSP for other test vehicles showed very similar trends. The small number of points in the lower right corner of Figure 6, indicating low NH_3 emissions for higher VSP events, can primarily be attributed to peaks where there were slight shifts in the time alignment between the NH_3 peak and the peak in VSP rather than outright anomalies. These points can generally be attributed to only one or two peaks within a typical cycle.

Figure 6 also shows that the relationship between NH_3 emissions and VSP can be fit using a 2nd order polynomial. Considering only positive power episodes, a correlation coefficient of $R^2 = 0.56$ was found for a 2nd order polynomial fit. Based on the number of data points for the cycle, this correlation coefficient is statistically significant at greater than a 99% confidence level. The correlation coefficients for the 2nd order polynomials for the remaining vehicles are presented in Table 6. The strongest correlation between NH_3 emissions and VSP was found for a LEV vehicle (L2) with a correlation coefficient of 0.85. The results for this vehicle are shown in Figure 7. The strong onset of NH_3 emissions for both vehicles at a VSP of approximately 25 m^2/s^3 is probably indicative of the conditions under which enrichment occurs.

3.5 NH_3 Emissions and Air/Fuel Ratio

The correlation between air/fuel (A/F) ratio and NH_3 emissions was also investigated. Specifically, under hard acceleration or high VSP conditions, there is a tendency for a vehicle to operate under rich A/F ratios. Figure 8 shows a real-time comparison between NH_3 emissions and instantaneous equivalence ratio (λ). These results indicate there is a correlation between A/F ratio and NH_3 emissions, with the highest NH_3 emissions generally found for sharply rich excursions in the equivalence ratio. Although there is a strong correlation between NH_3 emissions and equivalence ratio for very rich operation, this correlation is considerably weaker at closer to stoichiometric conditions. It should be noted that this correlation is statistically significant also. Specifically, as showed in Figure 9, moderate NH_3 emissions can be found under slightly lean conditions, whereas no NH_3 emissions are found under some slightly rich operating conditions.

Table 7 provides a summary of correlation coefficients of equivalence ratio vs. tailpipe-out NH_3 emissions. The correlation coefficients averaged 0.26 with a range from 0.10 to 0.52. In general, the correlation between A/F ratio and NH_3 was weaker than that between VSP and NH_3. In some previous studies, a strong linear relationship between NH_3 emissions and enrichment has been found (*12,20*). In other studies, however, high NH_3 emissions were found even when A/F ratios were not rich (*5*). In order to better understand the relationship between A/F ratio and NH_3 emissions further investigation is needed. Such studies could include other elements such as catalyst chemistry, which influences the formation of NH_3 emissions and is affected by A/F ratio.

3.6 Correlation Between Tailpipe NH_3 Emissions and Engine-Out Emissions

Another important factor in understanding NH_3 formation is the chemistry on the catalyst surface leading to NH_3 formation. A number of studies have shown that NH_3 is primarily formed due to reactions on the catalyst. Several reaction mechanisms exist for NH_3 formation on the catalyst including the water-gas shift reaction and the steam reforming reaction (*27,33*).

$$2NO + 2CO + 3H_2 \rightarrow 2NH_3 + 2CO_2 \qquad (NH_3 \text{ formation 1})$$

$$2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O \qquad (NH_3 \text{ formation 2})$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (\text{Water-gas shift reaction})$$

$$C_nH_{(2n+2)} + 2nH_2O \leftrightarrow nCO_2 + (3n+1)H_2 \qquad (\text{Steam reforming reaction})$$

For NH_3 production, Gandhi and Shelef (*25*) examined the relative contribution of hydrogen present in the exhaust compared with that formed from the water-gas shift and steam-reforming reactions. They concluded that hydrogen produced in the water-gas shift reaction is a major contributor to NH_3 formation.

Although the catalyst reactions were not directly measured as part of this study, some insight into these reactions can be obtained by examining the correlation between NH_3 emissions and engine-out emissions. For this comparison, engine-out CO, THC and NO_x over the combined set of hot running 505, MEC01v7 and NYCC cycles were investigated. A plot of NH_3 vs. CO emissions is presented in Figure 10 for a typical vehicle. For this vehicle, a linear correlation coefficient of 0.75 was found between CO and NH_3. A listing of the CO correlation coefficients for the remaining vehicles is presented in Table 7. The CO correlation coefficients averaged 0.67 over the fleet with a range from 0.34 to 0.94. Based on the number of data points utilized, these correlation coefficients are all statistically significant at greater than a 99% confidence level. With the exception of one vehicle (L1), all other vehicles had CO correlation coefficients of 0.56 or greater. The lower correlation for vehicle (L1) can be attributed primarily to slightly poorer time alignment between the CO and NH_3 emissions. Since CO is one of the principal reactants in the water-gas shift reaction, it is not surprising to find trends in NH_3 emissions correlated with those of CO. This correlation is consistent with the role of CO in forming NH_3 emissions via the water-gas shift reaction.

Correlations were also found for THC and NO_x with NH_3. As seen in Table 7, the average correlations for THC and NO_x are only 0.32 and 0.27, respectively, with the best correlation being only 0.57 for THC and 0.48 for NO_x. Although these correlations are statistically significant, they are considerably weaker than those found for CO and NH_3. This indicates that while THC and NO_x play a role in the formation of NH_3, the water-gas shift reaction with CO is probably the predominant rate limiting step in the NH_3 formation reaction.

4. Discussion

The major results of this study show that a number of factors can contribute to the formation of NH_3 in vehicle exhaust. NH_3 emissions vary considerably depending on the vehicle, cycle and operating mode. Higher NH_3 emissions were found for all vehicles on aggressive cycles. Modal emissions data show that NH_3 emissions are primarily generated during acceleration events, although for some vehicles NH_3 emissions are formed in the period immediately after catalyst light-off. The strongest correlations were found between both VSP and engine-out CO emissions and tailpipe NH_3 measurements. The correlation between engine-out CO and NH_3 emissions indicates that the water-gas shift reaction over the catalyst probably plays an important role in the formation of NH_3.

While this study provides insight into the correlations between various parameters and NH_3 emissions in vehicle exhaust, further study is needed to provide a better framework for understanding and modeling NH_3 emissions from vehicles. The fleet utilized in this study, for example, is primarily representative of late model technologies that contribute a relatively small portion of the total emission inventory. It is important to examine a wider range of vehicles to better understand how these relationships change for older technologies. It may also be important to better understand the relative impact of catalyst composition and air-fuel ratio on NH_3 emissions. Some more detailed catalyst experiments may also be worthwhile, to further investigate the relationships found. This could include, for example, injecting various components such as CO into the exhaust upstream of the catalyst to see how NH_3 emissions are affected.

Additional research on developing modal emission models for NH_3 is planned in conjunction with this study. First, the modal NH_3 emissions data will be used to calculate NH_3 emission rates using a VSP binning methodology. This methodology is being proposed for use in EPA's MOVES modeling framework (*1*). The modal NH_3 emissions data will also be utilized to develop a preliminary NH_3 module for CMEM that can subsequently be evaluated. Parameter sets for CMEM will be estimated for each vehicle as well as for a composite vehicle (*28*). While the number of vehicles that will be used in the development of the NH_3 module will be limited, it will provide information for the assessment of the data needs for including NH_3 in a broader context of emissions models.

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Table 1. Description of Test Vehicles

Vehicle ID	MY	OEM	Model	Certification	Displacement	Mileage	Test Weight	Dynamometer Road Load Coefficients		
						mi	lb	A (lb.)	B (lb./mph)	C (lb./mph^2)
SU1	2000	Honda	Accord	SULEV	2.3 L	11,958	3250	30.45	0.174	0.01914
SU2	2001	Nissan	Sentra CA	SULEV	1.8 L	6,592	3000	24.94	0.143	0.01568
U1	2001	Chrysler	Sebring	ULEV	2.4 L	19,677	3750	34.65	0.198	0.02178
U2	2001	Acura	CL	ULEV	3.2 L	20,523	3750	34.65	0.198	0.02178
L1	2000	Jeep	Grand Cherokee	LEV	4.7 L	29,571	4500	49.88	0.285	0.03135
L2	2001	Ford	Taurus	LEV	3.0 L	23,553	3625	34.13	0.195	0.02145
L3	2001	Chevrolet	Cavalier	LEV	2.4 L	22,482	3125	25.46	0.146	0.01601
L4	2001	Chevrolet	Silverado	LEV	5.3 L	8,380	4750	48.04	0.275	0.03020

Table 2. Properties of the Test Fuel

API Gravity	66.3 @ 60/60
RVP	6.7 psi
Base Sulfur	5 ppmw
Benzene	0.1 wt %
Aromatics	16.4 wt. %
	14.0 vol. %
Olefins	0.5 vol. %
T50	214.3°F
T90	243.6°F

Sulfur doping levels: Nominal 30 ppmw: 1st batch 30 ppmw and 2nd batch 31.6 ppmw

Table 3. Testing Cycle Descriptions

	Unit	FTP75	Hot Running 505	NYCC	US06	MEC01v7
Distance Traveled	**miles**	11.04	3.57	1.18	8.01	23.64
Duration	**seconds**	1874	505	598	596	1955
Average speed	**mph**	21.2	25.4	7.1	48.4	43.5
Maximum speed	**mph**	56.6	56.6	27.7	80.3	80.8

Table 4. Summary of Emissions (Unit: g/mi)

		SU1		SU2		U1		U2		L1		L2		L3		L4		Average
		OE	Aged	OE	Aged	OE	Aged	OE	Aged	OE	Aged	OE	Aged	OE	Aged	OE	Aged	
FTP	NH_3	0.002	0.006	0.003	0.002	0.023	0.012	0.009	0.026	0.029	0.027	0.001	0.002	0.001	0.002	0.028	0.085	**0.016**
	THC	0.022	0.020	0.010	0.014	0.034	0.032	0.036	0.055	0.100	0.098	0.057	0.065	0.048	0.055	0.084	0.119	**0.053**
	CO	0.145	0.181	0.176	0.161	0.458	0.430	0.295	0.732	1.158	1.531	0.522	0.549	0.877	1.097	1.082	1.422	**0.676**
	NO_x	0.018	0.022	0.007	0.009	0.026	0.024	0.065	0.070	0.103	0.188	0.039	0.036	0.072	0.049	0.127	0.124	**0.061**
	CO_2	345.0	346.1	327.6	328.3	406.0	406.5	402.1	395.3	578.5	537.8	434.1	432.8	340.0	334.7	534.5	550.0	**418.7**
Hot Running 505	NH_3		0.002	0.002	0.001	0.003	0.002	0.003	0.002	0.021	0.014		0.005	0.002	0.002	0.029	0.080	**0.012**
	THC		0.002	0.003	0.002	0.004	0.004	0.002	0.004	0.009	0.015		0.045	0.003	0.004	0.024	0.033	**0.011**
	CO		0.112	0.063	0.028	0.000	0.075	0.068	0.039	0.012	0.013		0.098	0.032	0.056	0.272	0.325	**0.085**
	NO_x		0.002	0.003	0.003	0.009	0.006	0.136	0.047	0.003	0.109		0.009	0.031	0.035	0.038	0.031	**0.033**
	CO_2		313.2	301.2	304.3	366.0	361.7	348.7	334.9	501.9	458.5		373.6	293.6	295.3	483.1	478.6	**372.5**
NYCC	NH_3		0.011	0.011	0.008	0.011	0.007	0.021	0.012	0.028	0.018		0.029	0.002	0.003	0.083	0.142	**0.028**
	THC		0.000	0.003	0.002	0.000	0.014	0.007	0.009	0.046	0.050		0.086	0.003	0.009	0.043	0.065	**0.024**
	CO		0.214	0.037	0.293	0.177	0.343	0.214	0.091	0.065	0.052		0.327	0.600	0.381	0.798	0.872	**0.319**
	NO_x		0.012	0.000	0.001	0.001	0.104	0.028	0.046	0.216	0.218		0.026	0.153	0.223	0.025	0.041	**0.078**
	CO_2		523.1	459.6	479.4	684.9	669.9	676.4	657.0	1040.5	940.1		753.9	505.8	494.8	917.7	896.9	**692.9**
US06	NH_3	0.007	0.002	0.030	0.023	0.138	0.095	0.089	0.101	0.231	0.207	0.031	0.045	0.029	0.028	0.064	0.197	**0.082**
	THC	0.006	0.004	0.003	0.003	0.038	0.045	0.033	0.026	0.084	0.089	0.057	0.111	0.014	0.015	0.064	0.064	**0.041**
	CO	1.167	0.450	5.562	4.071	17.004	15.916	8.081	7.311	7.833	3.048	3.139	4.494	2.632	1.897	0.858	1.283	**5.296**
	NO_x	0.005	0.008	0.004	0.003	0.066	0.109	0.068	0.198	0.094	0.141	0.006	0.013	0.120	0.090	0.093	0.181	**0.075**
	CO_2	316.1	311.6	330.8	322.6	372.4	371.4	335.4	327.3	524.2	473.1	352.8	354.2	281.8	278.0	475.2	471.4	**368.7**
MEC01v7	NH_3		0.003	0.071	0.059	0.098	0.104	0.099	0.081	0.190	0.197	0.078	0.071	0.081	0.100	0.065	0.148	**0.096**
	THC		0.004	0.004	0.003	0.060	0.079	0.076	0.083	0.155	0.191	0.153	0.203	0.020	0.032	0.078	0.105	**0.083**
	CO		6.880	9.892	7.599	34.191	38.410	20.230	22.267	25.343	35.138	13.674	14.087	7.125	6.185	9.381	10.397	**17.387**
	NO_x		0.015	0.005	0.009	0.029	0.031	0.029	0.050	0.048	0.076	0.010	0.020	0.091	0.106	0.081	0.153	**0.050**
	CO_2		289.0	300.2	301.7	331.6	334.3	305.0	302.7	462.0	420.3	339.0	323.1	256.7	257.1	453.2	440.2	**341.1**

Table 5. Comparison of Start NH_3 Emissions (Unit: g/mi)

Vehicle	Catalyst	Hot Running 505	FTP Bag1 Cold Start	FTP Bag3 Hot Start	CS-505	HS-505
SU1	**OE**	N/A	0.005	0.000	N/A	N/A
	Aged	0.005	0.007	0.003	0.002	-0.002
SU2	**OE**	N/A	0.009	0.001	N/A	N/A
	Aged	0.002	0.007	0.000	0.005	-0.002
U1	**OE**	0.003	0.019	0.012	0.016	0.009
	Aged	0.002	0.014	0.003	0.012	0.002
U2	**OE**	0.002	0.034	0.001	0.031	-0.001
	Aged	0.001	0.081	0.000	0.080	-0.001
L1	**OE**	0.021	0.071	0.039	0.050	0.019
	Aged	0.014	0.087	0.003	0.073	-0.011
L2	**OE**	0.003	0.001	0.000	-0.001	-0.003
	Aged	0.002	0.003	0.001	0.001	-0.001
L3	**OE**	0.002	0.002	0.001	-0.001	-0.002
	Aged	0.002	0.008	0.001	0.007	-0.001
L4	**OE**	0.029	0.034	0.015	0.005	-0.013
	Aged	0.080	0.099	0.067	0.019	-0.012

Table 6. Parameter Summary of Correlation between NH_3 emissions and VSP

(2^{nd} order polynomial correlation under positive power episodes)

Vehicle	Catalyst	$y=ax^2+bx+c$			
		a	**b**	**c**	R^2
SU1	**OE**	N/A			
	Aged	N/A			
SU2	**OE**	0.0154	-0.2374	0.5486	0.62
	Aged	0.0105	-0.1618	0.4507	0.42
U1	**OE**	0.0105	-0.0932	0.2764	0.57
	Aged	0.0108	-0.0855	0.2052	0.58
U2	**OE**	0.0061	0.0176	-0.0778	0.56
	Aged	0.0047	-0.0186	0.2627	0.53
L1	**OE**	0.0095	0.0212	0.1436	0.43
	Aged	0.0076	0.0921	-0.1183	0.52
L2	**OE**	0.0112	-0.1966	0.5785	0.85
	Aged	0.0088	-0.1123	0.3202	0.67
L3	**OE**	0.0141	-0.1942	0.3320	0.55
	Aged	0.0162	-0.2435	0.5995	0.55
L4	**OE**	0.0058	-0.0668	0.3612	0.46
	Aged	0.0059	0.0354	0.4581	0.71

Table 7. Summary of Correlation Coefficients (R^2) of

Engine-Out Emissions and Equivalence Ratio (λ) vs. Tailpipe-Out NH_3 Emissions

MY	Vehicle	CO		THC		NO_x		λ	
		OE	Aged	OE	Aged	OE	Aged	OE	Aged
2000	**SU1**	N/A*		N/A*		N/A*		N/A*	
2001	**SU2**	0.80	0.66	0.29	0.12	0.20	0.16	0.38	0.23
2001	**U1**	0.57	0.61	0.44	0.48	0.25	0.22	0.22	0.21
2001	**U2**	0.75	0.58	0.22	0.20	0.28	0.26	0.30	0.26
2000	**L1**	0.34	0.39	0.18	0.21	0.18	0.34	0.13	0.39
2001	**L2**	0.94**	0.90	0.50**	0.52	0.30**	0.34	0.52**	0.34
2001	**L3**	0.77	0.67	0.26	0.24	0.27	0.19	0.15	0.17
2001	**L4**	0.78	0.65	0.31	0.57	0.32	0.48	0.10	0.29

*: NH_3 emissions are too low to compare; **: MEC01v7 cycle only.

Figure 1. Average Emissions vs. Cycles

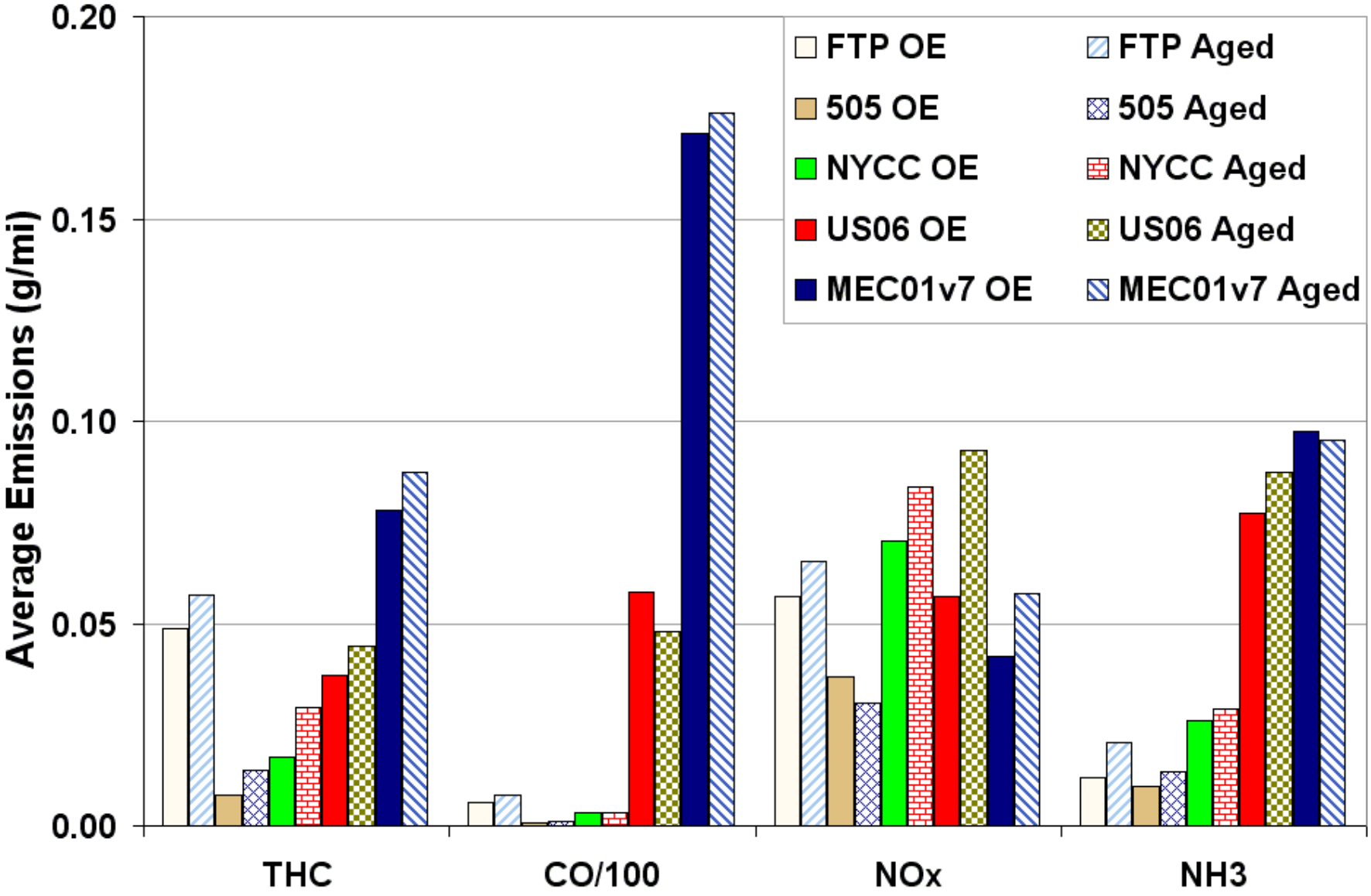

Figure 2. NH_3 Emissions vs. Cycles

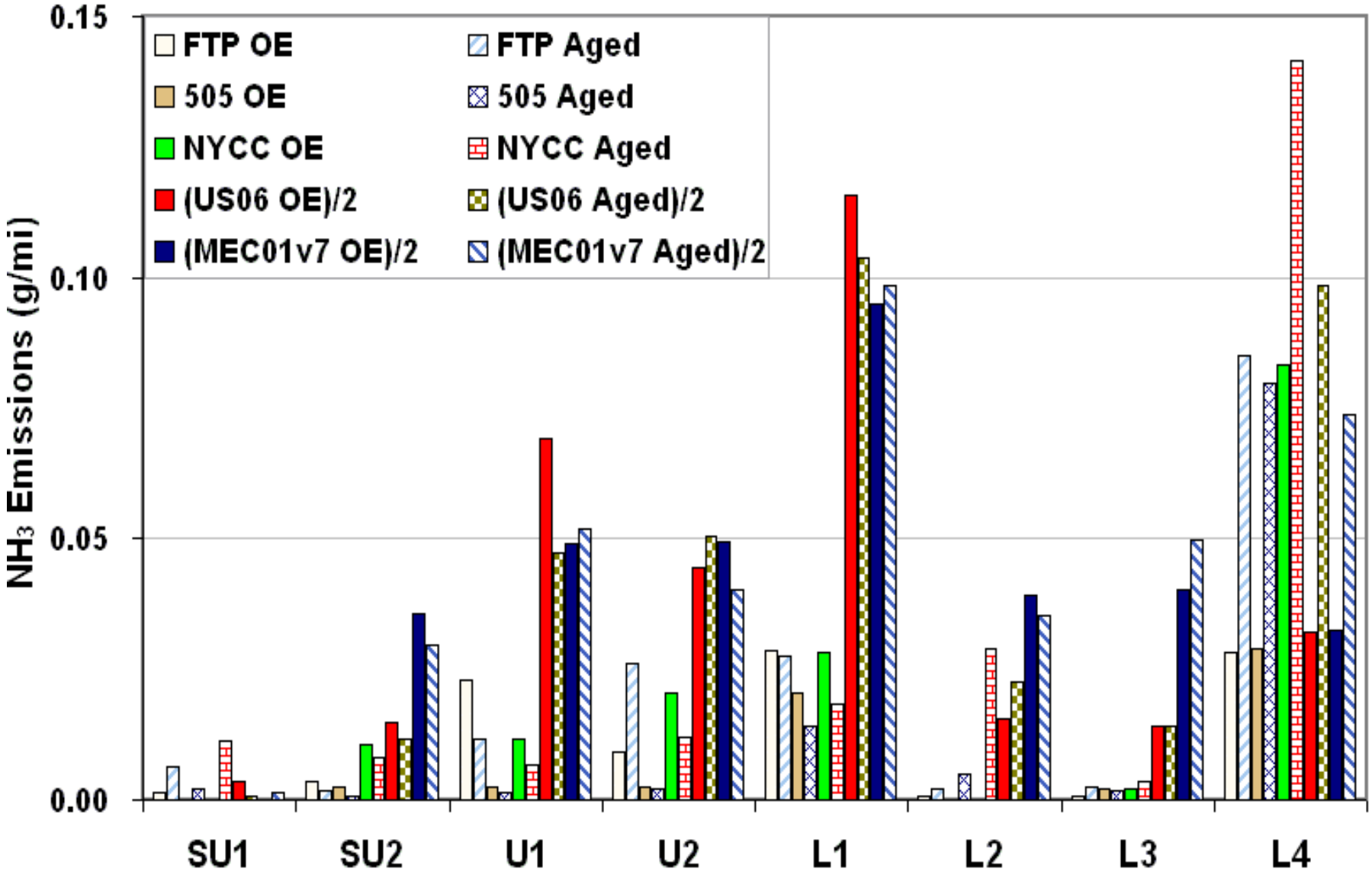

Figure 3. Second-by-Second Data of NH_3 Emissions for FTP/NYCC

(Vehicle U2, OE Cat.)

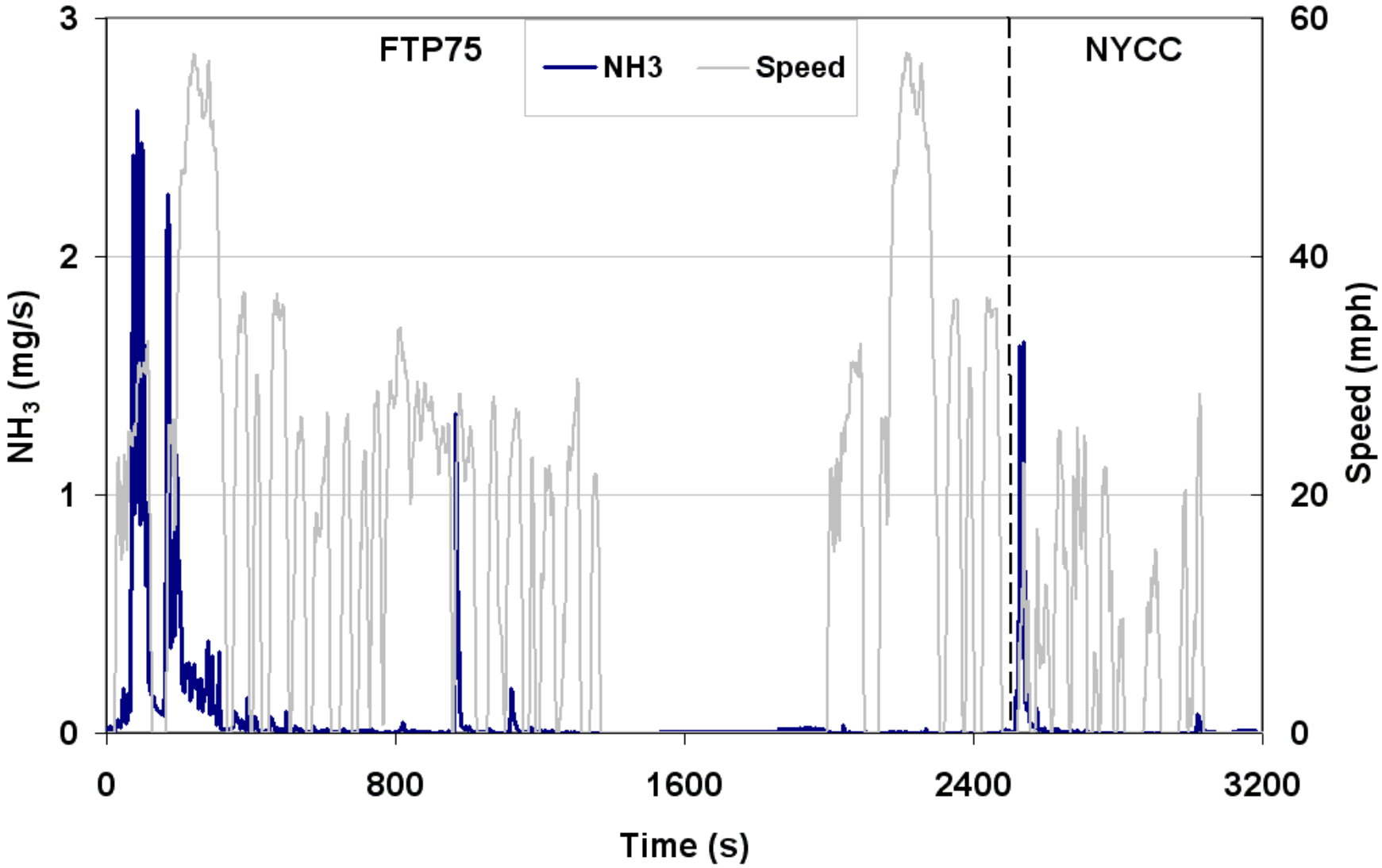

Figure 4. Second-by-Second Data of NH_3 Emissions for US06/MEC01v7

(Vehicle U2, OE Cat.)

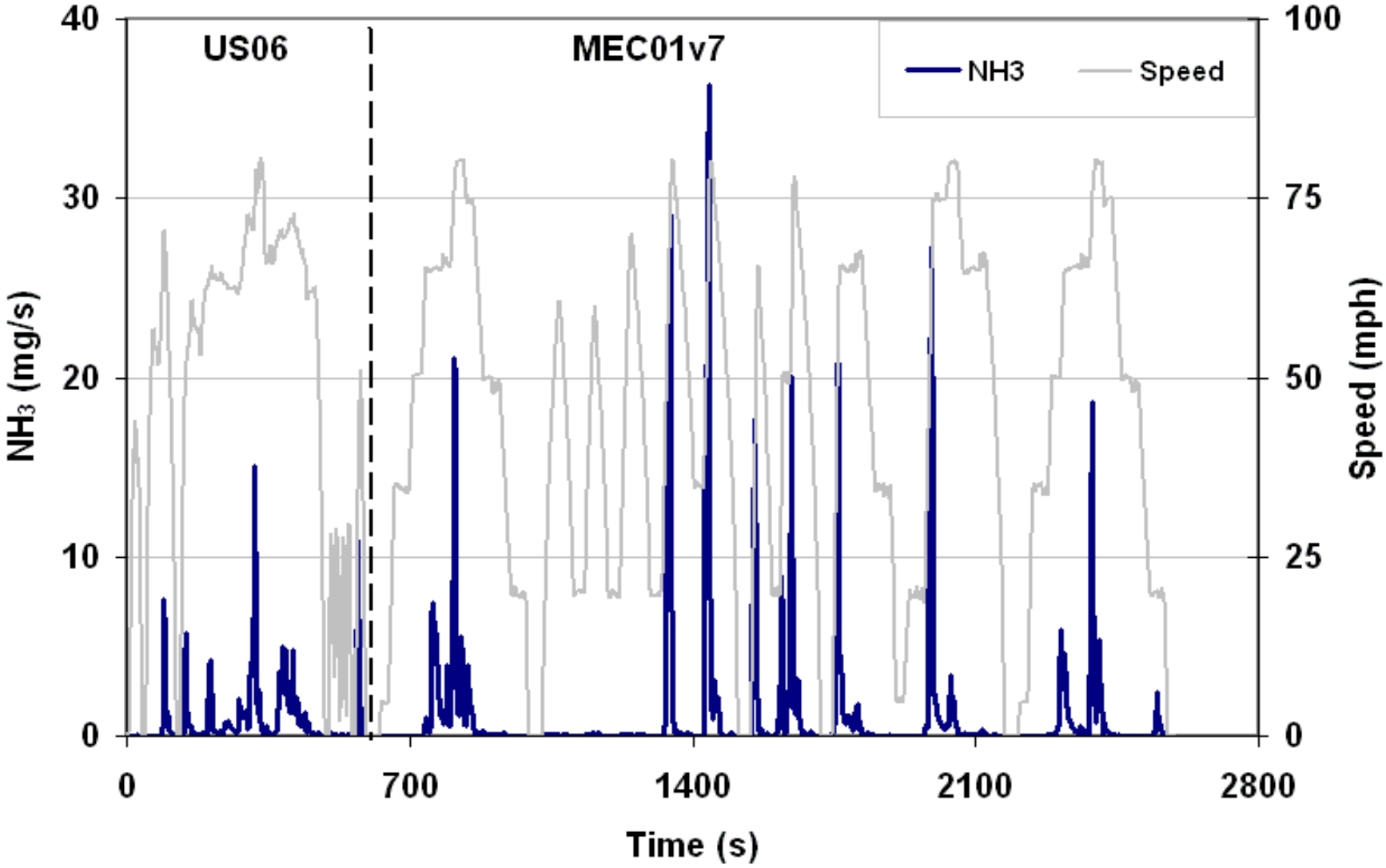

Figure 5. NH_3 Emissions at FTP Cold/Hot Start and Hot Running 505

(Vehicle U2, OE Cat.)

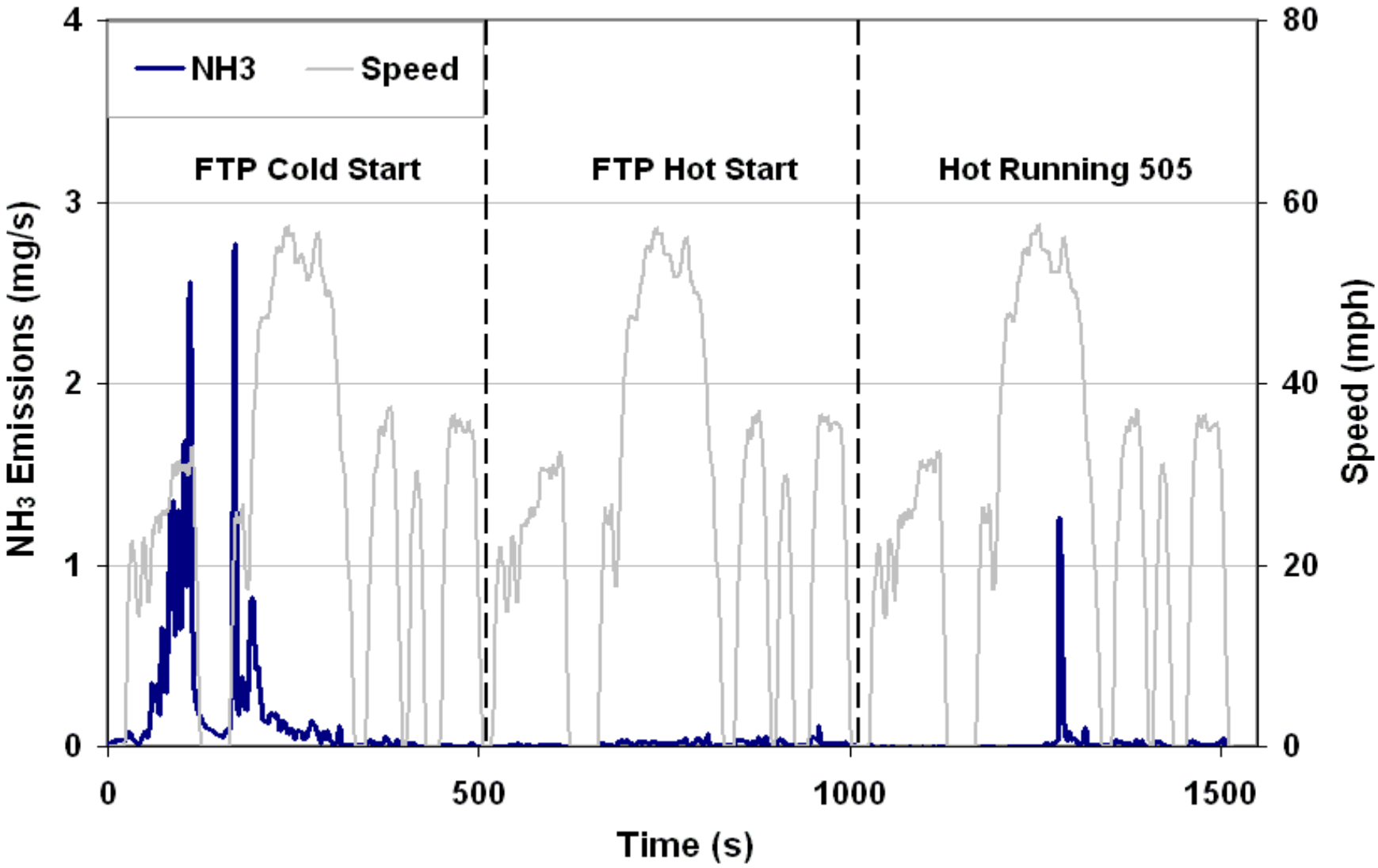

Figure 6. NH_3 Emissions vs. Vehicle Specific Power (VSP)

(Vehicle U2, OE Cat.)

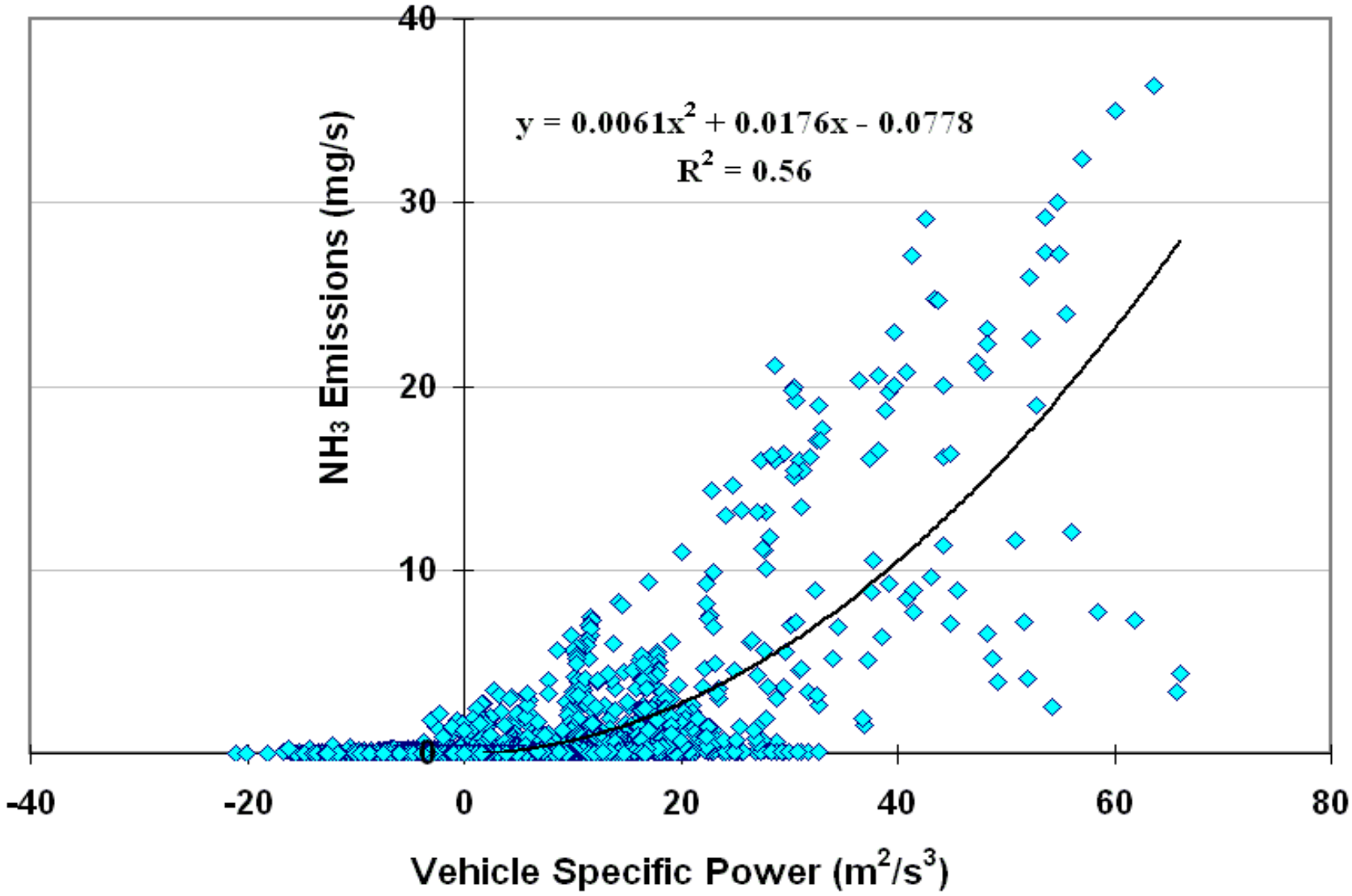

Figure 7. NH_3 Emissions vs. Vehicle Specific Power (VSP)

(Vehicle L2, OE Cat.)

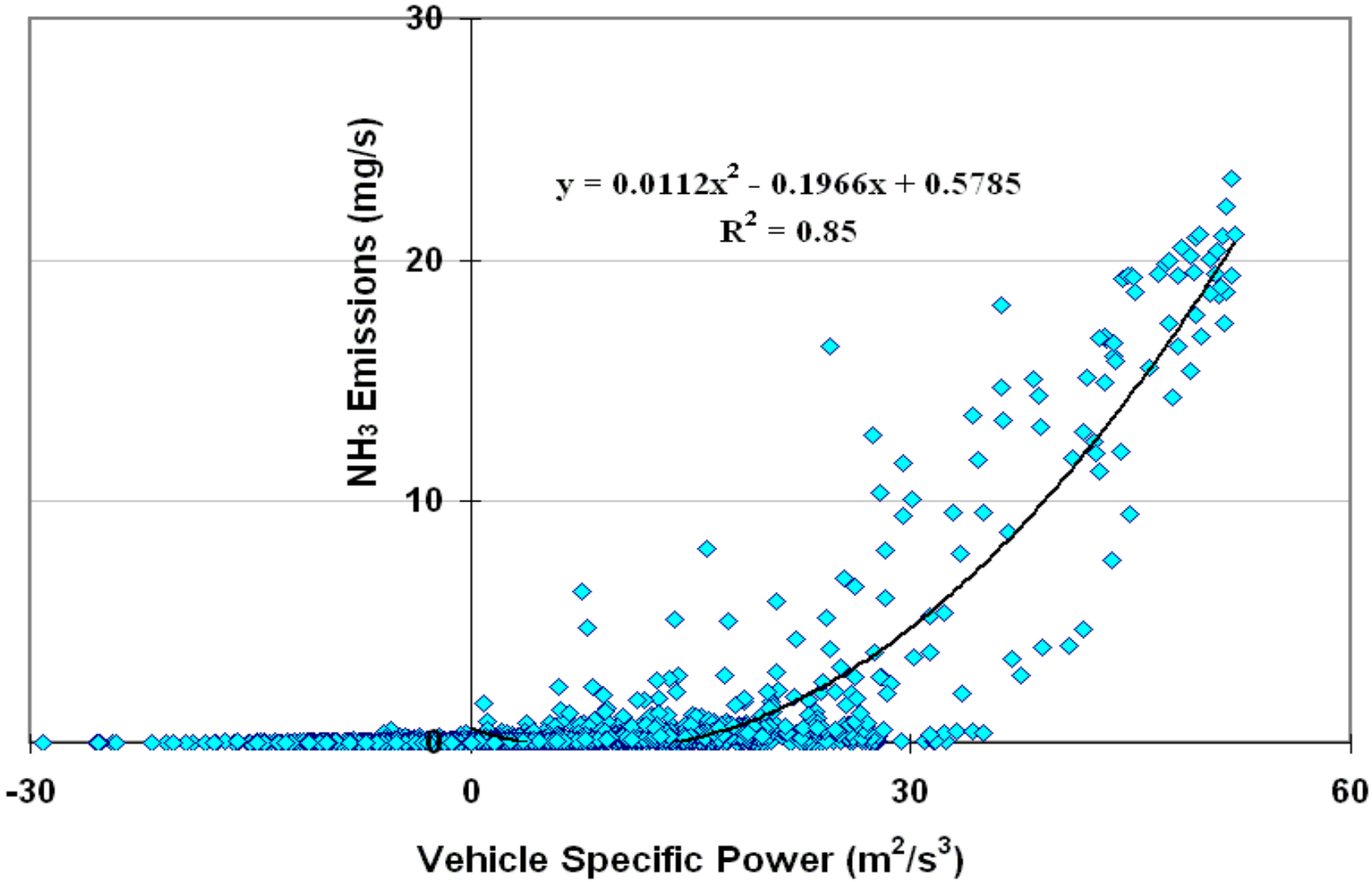

Figure 8. Real-Time Comparison of NH_3 Emissions vs. Equivalence Ratio (λ)

(Vehicle U2, OE Cat.)

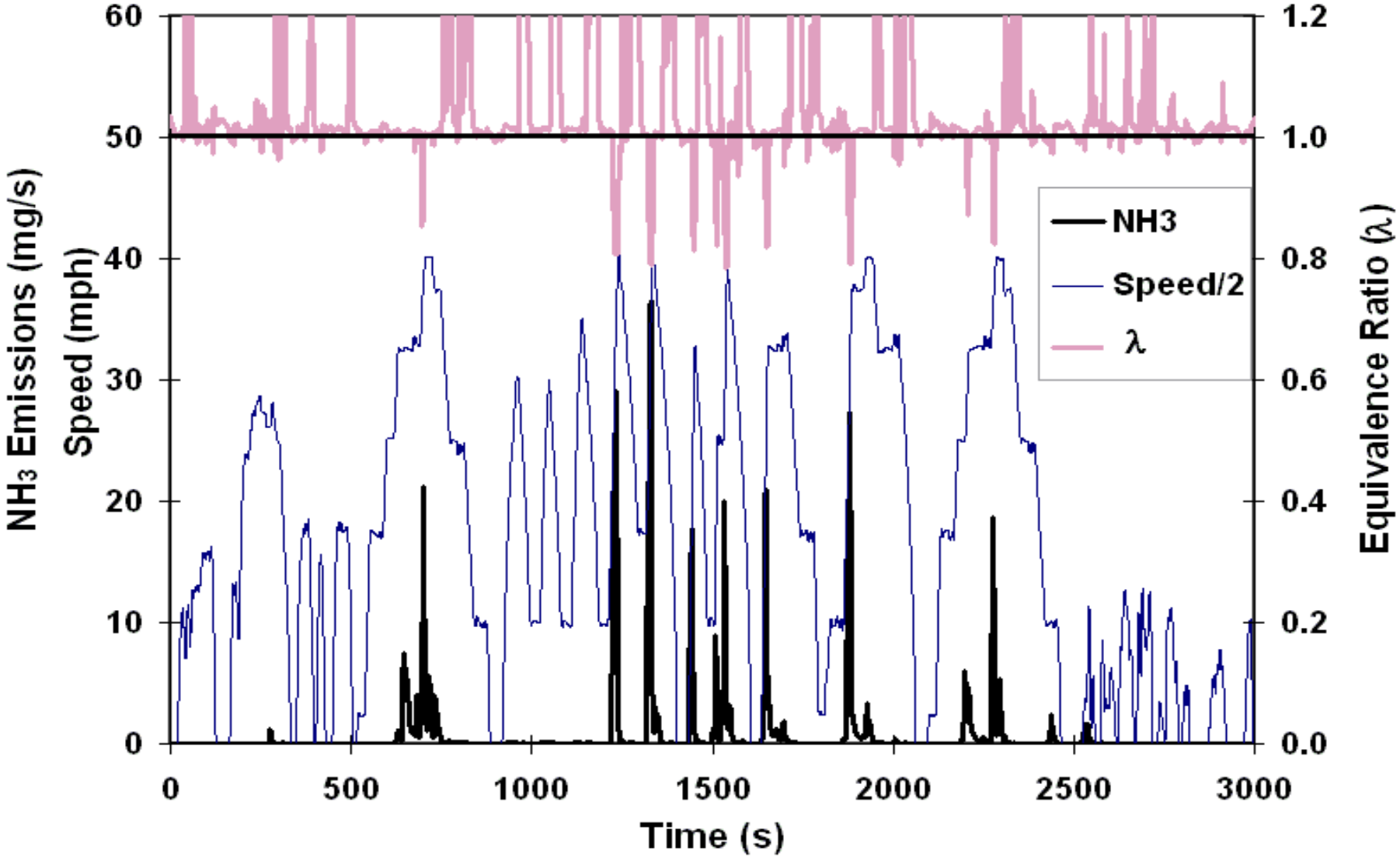

Figure 9. NH_3 Emissions vs. Equivalence Ratio (λ)

(Vehicle U2, OE Cat.)

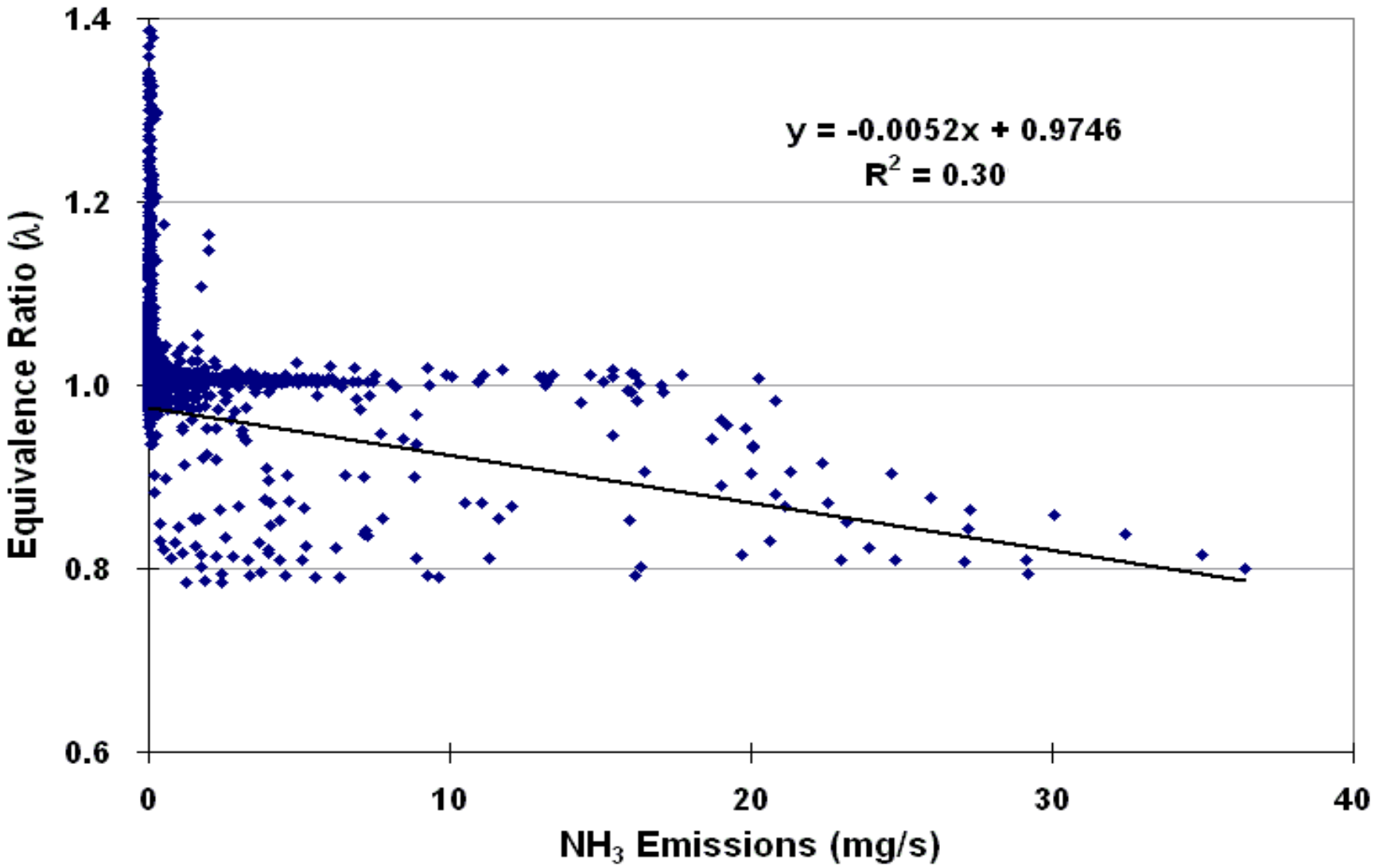

Figure 10. Engine-Out CO Emissions vs. NH_3 Tailpipe Emissions

(Vehicle U2, OE Cat.)