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AMMONIA EMISSION ASSESSMENT FROM GASOLINE AND DIESEL ENGINES
UNDER UTAH SPECIFIC CONDITIONS

by

Motasem Suleiman Abualqumboz

A thesis submitted in partial fulfillment of the
requirements for the degree

of

MASTER OF SCIENCE

in

Civil and Environmental Engineering

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2021

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ABSTRACT

Ammonia Emission Assessment from Gasoline and Diesel Engines under Utah Specific
Conditions

by

Motasem Suleiman Abualqumboz, Master of Science

Utah State University, 2021

Major Professor: Dr. Randal S. Martin
Department: Civil and Environmental Engineering

This study aims to quantify ammonia (NH_3) emission rates from the on-road gasoline and diesel motor vehicles fleet of the Wasatch Front, Utah. For this purpose, a portable Pollution Emissions Monitoring System (PEMS) was used to estimate NH_3 emission rates from a representative fleet of 53 in-use light-duty (LD) gasoline and diesel vehicles over a total of 166 on-road Real Driving Emissions (RDE) tests. The post-catalyst concentrations of ammonia precursors, nitrogen oxides (NO_x) and carbon monoxide (CO) were also measured.

The entire gasoline and diesel vehicles test sample had an average ammonia emission rate of 55.6 mg/mile. This would yield an estimated 1,496.5 metric tons per year of NH_3 emissions from the on-road motor vehicles of the Wasatch Front. Thus, limiting the number of old on-road vehicles with aged catalytic converters by replacing them with newer vehicles or repairing their exhaust control devices would significantly reduce NH_3

emission rates from motor vehicles fleet. The average NH₃ emission rates of gasoline and diesel motor vehicles were 62 and 10.7 mg/mile, respectively. The results also showed that ammonia emission rates from tested gasoline and diesel motor vehicles within different classifications were statistically different. For instance, tested Tier 0, Tier I, NLEV, Tier II and Tier III gasoline motor vehicles had average emission rates of 413.8, 119.7, 156.5, 38.2 and 9.5 mg/mile, respectively. Vehicles' characteristics including odometer reading, engine displacement and model year, and the concentrations of post-catalyst exhaust gases including CO and NO_x were strongly correlated with post-catalyst exhaust emissions of ammonia from gasoline and diesel motor vehicles. The vehicle specific power (VSP) parameter was strongly correlated ($r > 0.5$) with only NH₃ mass emission rates from gasoline motor vehicles. Lastly, higher ammonia emission rates were measured from most tested vehicles in the first lap than in the consecutive second and third laps.

This study concludes that the on-road gasoline and diesel motor vehicles fleet of the Wasatch Front contribute to anthropogenic ammonia emissions into the atmosphere. The study also concludes that vehicle characteristics, ammonia precursors concentration and driving conditions could impact ammonia emission rates from the on-road vehicles fleet.

PUBLIC ABSTRACT

Ammonia Emission Assessment from Gasoline and Diesel Engines under Utah Specific Conditions

Motasem Suleiman Abualqumboz

This study aims to quantify ammonia (NH_3) emission rates from the on-road gasoline and diesel motor vehicles fleet of the Wasatch Front, Utah. For this purpose, a portable Pollution Emissions Monitoring System (PEMS) was used to estimate NH_3 emission rates from a representative fleet of 53 in-use light-duty (LD) gasoline and diesel vehicles over a total of 166 on-road Real Driving Emissions (RDE) tests. The post-catalyst concentrations of NH_3 precursors, nitrogen oxides (NO_x) and carbon monoxide (CO) were also measured. The outcomes of this study showed that a motor vehicle in the Wasatch Front would emit 55.6 mg for every traveled mile. The average NH_3 emission rates of gasoline and diesel motor vehicles were 62 and 10.7 mg/mile, respectively. Together, the on-road gasoline and diesel motor vehicles in the Wasatch Front produce an estimated 1,496.5 metric tons of NH_3 every year. The study also showed that vehicle characteristics (model year, mileage reading, engine displacement and number of cylinders), the concentration of NH_3 precursors (carbon monoxide and oxides of nitrogen) and driving conditions impact NH_3 emission rates from the on-road vehicles fleet. Thus, limiting the number of old on-road vehicles with aged catalytic converters by replacing them with newer vehicles or repairing their exhaust control devices would significantly reduce NH_3 emission rates from motor vehicles fleet.

DEDICATION

This work is dedicated to my family.

ACKNOWLEDGMENTS

First and foremost, I acknowledge the immense contribution of my supervisor, Dr Randal S. Martin for his time and support throughout my study. I'm also grateful to my family, wife and friends who have been supporting me. I'm also grateful to the Division of Air Quality – Utah Department of Environmental Quality for funding this project. I also acknowledge the support of The Utah Water Research Laboratory (UWRL) at Utah State University (USU) and their staff members. Many thanks also to the Graduate Program Coordinator, Marlo Bailey and the department staff assistant, Haley Seiler.

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Motasem Suleiman Abualqumboz

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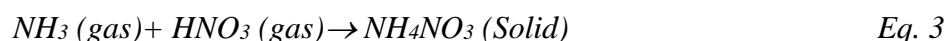
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CHAPTER I

INTRODUCTION

Ammonia (NH₃) is a colorless reactive gas with a sharp characteristic odor. It is an inorganic chemical compound composed of a single nitrogen atom (N) covalently bonded to three atoms of hydrogen (H). Ammonia is one of the most abundant alkaline gases in the atmosphere and is the third most abundant nitrogen-containing atmospheric compound after nitrogen (N₂) and nitrous oxide (N₂O) gases (Kean et al. 2000). Because of that, NH₃ plays a key role in atmospheric chemistry. For instance, it contributes to forest decline and vegetation damage, visibility problems and formation of photochemical smog, dry and wet deposition, and the eutrophication process in lakes (Behera et al. 2013; Moeckli et al. 1996). Nevertheless, the biggest environmental concern regarding atmospheric NH₃ is its contribution to the formation of fine secondary particles with an aerodynamic diameter of less than 2.5 microns (PM_{2.5}) such as ammonium sulfate ((NH₄)₂SO₄) and ammonium nitrate (NH₄NO₃) (Eq. 1-Eq. 3). Because of their small size, (NH₄)₂SO₄ and NH₄NO₃ PM_{2.5} particles can penetrate deeply into human lungs and reach lung alveoli, which can result in several respiratory and cardiovascular diseases (Fann et al. 2012; Xing et al. 2016).



The contribution of atmospheric NH_3 to the formation of secondary $\text{PM}_{2.5}$ pollutants has been confirmed by several studies. For example, a study implemented by Kim et al. (2000) showed that particulate NH_3 compounds were found to be among the most abundant chemical components of $\text{PM}_{2.5}$ particles in samples collected by the authors. The study showed that NH_4^+ comprised 14-17 % of $\text{PM}_{2.5}$ mass measured in the South Coast Air Basin (SCAB) of California. Similarly, Schiferl et al. (2014) reported that inorganic aerosols made up out of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 comprised 50–60% of $\text{PM}_{2.5}$ mass measured in the Los Angeles basin in the summer and 40% in the winter. The study also reported that anthropogenic NH_3 emissions are responsible for more than half of the inorganic $\text{PM}_{2.5}$ particles measured throughout the state of California, USA. Similarly, previous studies have also shown that $\text{PM}_{2.5}$ particles along the Wasatch Front in the US State of Utah were comprised mostly of secondary aerosols, including ammonium chloride (NH_4Cl), $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 (Hammond et al. 2017; Kelly et al. 2013, 2017). Baasandorj et al. (2018) and (Martin et al. 2016) also reported that NH_4NO_3 makes up the bulk of the $\text{PM}_{2.5}$ particles along the Wasatch Front, accounting for approximately 90% of their total mass. More than 80% of Utah's population resides along the Wasatch Front. Hence, reducing fine particulate levels including NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 in the Wasatch Front's airsheds remains one of the most challenging problems facing air pollution regulatory agencies. As a result, accurate characterization and quantification of ammonia emissions from all sources, including gasoline and diesel motor vehicles is necessary to help regulators develop particulate matter reduction strategies (Battye et al. 2003).

Atmospheric NH_3 has long been known to be an emission from biological

processes in soil, biomass burning, ammonia-based chemical fertilizers, sewage treatment plants, and animal wastes decay processes (Behera et al. 2013; Chang et al. 2016). In Utah, the 2017 National Emission Inventory (NEI) estimated that 85% (36,142.67 ton) of NH_3 emissions were from stationary sources (Figure 1).

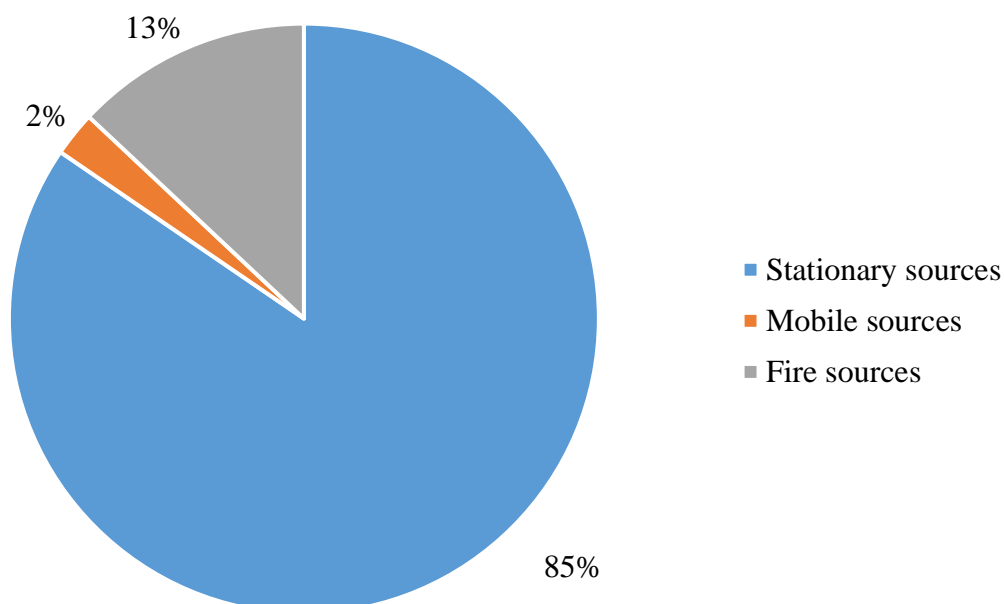


Figure 1. The 2017 National Emission Inventory (NEI) of ammonia in the United States. (EPA 2020)

As Figure 1 presents, motor vehicles were linked with 1,047.04 tons of NH_3 emission which represents 2% of total ammonia emission into the atmosphere. However, early studies indicate that substantial amounts of atmospheric NH_3 may also be attributed to gasoline motor vehicle fleets because of their Three-Way Catalyst (TWC) (Bradow & Stump, 1977; Cadle & Mulawa, 1980; Cadle, et al., 1979; Gregori et al., 1989; Smith & Carey, 1982; Urban & Garbe, 1979). Three-way catalyst converters are small canisters

designed to control exhaust emissions of carbon monoxide (CO), unburned hydrocarbons (HC), and nitrogen oxides (NO_x) from gasoline engines. Similar to gasoline vehicles, diesel vehicles also started to show higher emissions of NH₃ than pre-catalyst diesel motor vehicles after the introduction of the Diesel Oxidation Catalysts (DOC) in 1975. Diesel Oxidation Catalyst are two-way oxidation catalysts that are mainly designed to oxidize CO and HC exhaust emissions of diesel motor vehicles.

Emissions rates of exhaust ammonia from gasoline and diesel motor vehicles have been estimated mostly using highway tunnel measurement studies (Emmenegger et al. 2004; Fraser and Cass 1998; Kean et al. 2000, 2009; Liu et al. 2014; Moeckli et al. 1996; Pierson and Brachaczek 1983), chassis dynamometer experiments (Borsari and Assunção 2017; Durbin et al. 2002, 2004, 2001; Heeb et al. 2006, 2008; Huai et al. 2003, 2004, 2005; Livingston et al. 2009; Mohn et al. 2004), and remote sensing technology (Baum et al. 2000, 2001; Burgard et al. 2006). Highway tunnel measurement studies estimated the rate of exhaust ammonia emissions from in-use gasoline motor vehicle fleets inside highway tunnels based on field atmospheric sampling of ammonia concentrations in tunnel's air, whereas the chassis dynamometer studies measured direct tailpipe ammonia emission rates from different types of vehicles with specific characteristics operated on a chassis dynamometer over various driving cycles that typically simulate and represent various real on-road driving behaviors. The remote sensing studies estimated ammonia exhaust emissions from on-road vehicles using remote sensing instrumentations (e.g., stand-off, open path lasers) to measure the concentrations of atmospheric ammonia near or across roadways.

In this study, direct tailpipe exhaust emissions of ammonia from a representative

sample of 53 light-duty gasoline- and diesel-powered motor vehicles have been measured using a portable Pollution Emissions Monitoring System (PEMS) over on-road Real Driving Emissions (RDEs). The RDEs tests were carried out on an urban driving testing cycle designed on a local road network within the city of Logan, Utah. The tested vehicles had the same tier level distributions as the on-road motor vehicles fleet of the Wasatch Front and Cache County. The PEMS modules were carried on tested vehicles and their ceramic exhaust emission sensors were mounted in the engine exhaust pipe of tested vehicles. Direct quantification of raw exhaust ammonia emissions using appropriate reliable portable instrumentation mounted on vehicles' tailpipes over on-road real driving conditions would result in better understanding of vehicles' contribution to total anthropogenic ammonia emissions.

CHAPTER II

HYPOTHESIS AND OBJECTIVES

Gasoline and diesel motor vehicles are linked with increased emissions rates of NH_3 into the atmosphere following the introduction of catalytic converters. The hypothesis of this study is that exhaust NH_3 is being emitted from gasoline and diesel motor vehicles at rates sufficient to be considered as a major contributor to atmospheric ammonia inventory, along with other main sources of ammonia such as the agriculture sector, and that application of currently available emission rates may not adequately reflect northern Utah's vehicle fleet and driving practices.

The overall goal of this study was to quantify NH_3 emission rates from on-road gasoline and diesel motor vehicles in the State of Utah using reliable portable Pollution Emissions Monitoring Systems (PEMS) that will be mounted on solicited test vehicles over a specified on-road urban driving testing route. The research focused objectives are summarized below.

Objective 1: Recruit gasoline and diesel vehicles test samples representative of the Northern Utah on-road light-duty gasoline and diesel vehicles fleet

The aim of this objective was to identify the population and the characteristics of the representative vehicle test samples that will be used to represent the northern Utah's on-road light-duty gasoline and diesel motor vehicles fleet. The total population of northern Utah's on-road gasoline and diesel light-duty motor vehicles with a Gross

Vehicle Weight Rating (GVWR) up to 12,000 lbs. was obtained from the State of Utah Department of Motor Vehicles (DMV). Registered on-road vehicles were first sorted based on their fuel type into gasoline and diesel motor vehicles. Finally, representative test samples of gasoline and diesel vehicles were selected.

Objective 2: Quantify NH_3 concentrations in the exhaust emissions of diesel and gasoline vehicles test sample over Real Driving Emissions (RDEs) tests

This objective mainly aimed to quantify NH_3 exhaust emissions of diesel and gasoline vehicles over Real Driving Emissions (RDEs) tests using a reliable portable Pollution Emissions Monitoring System (PEMS). The modules of selected PEMS were carried onboard tested vehicles and were wired with their sensors that were mounted on the tailpipe of tested vehicles. The selected PEMS was also used to measure NO_x concentrations in the exhaust of tested gasoline and diesel motor vehicles. Additionally, the concentration of other relevant exhaust gases including unburned HC, CO, and CO_2 were simultaneously monitored using a separate portable instrument. Carbon monoxide is an ammonia precursor, whereas HC and CO_2 concentrations could be used to explain measured ammonia concentrations. Under this objective, an urban-driving test cycle was identified on the local network of Logan City, UT near the Utah Water Research Laboratory (UWRL) to perform the RDEs tests.

Objective 3: Calculate and analyze NH_3 emission rates of tested diesel and gasoline motor vehicles

This objective mainly aimed to analyze obtained data from the RDEs tests and to

report the emission rates of NH_3 and other exhaust gases in milligrams per mile (mg/mile). This is because regulated exhaust emissions including CO, NO_x and HC are reported in mass per traveled distance. Prediction models such as the MOtor Vehicle Emission Simulator (MOVES) model also estimate exhaust emissions of on-road and off-road vehicles in mass per traveled distance. The Microsoft Office Excel, MATLAB and RStudio software packages were used to analyze the collected data from the real driving emissions tests. The analyses mainly included descriptive and inferential analyses, and correlation and regression analyses.

CHAPTER III

LITERATURE REVIEW

3.1. Exhaust emissions from motor vehicles

Air pollution from motor vehicles did not attract much attention until major air pollution emissions from industry and coal combustion were controlled in 1950s (Schultz et al. 2017). Also, the first occurrence of an eye- and nose-irritating pollutant in Los Angeles, USA that was later named “Photochemical Smog” furthered the attention of both regulators and citizens to automobiles’ air pollution (Kidd and Kidd 2006). Photochemical smog involves a mixture of pollutants that usually form when sunlight strikes NO_x and HC compounds (Hallquist et al. 2016). As a result, a brown haze usually forms above cities and other dangerous secondary air pollutants such as ozone (O_3) and peroxyacetyl nitrate (PAN) will also be generated. Since the large air pollution emissions from industry were already controlled and natural gas became the principal urban heating gas in the United States, the smog problem was inevitably caused by air pollutants originating from exhaust emissions of automobiles, which were the third common source of air pollutants after industry and wood combustion (De Nevers 2010). By 1954, it was confirmed by several studies that smog and other related air pollutants were largely formed from materials emitted from motor vehicles (Kidd and Kidd 2006).

Exhaust emissions of NO_x and unburned HC including fine particles of carbon-based compounds and vapors from unburned fuel were found to be the main pollutants

responsible for the smog formation problem. Because of that, the auto industry was forced by regulators to develop new technologies to better control automotive air pollution emissions and to meet stricter exhaust emission regulations that were imposed by the Motor Vehicle Control Act of 1965 and the Clean Air Act of 1970 (De Nevers 2010). In response, the automobile industry succeeded in developing the catalytic converters that become an integral part of vehicles' exhaust system (Figure 2).

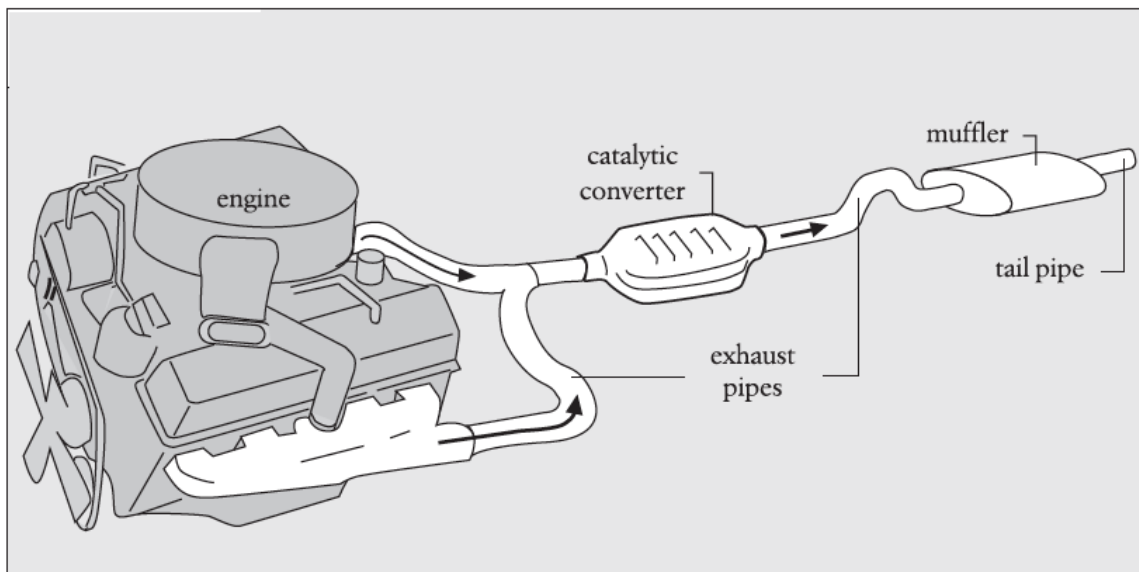


Figure 2. Idealized automotive exhaust system showing the catalytic converter (Kidd and Kidd 2006).

Catalytic converters are small canisters used to convert pollutant gases found in vehicles' exhaust emissions including CO, HC, and NO_x into relatively non-harmful gases such as CO₂, N₂ and H₂O. The unburned HC and NO_x compounds were targeted for control mainly because of their responsibility for smog formation, whereas CO was targeted due to its known toxicity to humans. Catalytic converters have been developed and their efficacy has been highly improved in order to control motor vehicles' exhaust

emissions and to comply with emission regulations as they keep getting stricter over time. Other technologies were also developed and included in the exhaust system of vehicles such as oxygen sensors for optimum operation of the combustion process and the convertors (Farrauto et al. 2019). Table 1 shows how the regulations have been getting stricter over time.

Table 1. Selected history of U.S. automobile air pollutant emission regulations in grams per mile (g/mile) (De Nevers 2010).

Year	Tailpipes emissions		
	CO	NO _x	HC
Pre-control (1960s)	87	3.6	8.8
1970	23	-	2.2
1972	39	-	3.4
1975	15	3.1	1.5
1980	7	-	0.41
1981	3.4	1	0.20
2000	3.4	0.4	0.08
2003	3.4	0.2	0.08
2016	4.2	0.07	0.01
2017	0.001	0.03 (combined NO _x and HC)	

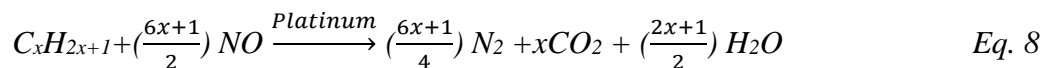
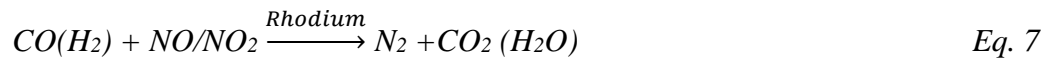
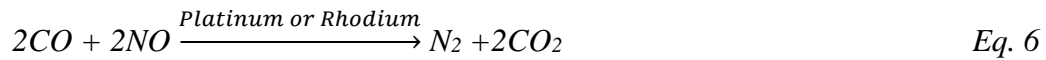
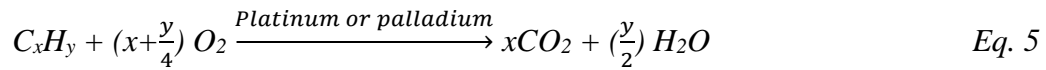
3.2. Types of catalytic converters and their effect on ammonia exhaust emissions

3.2.1. Types and purpose of catalytic converters

Catalytic converters are typically small canisters designed to control exhaust emissions of CO, HC, and NO_x from gasoline and diesel motor vehicles. They remove these pollutants from fuel combustion residues prior to their release into the environment by converting them into less-harmful compounds such as CO₂, H₂O, and N₂ (De Nevers 2010). This is usually done through sequential chemical oxidation and reduction reactions on converters' surfaces which are coated with rare earth catalysts such as platinum (Pt), palladium (Pd), and rhodium (Rh). Carbon monoxide and HC are ideally oxidized into CO₂ and H₂O, while NO_x compounds are reduced into N₂ gas. The rare metals coating the surfaces of catalytic converters are solid chemical catalysts that mainly help the oxidation and reduction reactions to occur faster by reducing the activation energy barrier of these reactions. These catalysts are not consumed during the reactions and are expected to keep functioning for around 10 years before they get exhausted (Ding et al. 2019).

The first generation of catalytic converters (1975-1980) were only oxidation catalytic converters. They were developed for oxidation of CO and unburned HC as shown in Eq. 4 and Eq. 5, respectively (Bartholomew and Farrauto 2011; Farrauto et al. 2016; Heck et al. 2016). The ceramic screens of these converters were coated with rare earth metals such as Pt and Pd that were found to be stable and highly active for CO and HC oxidation. Oxidation-only catalysts are still used on diesel-powered vehicles but gasoline-powered vehicles are now equipped with three-way catalytic converters. The

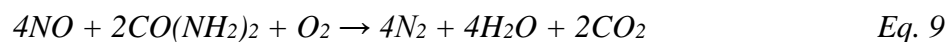
three-way catalytic convertor (TWC) was introduced in 1981 with an additional advantage of reducing NO_x (mostly NO and NO₂) emissions from motor vehicles. For that, Rh, a third rare earth metal which was found to be an excellent NO/NO₂ reduction catalyst, started to be used in manufacturing TWC convertors along with Pt and Pd catalysts (Shelef and Graham 1994). Reduction of NO_x emissions to N₂ gas occurs in different reactions as shown in Eq. 6 to Eq. 8 (Farrauto et al. 2019). Three-way catalytic convertors replaced the oxidation-only convertors on vehicles running on gasoline in 1981 and are the currently used exhaust control technology.



In 2010, a third type of catalytic converter was mandated for use on diesel vehicles along with the oxidation converters, known as Selective Catalytic Reduction (SCR) system. The SCR system aims to control the emissions of NO_x from diesel motor vehicles. It is an advanced emissions control technology system that injects liquid-reductant agents (usually automotive grade urea (CO(NH₂)₂) or ammonia) into the exhaust stream of diesel-powered motor vehicles. The injected liquid-reductant agent is usually referred to as Diesel Exhaust Fluid (DEF). The DEF normally starts a chemical

reaction that converts the NO_x into mostly N₂ gas and H₂O before being expelled through the vehicle tailpipe (Eq. 9 - Eq. 11). Small amounts of CO₂ would also be produced.

However, the excessive injection of urea may cause the emission of unreacted (slip) NH₃ to atmospheric environments (Miura et al. 2014).



3.2.2. Effect of catalytic converters on ammonia exhaust emissions

Aside from their ability to control exhaust CO, unburned HC, and NO_x emissions, oxidation and three-way catalytic converters have been associated with unintended increases in emissions of ammonia in the exhaust of gasoline and diesel motor vehicles (Fraser and Cass 1998). Numerous studies have shown that pre-catalyst vehicles had a very small and often neglectable emission rates of exhaust NH₃ (Cadle et al. 1979; Urban and Garbe 1979). On the contrary, motor vehicles equipped with catalytic converters have been linked with dramatically higher emissions of exhaust NH₃ as shown by plentiful laboratory (dynamometer) and on-road fleet studies. For instance, Cadle and Mulawa (1980) measured dynamometer-based emission rate of exhaust ammonia of 19-24 mg/mile for a gasoline vehicle equipped with a three-way catalytic converter. Upon removing the three-way catalytic converter and replacing it with a straight pipe, the exhaust NH₃ emission rate of the same vehicle dropped dramatically to 0.3-8 mg/mile.

The literature also shows that old gasoline vehicles (manufactured before the use of TWC convertors) fitted with oxidation-only catalysts have also resulted in unintended increases in exhaust ammonia emissions. However, exhaust ammonia emission rates from the more modern three-way catalyst-equipped vehicles are typically the highest. Early dynamometer studies showed that nominal ammonia emission rates for pre-catalyst gasoline vehicles, oxidation-only catalyst-equipped gasoline vehicles, and gasoline vehicles with properly operating TWC catalysts are 5, 10, and 35 mg/km, respectively (Bradow & Stump, 1977; Cadle & Mulawa, 1980; Cadle et al., 1979; Harkins & Nicksic, 1967; Harvey et al., 1983; Henein, 1975; Sawicki, Mulik, & Wittgenstein, 1978; Smith & Black, 1980; Smith & Carey, 1982; Urban & Garbe, 1979, 1980). Likewise, a comprehensive dynamometer NH₃ vehicular emissions inventory study that was made for the southern part of California, USA showed that the emission rates of ammonia for properly operating gasoline vehicles ranged from 2.5-5 mg/km for pre-catalyst vehicles, 2.5-5.7 mg/km for vehicles with oxidation-only catalyst, and 3.6-60.8 mg/km for vehicles equipped with three-way catalytic convertors (Dickson 1991).

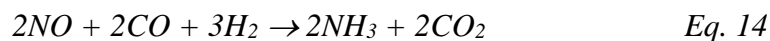
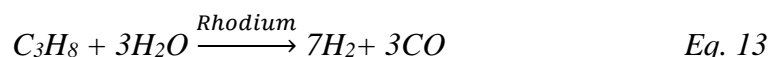
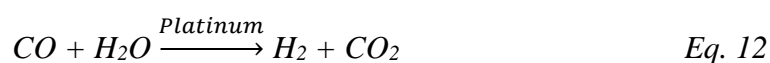
As compared with gasoline vehicles fitted with three-way catalytic convertors, diesel-powered vehicles fitted with oxidation catalysts and pre-catalyst diesel vehicles were also linked with low exhaust NH₃ emission rates, similar to those measured for gasoline vehicles fitted with oxidation-only catalytic convertors. Ammonia emissions from light-duty diesel vehicles had a range of 0 to 8 mg/km, while heavy-duty diesel vehicles could emit up to 17 mg/km of exhaust NH₃ (Cadle et al. 1979; Harvey et al. 1983; Henein 1975). Similar emissions rates of NH₃ ammonia from diesel vehicles were also suggested by Dickson (1991). However, an on-road in tunnel study done by Pierson

and Brachaczek (1983) showed that significant amount of NH_3 emissions attributed to diesel vehicles possibly originated from the livestock hauled by these vehicles. This perhaps explains the fact that most previous studies have been focusing on estimating exhaust ammonia emissions from gasoline-powered motor vehicles fitted with either oxidation or three-way catalytic converter. In addition, diesel-powered vehicles are small in numbers as compared with gasoline-powered vehicles that normally dominate vehicle fleets.

3.3. Ammonia formation in motor vehicles exhaust emissions

The process of exhaust ammonia formation has been linked with the reactions of nitric oxide and hydrogen gas over the surface of oxidation and three-way catalytic converters. The process normally starts with carbon monoxide reacting with water producing carbon dioxide and hydrogen gas as shown in Eq. 12 and Eq. 13 (Wang et al. 2015). The reaction shown in Eq. 13 usually occurs when $\lambda < 1$ under rich conditions over rhodium resulting in formation of more hydrogen molecules than under normal driving conditions. Lambda (λ) is the normalized air to fuel ratio which equals the ratio of actual air/fuel ratio to the stoichiometric air/fuel ratio. When λ is < 1 , this means that the vehicle is running under rich conditions because the actual air/fuel ratio is less than the stoichiometric air/fuel ratio of approximately 14.9 lbs. air/lbs. fuel (assuming fuel is C_3H_8). This also means that the engine is not getting enough air to optimally combust the fuel. Contrarily, a motor vehicle would be running under lean conditions when the normalized air to fuel ratio (λ) is greater than 1. Lean conditions indicate that the engine is getting excess air to combust the fuel and hence, the actual air to fuel ratio is greater

than 14.9 lbs. air/lbs. fuel. Under rich conditions ($\lambda < 1$), more hydrogen molecules would be formed than under normal driving conditions as clearly shown in Eq. 13. Following hydrogen gas formation, ammonia forms as an outcome of the reaction between the produced hydrogen gas and nitric oxide. The reaction of hydrogen gas and nitric oxide can occur through two different pathways as shown in Eq. 14 and Eq. 15. Both pathways of reaction result in two molecules of ammonia.



Formation of exhaust ammonia over the catalytic convertors of gasoline motor vehicles could be further increased under fuel-rich driving conditions when reducing agents are normally present. This is because these conditions favor reducing processes over the surface of catalytic convertors. Due to incomplete combustion of fuel under fuel-rich conditions, more CO would form and be available to react with H₂O causing more H₂ to be generated (Eq. 12). In addition, unburned hydrocarbons would react with water and result in 7 moles of H₂ per 1 mole of HC (Eq. 13). All this H₂ gas will lead to more exhaust ammonia upon reacting with NO compounds that exist normally in exhaust emissions. Cadle & Mulawa (1980) forced a three-way catalyst-equipped vehicle to run over conditions richer than 13.5 air/fuel ratio by adjusting the fuel injection controls. As a result, the vehicle caused approximately 108-268 mg of exhaust ammonia to emitted per

mile. However, running the same vehicle at normal conditions near-stoichiometric air/fuel mixing ratios resulted in emitting exhaust ammonia at rates of 19-24 mg/mile (Cadle and Mulawa 1980). In addition to aggressive driving behavior, failure of oxygen sensors to control the air-fuel ratio to be running at near-stoichiometric conditions could also result in rich air-fuel ratio conditions.

Higher NH_3 emissions could also result due to malfunctioning TWC converters that no longer efficient in controlling overall exhaust emissions (Cadle and Mulawa 1980; Fraser and Cass 1998). In fact, vehicles with malfunctioning TWC converter and/or oxygen sensors were linked with an extremely higher rates of exhaust ammonia emissions than vehicles running with properly operating converters. Dickson (1991) estimated that vehicles with malfunctioning TWC could emit up to 268.1 mg of NH_3 per a mile (Dickson 1991). This is almost three times the maximum emission rate of ammonia of vehicles with properly working converters of 97.8 mg/mile as reported by the same study.

Fuel composition such as the percentage of sulfur has also shown to cause variation in exhaust ammonia formation over the surface of TWC converters as it is known for adversely impacting the efficiency of catalytic converters for regulated contaminants (Benson et al. 1991). However, some chassis dynamometer studies reported that the content of sulfur has different impacts on formation rates of exhaust ammonia. For instance, (Durbin et al. 2002) showed that ammonia emissions rates were inversely proportional to the fuel's sulfur content. The study showed that increasing fuel's sulfur content by 11 times from 30 to 330 ppm_w resulted in 87 % ammonia reduction from 38 to 5 mg/mile for a Transitional Low-Emission Vehicle (TLEV) passenger vehicle over the

FTP cycle (Durbin et al. 2002). These outcomes are in line with the findings of several studies including (Summers and Baron 1979) that suggested that sulfur compounds had the ability to inhibit ammonia formation over catalytic convertor surfaces by poisoning ammonia formation reaction sites. Despite that, the study of Durbin et al. (2002) showed that decreasing fuel's sulfur content caused exhaust ammonia emissions to drop from 237 to 146 mg/mile resulting in 62 % ammonia reduction when the same vehicle ran over the US06 driving cycle. The same trend was also reported for another vehicle tested by the authors. This relationship between ammonia emission rates and fuel sulfur content was also confirmed by Borsari and Assunção (2017). The authors explained that, although the observed difference in ammonia emissions rates caused due to different sulfur content was statistically insignificant, the fuel with higher sulfur content resulted in higher emissions rates of ammonia over the FTP driving schedule. Similarly, Baronick et al. (2000) supported a positive relationship between sulfur content and formation of exhaust ammonia over catalyst surfaces. The authors showed that decreasing fuel sulfur content resulted in lowering exhaust ammonia emissions. However, the same study concluded that fuel sulfur content had little impact on formation of exhaust ammonia emissions. All these studies conclude that fuel sulfur content has uncertain impact of formation of ammonia over the surface of TWC convertors.

3.4. Measurement of exhaust ammonia emissions

Accurate estimation and quantification of exhaust ammonia emissions from mobile sources is necessary as these emissions can significantly contribute to the total atmospheric ammonia inventory. This will help in better understanding of vehicles'

contribution to atmospheric particulate matter inventory. It also helps regulators and stakeholders in planning, facilitating, and implementing effective reduction strategies of secondary particulate matter pollutants especially in areas where these particles occur at elevated concentrations and violate the applicable standards due to large number of motor vehicles. Additionally, reliable estimations of exhaust ammonia coming out of mobile vehicles' tailpipes would help the automotive industry and manufacturers in better modifying and improving catalytic converter performance in order to cause significant reduction in emissions of exhaust ammonia and the consequently PM pollutants.

Therefore, a growing interest in estimating precisely the emissions of exhaust ammonia from mobile sources has been of interest over the past few decades. For this purpose, the researchers have been using different measurement methodologies, mainly on-road in-tunnel field measurements and chassis dynamometer studies. In addition, a few studies employed the remote sensing technology for the estimation of exhaust ammonia from motor vehicles.

3.4.1. On-road in-tunnel measurement studies

On-road in tunnel measurement studies estimate the emission rates of exhaust ammonia from in-use motor vehicles based on field measurements inside roadway tunnels over a specified period of time. Most on-road in tunnel measurement studies measured atmospheric ammonia concentration at tunnel exit portals. Hence, exhaust ammonia emission rates reported by these studies are believed to represent the cumulative emissions of exhaust ammonia in the whole tunnel since the air carrying exhaust ammonia emissions accumulate at tunnels' exit portals before leaving the tunnels

due to vehicles' movement towards the exit. Motor vehicles inside tunnels create a piston air flow as they move from tunnels' entrances to their exit (Fraser and Cass 1998). The air piston impact created due to vehicles' movement is how the air inside tunnels is mostly exchanged. Most ventilation systems work only in case of dangerous situations including fires, reduced visibility, or accumulation of high carbon monoxide levels. This fact is supported by many on-road in-tunnel measurement studies that reported remarkably higher ammonia concentrations at the exit of tunnels as compared with ammonia concentrations measured at their entrances. For instance, Kean et al. (2000) showed that ammonia concentrations at tunnel exits were as high as 10 times higher than at tunnel entrance. This could also be due to the fact that people usually accelerate as they leave the tunnel causing the engine to run over rich conditions and consequently, higher emission rates of ammonia occurs. Another important note is that almost all the on-road tunnel studies were carried out in tunnels where mostly gasoline-powered vehicles including personal vehicles and light-duty trucks dominated the traffic flow.

On-road in tunnel measurement studies provide useful data for estimation of exhaust ammonia emissions from different motor vehicles fleets. However, these studies have certain limitations. Most importantly, on-road in tunnel measurement studies targeted fleets of vehicles that were driving on highway roads at almost constant high speed over a hot-stabilized operating mode (Kirchstetter et al. 1999). This driving condition normally cause lower emissions rates of exhaust ammonia as compared with other driving modes and conditions Livingston et al. (2009). Hence, this driving condition may not be taken as representative for all other driving conditions that produce significantly higher ammonia emissions. For instance, Fraser and Cass (1998) reported

that upon analyzing the videotape of a camera installed at a traffic turn-out within the Van Nuys Tunnel, the recorded speeds of all vehicles in the tunnel during the measurement period were generally uniform and no congestion that may result in deceleration and acceleration was observed at any point. Similarly, Kean et al. (2000) highlighted the fact that no stalled vehicles were observed at the time of measurements and heavy acceleration and stop-and-go driving conditions were rarely observed. These traffic conditions are identical to those observed in almost all on-road in tunnel measurement studies reviewed within the literature.

In addition to what has been mentioned, having a high number of vehicles in a tunnel would result in different mixing ratio of air as compared with times where the traffic flow is small, especially since these studies are usually carried out during rush hours and with the ventilation fans often turned off. Large traffic flow causes more mixing of air than small traffic flow. Additionally, the longitudinal airflow inside the tunnels is usually caused by the flow of traffic through the tunnel and prevailing winds; however, the magnitude and the direction of wind were not reported or examined for correlation with ammonia emissions. The influence of possible air exchange through the openings between tunnels' neighboring sections was also not studied. The effect could be greater in the case of two neighboring sections with opposite traffic directions. Moreover, most on-road in tunnel measurement studies only provided an estimation of traffic flow (number of cars) and vehicle type inside tunnels, regardless of their different and unique exhaust emission rates due to many parameters such as catalytic convertor condition, mileage on the vehicle, the load in the vehicle, the air/fuel ratio, the driving patterns of drivers, and many other parameters. Therefore, it was challenging to the authors of these

studies to come up with a practical way to assign ammonia emissions rate to specific vehicles group and to determine the contribution of each vehicle's category. As a result, air quality regulators would not be able to identify and locate the responsible vehicle type or characteristic for ammonia emissions that may be marked for regulation. For instance, Fraser and Cass (1998) reported that it was impossible to determine if the measured high ammonia emissions were caused due to a small number of vehicles running under very rich conditions or due to a large number of vehicles running under less rich conditions.

Lastly, ammonia losses to sampling apparatus and tunnel surfaces because of its stickiness have been shown to be a concern of many studies (Sutton et al. 1998). Ammonia losses to tunnels walls and sampling tubes and containers could be more problematic especially in the case of low exhaust ammonia concentrations. For instance, Kean et al. (2000) carried out a side-by-side measurement of ammonia using identical sampling devices except for a Teflon inlet tube and cyclone. The results showed that the losses of ammonia to the surfaces of the inlet sampling tube and the cyclone ranged between 1 and 13%, with an average of 7%. Likewise, Cadle and Mulawa (1980) reported that losses of amines and ammonia samples to the walls of transfer tubes and collection containers varied from 20-100% depending on the condition and type of sampling apparatus. For instance, a stainless-steel fitting installed in the sampling system was found to be responsible for removing as much as 90% of the amines. The study also emphasized that the efficiency of sample collection using new sample lines dropped from 100% to almost 80 % at the end of the project. The effect of contaminated walls of sampling apparatus on ammonia loss has also been highlighting by Pierson and Brachaczek (1983) who showed that using sampling dilution tubes with soot deposits

accumulated over a long time deeply affected the results as compared with a clean dilution tube. In fact, the outcomes of their study showed that the recoveries were only 10-50% when an uncleaned dilution tube was used. The problem of ammonia stickiness to tunnels' walls and stainless-steel sampling tubes has also been observed by Moeckli et al. (1996) who reported that ammonia concentrations stayed at high levels even at nighttime where traffic flow was considerably lower than daytime. The authors, however, assumed that this only affected low concentration values. These findings signify the importance of having well-designed and carefully-monitored sampling systems of exhaust ammonia as wall deposits could play a governing role in reporting inaccurate emissions rates. Typically, Teflon lines and fittings are preferable to steel fittings and new clean apparatus are also preferred to old contaminated apparatus. Ammonia could also be lost during samples collection process if ammonia exhaust emissions carried in tunnels air and/or ammonia salts collected on filters react with acids (e.g. H_2SO_4) that may originate from the ambient air or/and other vehicles emissions (Truex et al. 1980).

3.4.2. Chassis dynamometers studies

Chassis dynamometers are devices for measuring torque, force, or power available from a vehicle's rotating shaft. They have been used by many studies for quantifying raw exhaust emissions coming out of vehicles' tailpipes under different circumstances such as various vehicle speed and changing engine load. A schematic diagram of the dynamometer experimental setup is shown in Figure 3. Chassis dynamometer studies rely on having different types of vehicles with specific characteristics operated over different simulated driving cycles. Chassis dynamometer

driving schedules are primarily used to simulate and represent various real on-road driving behaviors and under different conditions and situations. For instance, aggressive driving behavior with high speed and rapid acceleration is usually represented by the US06 driving schedule, while NYCC driving schedule represents driving at low speed with multiple stops. The common driving cycles used are shown in Table 2.

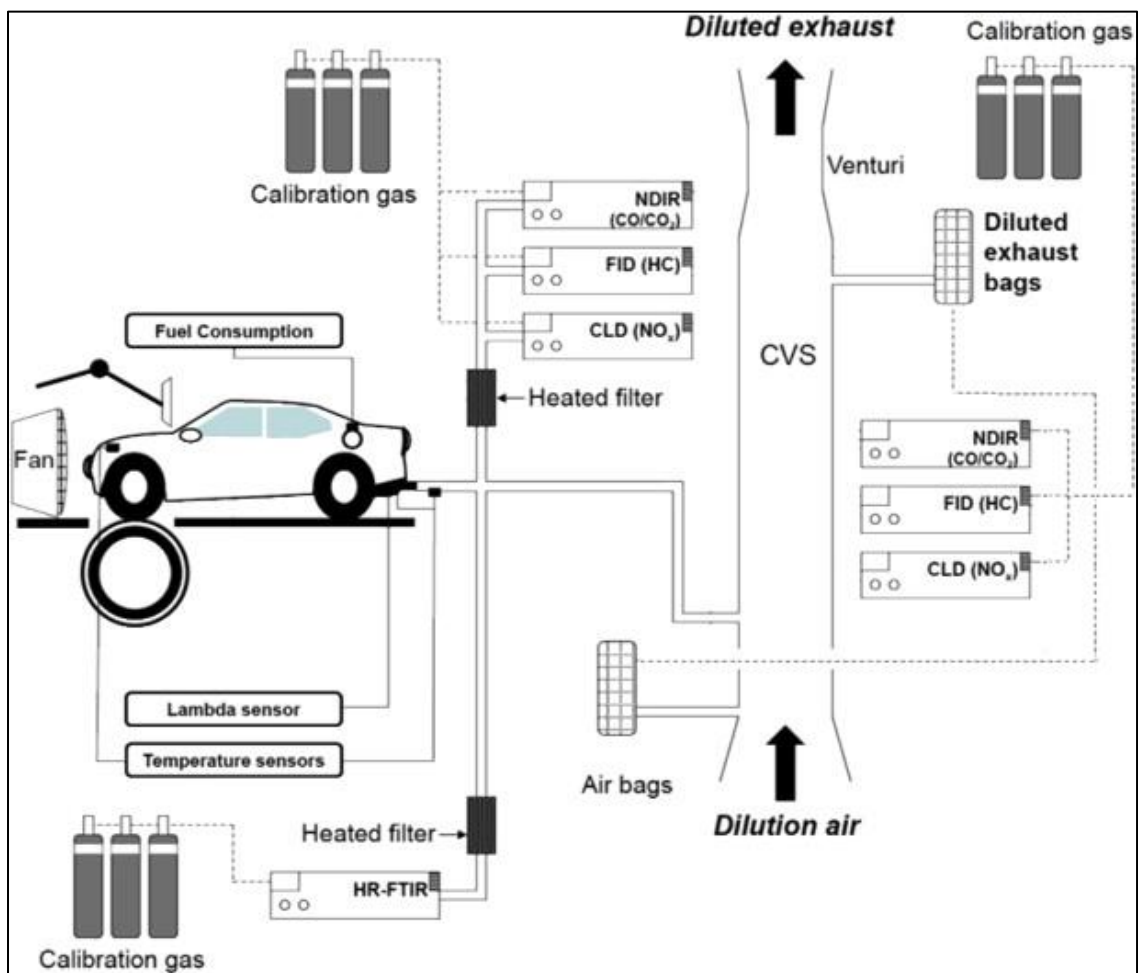


Figure 3. Schematic diagram of the dynamometer experimental setup (Suarez-Bertoa et al. 2014).

Table 2. Common chassis dynamometers driving schedules.

Cycle	Description
Federal Test Procedure (FTP-75)	A three-phase cycle used for certification of exhaust emissions and testing of fuel economy of light-duty vehicles. It consists of Cold Start Transient phase, Stabilized phase, and lastly Hot Start Transient phase. The last phase usually done after a 10 minutes Hot Soak period.
Supplemental Federal Test Procedure (SFTP SC03)	Used to represent the engine load and emissions associated with the use of air conditioning (A/C) of the vehicle certified over the FTP-75 cycle.
Supplemental Federal Test Procedure (SFTP US06)	Used as a representation of aggressive, high speed and/or high acceleration driving behavior, rapid speed fluctuations, and driving behavior following startup.
New York City Cycle (NYCC)	Developed to simulate low-speed urban driving with frequent stops of light-duty vehicles in highly populated areas with congested traffic.
California Unified Cycle (UC)	Designed specifically for Los Angeles driving patterns. As compared with the FTP-75 cycle, this cycle has higher speed, higher acceleration, fewer stops per mile and less idle time. It is also applicable for testing vehicles with direct ozone reduction technologies.

Air quality researchers started using the chassis dynamometers for conducting their exhaust ammonia studies mainly in order to overcome the limitations and constraints of on-road tunnel measurement studies. Unlike on-road tunnel measurement studies, dynamometer studies allowed raw exhaust measurements of ammonia emissions directly out of vehicles' tailpipes. Chassis dynamometers studies have also made it possible to have a real-time profiles of ammonia emission for certain vehicles with specific unique characteristics. The impact of different parameters and factors such as vehicles type and model year were examined too in some dynamometer studies, whereas the on-road tunnel measurement studies were able to only report the traffic flow and, in some cases, the different types of vehicles fleet received in the tunnel at the time of measurement.

Furthermore, chassis dynamometers studies examine exhaust ammonia emissions under various driving behaviors and operating conditions. For instance, dynamometer studies were able to estimate ammonia emissions rates from motor vehicles over several operating conditions such as aggressive driving behavior (US06 cycle) and low-speed urban driving with frequent stops (NYCC cycle), whereas motor vehicles that were included in on-road tunnel measurement studies operate under steady state, hot stabilized operating conditions without any consideration of the variable ammonia emissions rates caused due to other conditions. This leads to probable underestimation of exhaust ammonia emissions as running the vehicles on highways under steady state hot stabilized operating conditions usually results in less ammonia emissions than due to other driving conditions.

3.4.3. Real Driving Emissions (RDEs) studies

Recent studies such as (Mendoza-Villafuerte et al. 2017) used onboard Pollution Emissions Monitoring System (PEMS) for measuring NH_3 exhaust emissions of motor vehicles. Targeted vehicles would be tested over RDEs tests on designed urban-driving test cycles. An example of these PEMS is the ECM miniPEMS that are used in this study. The ECM miniPEMS has been recently used by (Bodisco et al. (2019),; Prakash and Bodisco (2019),; Shahariar et al. (2019), and; Tang et al. (2020) for measuring vehicle exhaust emissions. For instance, Bodisco et al. (2019) used the ECM miniPEMS to investigate the emissions of NO_x of a modern commercial passenger vehicle. The tests were carried out over a one-hour urban driving testing route that contains a mix of urban (<60 km/h), rural (<90 km/h) and motorway (>90 km/h) roads. Similarly, Shahariar et al. (2019) used the ECM miniPEMS to investigate the real-time NO_x emissions from a heavy-duty diesel truck. The tests were done on a route that had a combination of a flat and hilly roads segments.

CHAPTER VI

MATERIALS AND METHODS

4.1 Study area-Wasatch front-UT:

The Wasatch Front and Cache County is where more than 80% of the Utah population is located. It is a narrow strip of land located in the north-central part of the State of Utah. It is bordered by the Wasatch Mountains on the east and by the Great Salt Lake, Utah Lake, and smaller mountain ranges on the west. The Wasatch Front includes six counties: Box Elder, Davis, Salt Lake, Tooele, Utah, and Weber (Figure 4).

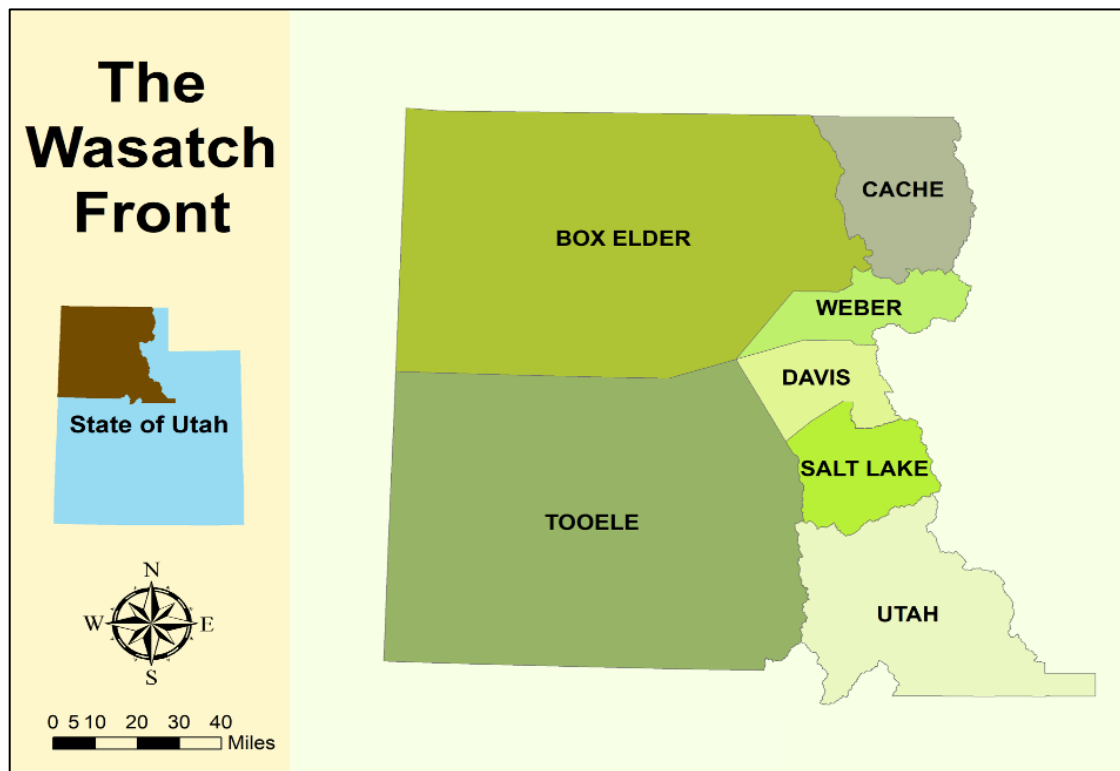


Figure 4. Counties of the Wasatch Front (raw data were obtained from the Utah Automated Geographic Center (Utah Geospatial Resource Center 2020)).

The seven counties were non-attainment areas for PM_{2.5} as of 2020 (EPA 2021). Additionally, in January 2004, Cache County had the worst ever, non-fire related PM_{2.5} pollution episode in the United States. The 24-hr PM_{2.5} concentration was recorded at 132.5 µg/m³, which is almost four times the EPA National Ambient Air Quality Standard (NAAQS) of 35 µg/m³ (Cipollone et al. 2015; Hammond et al. 2017; Malek et al. 2006).

Based on the data obtained from the Utah Division of Motor Vehicles (DMV), the seven counties of the Wasatch Front had approximately 1,936,849 registered LD gasoline, diesel and electric motor vehicles with a Gross Vehicles Weight Rating (GVWR) up to 12,000 pounds as of February 2019. Light-duty gasoline vehicles represented 94.3% of the on-road fleet with 1,826,584 vehicles, whereas diesel cars and truck represented only 5.5% of all registered vehicles. Electric vehicles were only 4,736 vehicles that represented 0.2% of the whole fleet. For this research, only gasoline and diesel motor vehicles were targeted as they produce exhaust emissions. Electric vehicles were discarded as they cause no exhaust emissions to be produced. The population of gasoline and diesel motor vehicles of each county of the Wasatch Front is shown in Table 3. Gasoline motor vehicles are expected to cause a significant amount of NH₃ emissions because of their three-way catalytic converters and as they represent most of the on-road vehicles fleet of the Watch Front. Light-duty diesel vehicles are expected to emit lower emission rates of NH₃ as compared with gasoline motor vehicles (Pierson and Brachaczek 1983). Light-duty diesel vehicles lack the TWC converters and they also represent a small portion of the Wasatch Front on-road vehicle fleet.

For this research, the project target goal was to test 50 or more light-duty gasoline and diesel motor vehicles with Gross Vehicle Weight Rating (GVWR) up to 12,000 lbs. to represent the on-road light-duty vehicle fleet along the Wasatch Front. A representative sample of 53 vehicles were successfully tested. The representative sample consisted of 47 gasoline motor vehicles and 6 diesel motor vehicles.

Table 3. The 2019 population of gasoline and diesel vehicles of the Wasatch Front.

	County	Gasoline vehicles population	Diesel vehicles population
1	Box Elder	47,907	5,784
2	Cache	84,717	5,182
3	Davis	243,709	10,860
4	Salt Lake	834,487	43,831
5	Tooele	56,403	5,304
6	Utah	381,434	21,850
7	Weber	177,927	12,718
	Total	1,826,584	105,529

4.2. Vehicle recruitment: Gasoline and diesel vehicles test samples

4.2.1 Gasoline motor vehicles test sample

A representative sample of $n = 47$ LD gasoline vehicles was chosen to represent the Wasatch Front on-road LD gasoline vehicle fleet. The gasoline motor vehicles sample was selected so that numbers of vehicles certified to each EPA tier level is equivalent to the fractions certified to each tier level in the Wasatch Front. The tiers were Pre-Tier 0

(≤ 1980), Tier 0 (1981-1993), Tier I (1994-2000), NLEV (2001-2003), Tier II (2004-2016) and Tier III (2017-2025). The tier-level criterion was chosen to replicate the on-road gasoline motor vehicles fleet of the Wasatch Front because the U.S. EPA normally assigns each major revision of on-road vehicle tailpipe and evaporative emission standards to a “Tier level”. Hence, the vehicles of the same tier level are expected to have similar exhaust emissions for the regulated pollutants since they have the same regulations. The on-road gasoline motor vehicle fleet of the Wasatch Front were first assigned to the appropriate tier level based on their model year as shown in Table 4, and then a distributed representative sample of $n = 47$ LD gasoline vehicles was selected (Figure 5).

Table 4. Population and tier level distribution of gasoline light-duty vehicles fleet of the Wasatch Front as of February 2019.

Model Year (MY)	Tier Standard	Gasoline vehicles population
< 1981	Pre-Tier 0	24,667
1981 -1993	Tier 0	42,304
1994 - 2000	Tier 1	183,726
2001 - 2003	NLEV	174,037
2004 - 2016	Tier 2	1,163,123
2017 +	Tier 3	238,728
Total		1,826,584

The approach used in this study for designing the test sample helped the authors in overcoming the problem of recruiting vehicles from smaller-population tier levels as they were small in number. A gasoline vehicle test sample of 47 LD vehicles would allow

the use various statistical analyses. The number of vehicles within each tier level group also helped in having a more representative average for the vehicles of the same tier level. This is because vehicles of the same tier level have different characteristics such as model year, engine size, and odometer reading. The impact of the unique characteristics of vehicles was also examined due to having enough vehicles within each tier level for running various statistical analyses.

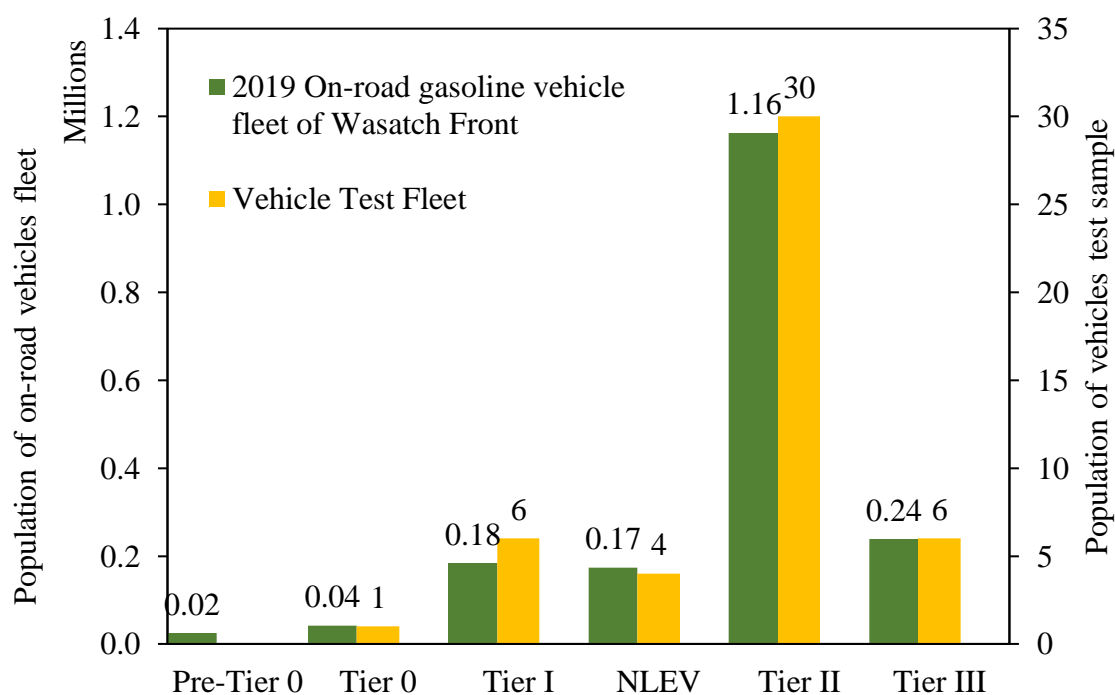


Figure 5. Vehicular profile of the Wasatch Front and current study.

The model year of tested vehicles was not pre-defined. The research team continued to test gasoline vehicles of family members, friends, colleagues, Utah Water Research Laboratory and Utah State University Facilities until the total vehicles number needed for each tier level was completed. No Pre-Tier 0 (≤ 1980) vehicles were tested mainly because these likely vehicles emit negligible amounts of NH_3 due to the absence

of TWC converters (Cadle and Mulawa 1980; Gregori et al. 1989; Pierson and Brachaczek 1983). Besides, most of these vehicles are vintage vehicles and they rarely seen on-road.

4.2.2 Diesel motor vehicles test sample

The on-road light-duty diesel motor vehicles represented only 5.4 % of the on-road vehicles fleet of the Wasatch Front. Because of their small sample size and the difficulty in securing diesel vehicles for testing, the vehicles test sample of diesel vehicles was not selected based on their tier standard. However, it was decided to test vehicles with different exhaust control devices including the Diesel Oxidation Catalyst (DOC) and the Selective Catalytic Reduction (SCR) catalyst as shown in Table 5.

Table 5. Diesel motor vehicles test sample with their fitted exhaust control devices.

#	Vehicle	Oxidation Catalyst	Selective Catalyst reduction (SCR)
1	1999 Ford F5300	None	None
2	2008 Dodge RAM 2500	Yes	None
3	2003 Dodge RAM 2500	Yes	None
4	2006 Volkswagen Jetta	Yes	None
5	2017 Dodge RAM 2500	Yes	Yes
6	2013 Dodge RAM2500	Yes	Yes

The selection of diesel motor vehicles with different exhaust control devices to be included in the test sample helped in examining the impact of these different exhaust control devices on the emission rates of NH₃ from diesel vehicles. The test sample of

diesel motor vehicles of six vehicles included one vehicle with no converters, three vehicles with only DOC converter and two vehicles with both DOC and SCR converters. The 1999 Ford F5300 was tested on Stock and Fuel Economy modes.

4.3. Real Driving Emissions (RDEs) Tests

An urban on-road driving cycle was designed on the local road network within the City of Logan, Utah, on which to conduct the Real Driving Emissions (RDE) tests using the vehicles in the test sample. The cycle started and ended at the Utah Water Research Laboratory (UWRL), and had a total length of 5.3 miles. The test cycle (Figure 6) was coded as the UWRL-UDTC (Utah Water Research Laboratory-Urban Driving Test Cycle). The same testing cycle was recently used by Khader and Martin (2019). The UWRL-UDTC included residential and highway roads with 25, 40, and 45 mph speed limits areas. The cycle had variable grades, including low and steep uphill and downhill road segments. In addition to three traffic lights located at the intersection of Center St and N 200 E St, N 200 E St and E 400 N St, and E 400 N and N 600 E, the route had two 4-way stop signs where vehicles had to come to a complete stop and yield to vehicles arriving first at the stop sign. The first 4-way stop sign is located where the Canyon Road meets with the N 600 E St and the second 4-way stop sign is located where N 200 E St and E 100 N St meet at an intersection. The route also included a 2-way stop sign that requires vehicles to completely stop and yield to crossing traffic. The 2-way stop sign is located where the Canyon Road intersects with the Center St. Lastly, the cycle included many pedestrian crossings and a school zone with a reduced speed limit from 40 to 25 mph. Based on what has been mentioned about the UWRL-UDTC, the calculated NH₃ emission rates most likely reflect the effect of many driving conditions, including stop-

and-go, high-speed highway and low-speed urban driving, acceleration/deceleration, and uphill and downhill driving conditions. Triplicate RDE tests were conducted for all tested vehicles.

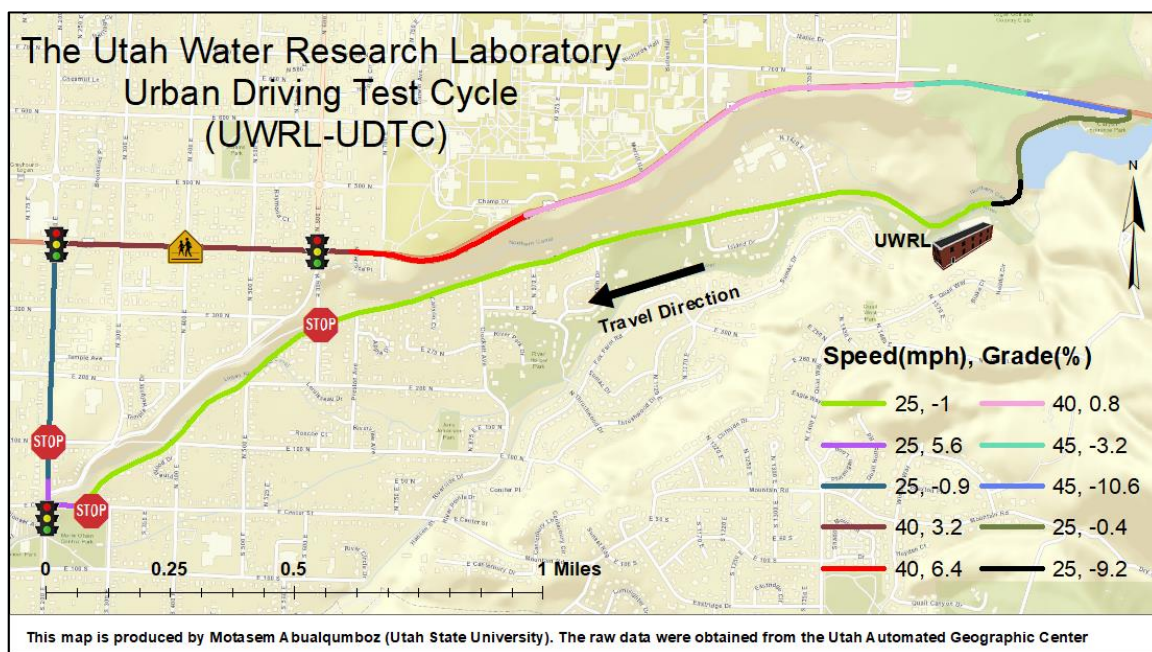


Figure 6. The Utah Water Research Laboratory-Urban Driving Test Cycle (UWRL-UDTC).

Tested vehicles were driven to the UWRL to be equipped with testing instruments. The instruments were allowed to warm up for approximately 10 minutes before the on-road RDE tests with the vehicle's engine turned off. The on-road RDE tests were conducted with slightly warmed vehicle engines and were accomplished between January and September of 2020. The researcher drove tested vehicles over the testing cycle only when vehicle owners were unavailable to drive the test cycle themselves. In those cases, the owners delivered their vehicles to the UWRL and gave permission to the researcher to drive the vehicles over the designed testing cycle. The researcher had a valid U.S. driving license and an accident-free driving record at the time of testing.

Vehicle owners who participated in the on-road tests were accompanied by the researcher and were asked to drive normally and adhere to traffic rules. No other instructions were given to them. Because of the COVID-19 pandemic, gasoline vehicles that were tested during the pandemic were sanitized after the on-road tests. The researcher and vehicle owners practiced social distancing during the on-road RDE tests and used face coverings to limit the spread of the COVID-19 virus.

The characteristics of tested gasoline and diesel vehicles including type (Passenger Car (PC), Multi-Purpose vehicle (MPV) and Light-Duty Truck (LDT)), make, model, model year, Emission Standard Tier (Tier 0, Tier I, NLEV, Tier II and Tier III), fuel type (Gasoline, Diesel), engine size and number of cylinders, odometer reading, and the Gross Vehicle Weight Rating were recorded. In addition, the vehicle's owner information, the atmospheric pressure (mmHg) at the time of testing, and vehicle's tailpipe diameter were obtained.

4.4 Measuring Equipment:

4.4.1. The ECM miniPEMS

Exhaust concentrations of NH_3 and NO_x of gasoline and diesel motor vehicles were measured in parts per million (ppm) using the portable ECM (Engine Control and Monitoring) miniPEMS. The ECM miniPEMS uses different modules and sensors for gasoline and diesel motor vehicles. The ECM miniPEMS modules were carried onboard the tested gasoline and diesel motor vehicles during the test, and were wired such that their ceramic exhaust emission sensors were mounted in the tested vehicle's engine exhaust using a 1.5"-diameter specially fabricated stainless-steel tube (Figure 7). The

ECM miniPEMS also recorded vehicle speed and revolution per minute (RPM) readings using several on-board diagnostics (OBD) readers that were connected to the tested vehicle's OBD II port. For vehicles made before 1996, the RPM and vehicle speed were recorded using a video camera as no OBD II port was available for those vehicles. The ECM miniPEMS also measured exhaust temperature using a Type J thermocouple.

The stainless-steel tube holding the sensors was inserted five inches inside test vehicle's tailpipe and extended for about 10 inches into the atmosphere to avoid ambient air interference. The sensors instantaneously measure NH_3 and NO_x concentrations once the emissions touch their ceramic sensors. This overcomes the problem of NH_3 adsorption/desorption to sampling tubes and tunnels walls because of the sticky nature of ammonia. As previously discussed, this problem was reported by several on-road tunnel studies including Heeb et al. (2006, 2008) and Mohn et al. (2004). The instantaneous measurement also prevents concentration loss due to reaction with acids potentially present in the ambient air or in emissions such as H_2SO_4 from on-road diesel motor vehicles (Truex et al., 1980). The effect of background ambient NH_3 concentrations reported particularly by on-road in-tunnel studies is also avoided by instantaneous NH_3 measurement. The ECM miniPEMS collected the NH_3 and NO_x concentrations as well as vehicle speed, engine RPMs and exhaust temperature information every 0.1 second. The ECM miniPEMS data, however, were averaged over a 1-second time period using the MATLAB software package. The reduction code is shown in Appendix A.

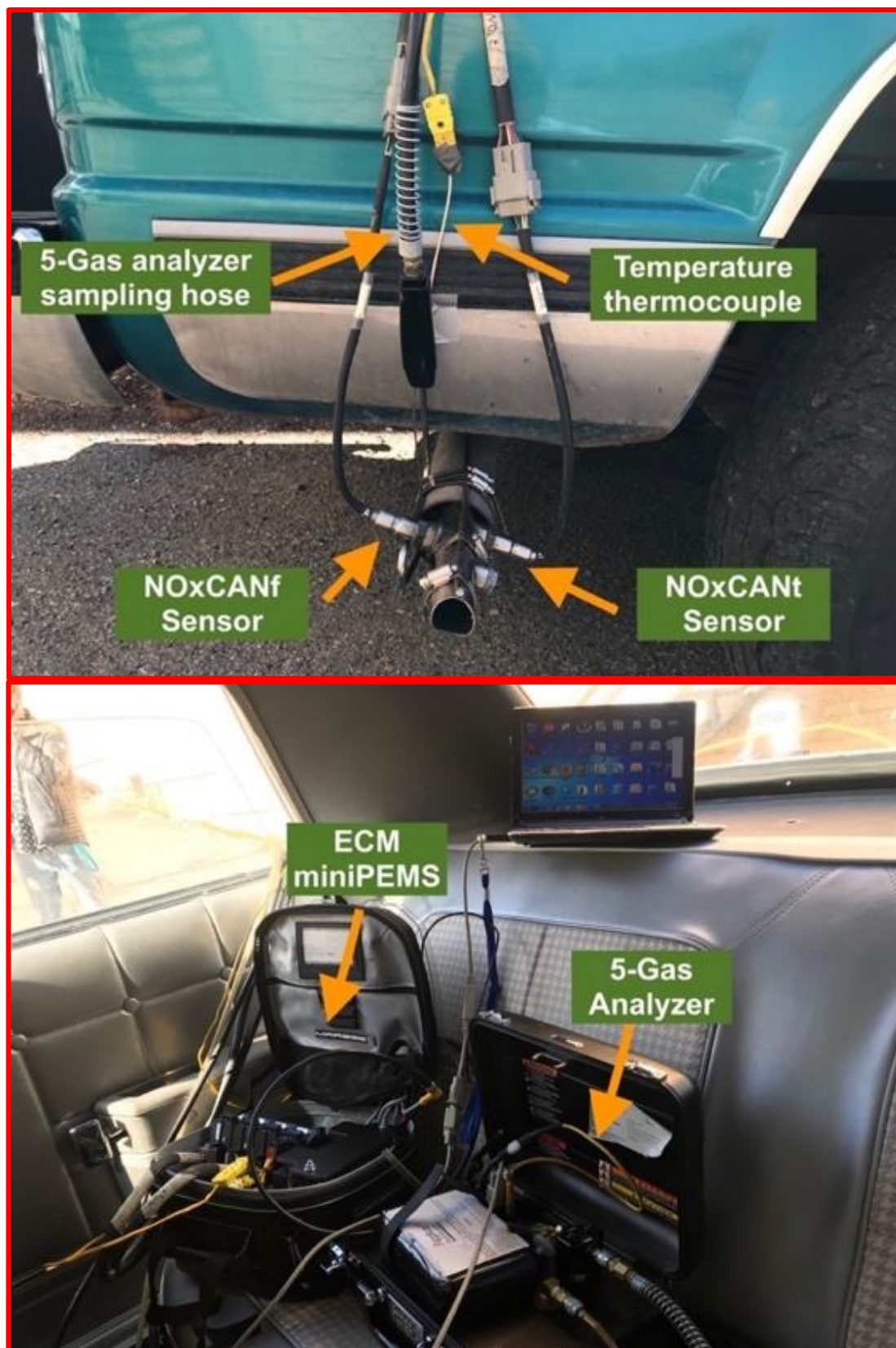


Figure 7. The ECM miniPEMS and 5-Gas analyzer instruments.

4.4.1.1. Gasoline motor vehicle (spark engine)

The ECM miniPEMS had two modules for measuring exhaust NH_3 and NO_x concentrations: NO_xCANt (Figure 8) and NO_xCANf (Figure 9). The NO_xCANf sensor is a NO_xCANt sensor fitted with an acid filter to absorb NH_3 emissions before reaching the sensor. The NO_xCANt sensor measured the concentration of both NH_3 and NO_x , whereas the NO_xCANf sensor measured only NO_x concentrations, as it was equipped with the acid filter. Ammonia concentrations were obtained by subtracting the NO_xCANf readings from the NO_xCANt readings. The acid filter had a high concentration of phosphoric acid (H_3PO_4). The NO_xCANt and NO_xCANf sensors are O_2 pumping type sensors with two cavities (Figure 10).



Figure 8. The NO_xCANt Module and sensor of the ECM miniPEMS.

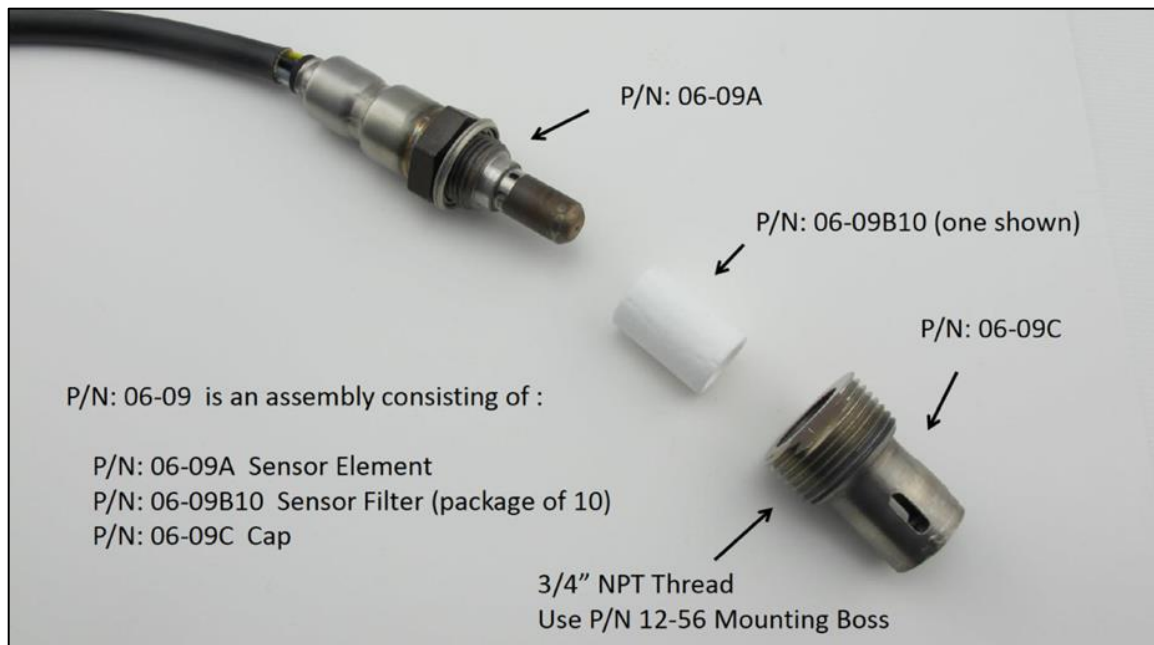


Figure 9. The NO_xCANf sensor of the ECM miniPEMS with the acid filter.

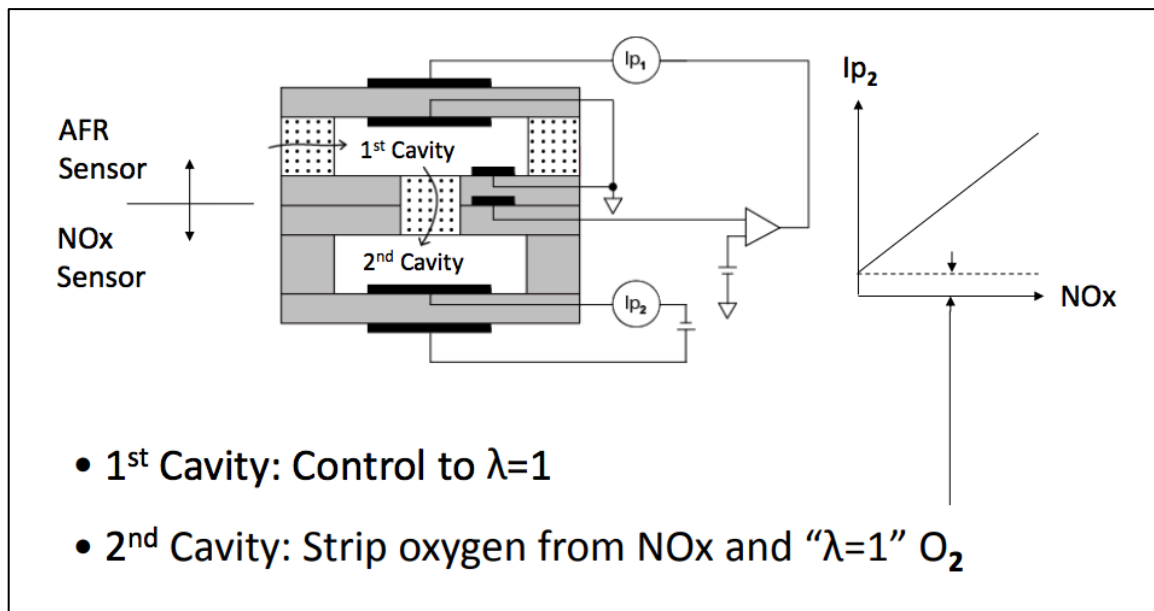


Figure 10. Operational schematic of the NO_xCANt sensors.

Exhaust emissions diffuse first into the 1st cavity where the O₂ pumping current (I_{p1}) is controlled to obtain a 0 % oxygen condition in the cavity. The I_{p1} is used to determine O₂ percentage in the exhaust. Gases from the 1st cavity next diffuse into the 2nd

cavity, where oxygen molecules are stripped from O_2 and NO_x compounds. The I_{p2} current is proportional to the O_2 and NO_x in the cavity. Since the O_2 percentage is reduced to near zero in the 1st cavity, the I_{p2} would largely be due to NO_x emissions. Hence, the I_{p2} is used to determine the amount of NO_x compounds in the exhaust emissions, as it would be proportional to their concentration.

4.4.1.2. Diesel motor vehicle

The ECM miniPEMS also had two modules for measuring NH_3 and NO_x concentrations in the exhaust of diesel motor vehicles: NO_xCANt (Figure 8) and NH_3CAN (Figure 11). The NO_xCANt sensor measured the concentration of both NH_3 and NO_x , whereas the NH_3CAN sensor only measured NH_3 concentrations. Exhaust concentrations of NO_x were obtained by subtracting the NH_3CAN readings from the NO_xCANt readings. Unlike the NO_xCANt and NO_xCANf sensors, the NH_3CAN sensor is a mixed-potential type sensor with only one cavity. The cavity has three electrodes, one is a ground and the two others have a different composition from each-other (conductive, but a different mix of metals). The voltage between the ground and each of the two other electrodes is measured and then a 3-dimensional plot of NH_3 versus those two voltages is generated. The sensor keeps running trials between NH_3 and the measured two voltages until the desired 3-dimensional plot is obtained and the concentration of NH_3 is determined.



Figure 11. The NH₃CAN Module of the ECM miniPEMS.

4.4.2. The 310-0220 Applus Autologic 5-Gas Portable Vehicle Gas Analyzer

In addition to the ECM miniPEMS, an Applus Autologic 5-Gas Portable Vehicle Gas Analyzer (model 310-0220) was used to measure the concentrations of CO, HC, and CO₂ compounds in gasoline and diesel motor vehicles exhaust emissions. The concentrations of unburned HC were reported in ppm, whereas the CO and CO₂ concentrations were reported in percentages. The CO and CO₂ percentages were multiplied by 10,000 to convert them into ppm. The 5-gas analyzer interfaced to laptop computers via serial ports to collect emissions data every second. The lag-time between the 5-Gas analyzer and the ECM miniPEMS was 6 seconds in favor of the ECM miniPEMS as the 5-Gas analyzer used sensors that were external to the tailpipe and were transferred to the control module through a sampling hose (Figure 7). This same analyzer was recently used by Khader and Martin (2019).

4.5. Calculation and analysis of emission rates (mg/mile):

4.5.1. The 1-second averaged total exhaust emission volume (V_{Total, m^3})

The 1-second averaged total volume of exhaust emissions corresponding of the approximate 600-second on-road RDEs tests was calculated to convert each pollutant's mass concentrations to mass per time, and ultimately to mass per distance. The exhaust velocity ($V_{Measured, m/s}$) and temperature ($T_{Measured, °F}$) of each tested vehicle were measured at at least three RPMs using the Extech 407113 Heavy-Duty CFM Metal Vane Anemometer (Figure 12). This was done while the tested vehicle was at idle condition.



Figure 12. Electric high temperature metal probe anemometer.

The actual flow rate ($Q_{Actual, m^3/s}$) corresponded to each RPM reading was then calculated by multiplying the $V_{Measured, m/s}$ with the cross-sectional area of each vehicle's tailpipe ($A_{Tailpipe, m^2}$). The calculated $Q_{Actual, m^3/s}$ at various RPMs and the corresponding measured $T_{Measured, ^\circ F}$ were used after that to calculate the equivalent standard exhaust flow rates ($Q_{Standard, m^3/s}$) using Eq. 16.

$$Q_{Standard} = Q_{Actual} \times \frac{Atm. Pressure Measured}{Atm. Pressure Standard} \times \frac{Temperature Standard}{Temperature Measured} \quad Eq. 16$$

The standard temperature and pressure were used as 298.15 K and 1 atmosphere, respectively. The measured pressure was obtained at the time of testing using a mercury barometer located inside the Air Quality Lab in the UWRL. The flow rate was converted to standard conditions to allow for future calculations of on-road various actual conditions. Following that, the linear relationship between engine RPMs and the corresponding $Q_{Standard, m^3/s}$ was established for each tested vehicle. Examples of the linear relationship between engine RPMs and the corresponding $Q_{Standard, m^3/s}$ are shown in Figure 13. The R^2 of the linear relationship between engine RPM and the corresponding $Q_{Standard, m^3/s}$ of all vehicles ranged between 0.82 and 1.00 and had an average of 0.94. The linear relationships between RPMs readings and the corresponding $Q_{Standard, m^3/s}$ were expressed for each vehicle as a mathematical equation of the form shown in Eq. 17 as illustrated in Figure 13.

$$Q_{Standard} = Slope \times RPMs + y-intercept \quad Eq. 17$$

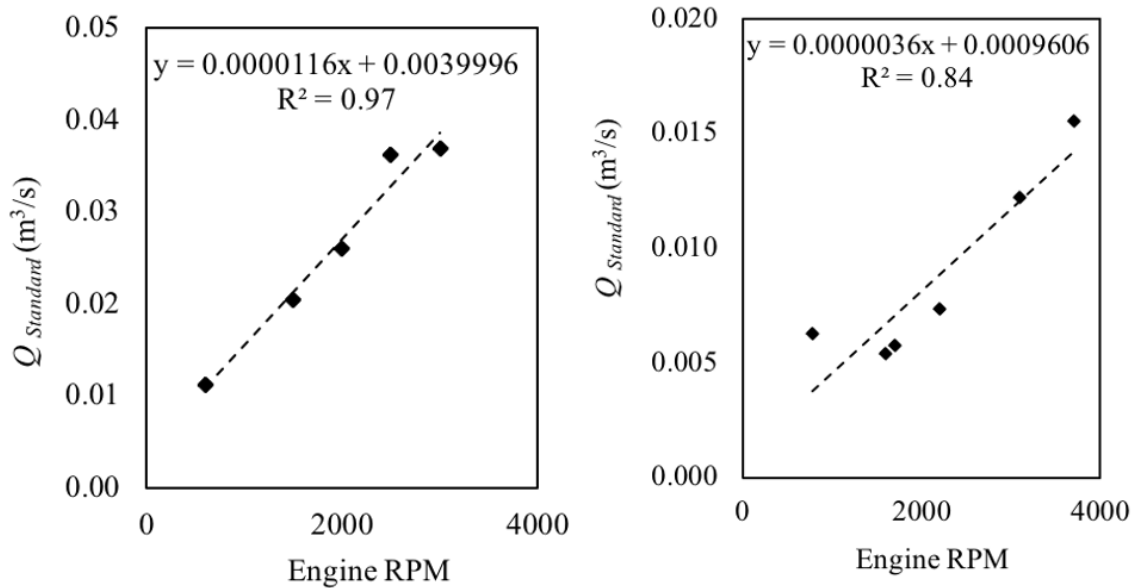


Figure 13. Examples of the derived linear relationships between engine RPMs and $Q_{Standard}$ (Left: 2007 Dodge RAM 1500 Light-Duty Truck (LDT), Right: 2019 Subaru Cross Trek Multi-Purpose Vehicle (MPV)).

The developed relationship between RPM readings and the corresponding $Q_{Standard, m^3/s}$ was used after that to calculate the $Q_{Standard, m^3/s}$ corresponding to all of the 1-second averaged RPM readings reported by the ECM miniPEMS over the approximate 600-second on-road RDEs tests. The $Q_{Standard, m^3/s}$ corresponding to each of the 1-second averaged RPM readings was then converted back to the equivalent $Q_{Actual, m^3/s}$ using the equation shown in Eq. 18.

$$Q_{Actual} = Q_{Standard} \times \frac{Atm. Pressure Standard}{Atm. Pressure Measured} \times \frac{Temp Measured}{Temp Standard} \quad Eq. 18$$

The $Temp_{Measured, F}$ represented the 1-second average exhaust temperature that was obtained during the tests using the Type J temperature thermocouples. The exhaust temperature was converted first to the appropriate absolute units (K). The standard atmospheric temperature and pressure were used as 298.15 K and 1 atmosphere,

respectively, and the measured pressure was the actual atmospheric pressure as recorded from a UWRL barometer. Lastly, the $Q_{Actual, m^3/s}$ corresponding to each 1-second averaged RPM was multiplied by 1 second to calculate the 1-second averaged total exhaust emission volume (V_{Total, m^3}) for each second of the approximate 600-second on-road RDEs tests.

4.5.2. The 1-second averaged emission rates (mg/mile)

The 1-second averaged tailpipe mixing ratios (ppm) were converted to mass concentration (mg/m^3) using the Ideal Gas Law equation as shown in Eq. 19. The atmospheric pressure was measured at the time of each test using a mercury barometer located inside the Air Quality Lab in the UWRL. The 1-second averaged exhaust temperature values were obtained during the tests using the Type J temperature thermocouple. The ideal gas constant (R) was taken as 62.36 mmHg-L/gmol-K.

$$\begin{aligned}
 & \text{Mass concentration } \left(\frac{g}{L} \right) = \\
 & \frac{\text{Concentration (ppm)} \times MW \left(\frac{g}{mol} \right) \times \text{Atm pressure (mmHg)}}{\text{Exhaust temperature (K)} \times \text{Ideal gas constant (R) (mm Hg-L/gmol-K)} \times 10^6} \quad \text{Eq. 19}
 \end{aligned}$$

The calculated mass concentrations using Eq. 19 were multiplied by total exhaust emission volume (Q_{Total, m^3}) to get the mass (mg) of each pollutant. The masses calculated at all seconds of the RDEs tests were then summed and divided by the UWRL-UDTC length of 5.3 miles to get the emission rates (mg/mile) for all gases.

4.5.3. Analysis of ammonia emission rates

The NH₃ data of emission rates were analyzed using the Microsoft EXCEL and RStudio statistical tools. The assembled R code is shown in Appendix B.

4.5.3.1. Descriptive and inferential analyses

The descriptive analyses included the minimum, maximum, average, standard deviation, 25th, 50th and 75th percentiles and the 95% confidence level, whereas the inferential analyses included the t-test for comparing ammonia emissions rates of two groups, and the ANOVA test for examining the difference in NH₃ emissions rates of three or more groups of data. Boxplot and histogram plots were also used to summarize NH₃ data.

4.5.3.2. Correlation and regression analyses

The Pearson's correlation coefficient (r) was used to measure the linear correlation between NH₃ emission rates and several vehicles' characteristics and other post-catalyst exhaust gases including NO_x, CO, HC, and CO₂. The factors that showed good correlation to NH₃ emission rates from gasoline motor vehicles were used to build a linear prediction model using the Stepwise Regression (SR) analysis (Eq. 20).

$$y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \dots + \beta_n X_n + \varepsilon \quad \text{Eq. 20}$$

Where, y is the dependent variable, β_0 is the intercept, $\beta_1, \beta_2, \dots, \beta_n$ are the regression coefficients of the independent variables X_1, X_2, \dots, X_n and ε is the residual error. The SR analysis is a step-by-step approach, where inconsequential variables are

removed from the regression analysis, allowing only important variables to be present. The analysis starts by choosing the important variables that contribute substantially to the analysis and subsequently adding the variable that would improve the data most.

4.5.3.3. Vehicle specific power

The Vehicle Specific Power (VSP) parameter is a direct measure of the road load on a vehicle which characterizes vehicles and driving profiles using real-world on-road measured data. VSP parameter is also often used by regulatory agencies and investigators to normalize pollutant emissions. The VSP for light-duty vehicles is calculated using the second-by-second speed values and road grades as shown in Eq. 21 (Jiménez-Palacios 1999).

$$VSP = v \times [1.1 \times a + 9.81 \times \text{grade} (\%) + 0.132] + 0.000302 \times v^3 \quad \text{Eq. 21}$$

Where *VSP* is the vehicle specific power in kilowatts per metric tons (kW/ton), *v* is the speed of tested vehicles in meters per second (m/s), *a* is the acceleration of tested vehicles (m/s²) and *grade* is the travel path's vertical rise divided by the horizontal run (%). The vertical rise was obtained from the GPS of the ECM miniPEMS, whereas the horizontal run was obtained by multiplying vehicles' velocity by the time of the travel at that velocity. The second-by-second VSP values were then grouped into the corresponding VSP mode shown in Table 6. These modes are typical of established protocols (Khan and Frey 2016).

The MOtor Vehicle Emission Simulator (MOVES) model was developed by the U.S. Environmental Protection Agency (USEPA) to estimate emissions from on-road and

off-road vehicles in the United States. In the MOVES model, emissions are now defined as a function of speed and vehicle specific power (VSP) for light-duty vehicles which reflects acceleration and speed impacts on work and engine load (J. Liu et al. 2017).

Table 6. VSP mode and corresponding power requirements (kW/Metric ton).

VSP Mode	Power (kW/ton)	VSP Mode	Power (kW/ton)
1	$VSP < -2$	8	$13 \leq VSP < 16$
2	$-2 \leq VSP < 0$	9	$16 \leq VSP < 19$
3	$0 \leq VSP < 1$	10	$19 \leq VSP < 23$
4	$1 \leq VSP < 4$	11	$23 \leq VSP < 28$
5	$4 \leq VSP < 7$	12	$28 \leq VSP < 33$
6	$7 \leq VSP < 10$	13	$33 \leq VSP < 39$
7	$10 \leq VSP < 13$	14	$VSP > 39$

4.6. Quality control

The sensors of the ECM miniPEMS were factory-calibrated and again calibrated at the UWRL using a certified NH₃ standard calibration gas from Airgas Specialty Gases. The ECM miniPEMS was also calibrated against the bench-scale Picarro cavity ringdown spectrometer (Model G2103). The Picarro base station NH₃ analyzer is a reliable and accurate instrument and is usually calibrated using two standard gases. The 5-Gas analyzer was calibrated frequently using a certified blend gas from Airgas Specialty Gases.

The NO_xCANf sensor was fitted with a new acid-impregnated filter for each vehicle, despite the fact that the ECM company recommendations stated that each filter could be used for more than one vehicle. Moreover, two filters from different filter batches were tested before and after the on-road RDE tests were conducted to check that the H₃PO₄ acid was not totally consumed during the tests. The initial (before the RDEs test) concentrations of H₃PO₄ acid of two filters from the First and Second filters batches were measured at 691 and 2900 mg/L, respectively. The final (after the RDEs test) concentrations of H₃PO₄ acid of two filters from the First and Second filters batches were 300 and 2180 mg/L, respectively. The H₃PO₄ acid contained in the filters of the First and Second filters batches was sufficient as the final (after the RDEs test) concentrations indicate that the H₃PO₄ acid was not totally consumed during the tests. The ECM data files were checked for any errors that may have occurred during the collection and/or retrieving of data and to align the data from the different modules.

CHAPTER V

RESULTS AND DISCUSSION

5.1. Vehicle test fleet

A total of 166 on-road RDEs tests were carried out using 53 LD gasoline and diesel motor vehicles with a GVWR up to 12,000 pounds. Two gasoline vehicles were tested in triplicate on two separate occasions and one diesel vehicle was tested twice over stock and fuel economy modes. The triplicate NH₃ emission rates of tested vehicles and their averaged emission rates are shown in Table 7. A single measurement was obtained only for one gasoline vehicle due to technical issues that occurred during the on-road RDEs test. The characteristics of tested motor vehicles are also presented in Table 7. The characteristics included fuel type (Gasoline (G) and Diesel (D)), make, model, model year, EPA Emission Standard Tier (Pre-Tier 0, Tier 0, Tier I, NLEV, Tier II, Tier III) and odometer reading (miles). Additionally, detailed vehicle specific information including vehicle driver (Researcher (R) and vehicle Owner (O)), vehicle type (Passenger Car (PC), Multi-Purpose Vehicle (MPV) and Light-Duty Truck (LDT)), engine size (liters), number of cylinders and vehicle's GVWR (US pounds) is shown in Appendix C. The driver factor was added in this study because driving the same car by the researcher could result in different exhaust emissions than if it was driven by the owner (Khader and Martin 2019). The three-run average emission rates of CO, NO_x, HC and CO₂ for each vehicle is also presented in the Table 7. The 5-Gas analyzer did not produce useable data during the RDEs test of five vehicles. Tested gasoline motor vehicles were all fitted with

the TWC converter, whereas one diesel motor vehicle had no catalyst, three diesel vehicles had only the DOC converter and two diesel vehicles had both DOC and SCR converters. The 1999 F5300 light-duty diesel truck was tested at the stock and fuel economy modes.

Table 7. Characteristics of tested gasoline and diesel vehicles and their post-catalyst NH₃, NO_x, CO, HC and CO₂ emission rates. G = Gasoline, D = Diesel.

#	Fuel	Tier Level	Mileage (mile)	Emission rate							
				mg/mile							g/mile
				NH ₃ (1 st run)	NH ₃ (2 nd run)	NH ₃ (3 rd run)	Average NH ₃	NO _x	CO	HC	CO ₂
1	G	Tier 0	284117	465.5	387.7	388.2	413.8	580.7	16781.2	916.9	840.3
2	G	Tier I	161603	120.2	80.0	85.5	95.2	72.3	2397.9	741.1	205.9
3	G	Tier I	184545	78.7	73.7	72.5	74.9	197.0	653.4	49.5	354.0
4	G	Tier I	200624	109.0	63.5	69.0	80.5	165.0	993.2	131.7	281.2
5	G	Tier I	160714	331.2	203.9	233.8	256.3	504.6	2018.0	5741.6	890.2
6	G	Tier I	188405	216.0	127.5	122.0	155.2	76.3	1300.3	7338.2	791.6
7	G	Tier I	171099	117.5	26.5	24.3	56.1	25.6	778.7	94.1	450.9
8	G	NLEV	267031	426.4	290.8	282.8	333.3	480.2	4582.6	284.4	728.5
9	G	NLEV	249362	9.4	7.3	5.9	7.5	17.4			
10	G	NLEV	221711	334.4	247.9	208.3	263.5	141.4	3886.9	197.4	472.2
11	G	NLEV	122918	39.8	13.1	11.3	21.4	4.3	9.6	37.7	236.8
12	G	Tier II	137724	36.5	36.3	27.1	33.3	10.7	186.4	9.2	236.7
13	G	Tier II	150872	20.2	15.1	17.9	17.7	11.4			
14	G	Tier II	124689	18.5	3.5	2.9	8.3	3.8			
			124817	52.4	3.4	2.8	19.5	23.2			
15	G	Tier II	214484	60.9	55.7	55.3	57.3	83.4	3272.0	47.6	639.7
			216506	95.2	61.5	62.1	72.9	80.2	2555.0	47.5	644.9
16	G	Tier II	166095	305.6	90.9	90.7	162.4	57.0	741.2	27.7	278.9
17	G	Tier II	134613	92.6	53.1	50.1	65.3	26.1	848.8	4053.0	308.3
18	G	Tier II	40680	32.8	21.4	25.7	26.6	5.7	175.9	21.4	305.1

#	Fuel	Tier Level	Mileage (mile)	Emission rate							
				mg/mile							g/mile
				NH ₃ (1 st run)	NH ₃ (2 nd run)	NH ₃ (3 rd run)	Average NH ₃	NO _x	CO	HC	CO ₂
19	G	Tier II	136262	27.0	10.8	13.9	17.2	9.2	55.4	47.6	309.0
20	G	Tier II	63570	27.0	27.3	25.7	26.6	57.8	390.4	39.7	370.9
21	G	Tier II	57976	25.6	8.2	7.4	13.8	5.9	124.4	5.4	149.9
22	G	Tier II	33320	16.2	3.0	5.7	8.3	10.9	80.7	1.6	141.6
23	G	Tier II	192228	146.8	73.8	60.0	93.5	7.3	895.2	4025.3	330.9
24	G	Tier II	165808	201.1	52.7	63.0	105.6	16.0	505.9	28.3	269.0
25	G	Tier II	104870	48.1	28.0	25.3	33.8	24.5	372.8	15.6	98.7
26	G	Tier II	136804	97.9	82.4	78.2	86.2	23.5	727.4	18.4	191.8
27	G	Tier II	126928	241.6	39.1	0.3	93.7	79.5	2025.9	23.6	483.1
28	G	Tier II	30145	4.3	2.7	2.5	3.2	1.3	34.1	1.6	131.7
29	G	Tier II	53982	50.7	21.2	20.8	30.9	6.6	147.3	0.1	399.4
30	G	Tier II	13602	53.5	16.6	24.6	31.5	21.9	243.2	12.1	375.5
31	G	Tier II	50432	12.4	3.3	3.4	6.4	7.7	4.5	11.5	356.4
32	G	Tier II	67634	19.7	3.5	6.1	9.8	6.5	29.3	32.9	354.3
33	G	Tier II	19747	88.4	67.7	66.1	74.0	11.4	1078.8	18.0	376.1
34	G	Tier II	92976	8.1	3.4	3.2	4.9	4.0			
35	G	Tier II	93642	78.7	46.4	30.4	51.8	88.8	1427.3	4.7	381.3
36	G	Tier II	45238	14.5	9.7	9.3	11.2	6.7	31.1	0.0	129.6
37	G	Tier II	16564	19.8	5.2	8.3	11.1	5.2	156.8	15.6	218.9
38	G	Tier II	125429	10.5	3.6	2.8	5.6	13.3	96.6	334.1	220.4
39	G	Tier II	15769	5.4	5.3	6.2	5.6	0.6	215.4	8.0	80.6
40	G	Tier II	14107	14.0	5.2	4.2	7.8	6.1	108.9	39.4	360.0
41	G	Tier II	15536	38.3	22.6	18.1	26.4	8.9	71.3	12.4	374.7
42	G	Tier III	5654	17.6	NA	NA	17.6	5.1	378.7	28.2	397.2
43	G	Tier III	33374	3.6	1.2	1.2	2.0	1.2	5.8	0.0	133.0
44	G	Tier III	9365	12.5	4.1	2.7	6.4	1.2	84.0	7.1	163.9
45	G	Tier III	3618	23.5	9.4	11.3	14.7	15.6	864.1	16.5	414.4
46	G	Tier III	8006	3.8	2.7	2.9	3.1	3.4	15.5	27.8	264.3

#	Fuel	Tier Level	Mileage (mile)	Emission rate							
				mg/mile							g/mile
				NH ₃ (1 st run)	NH ₃ (2 nd run)	NH ₃ (3 rd run)	Average NH ₃	NO _x	CO	HC	CO ₂
47	G	Tier III	3439	28.3	5.1	6.5	13.3	3.4	83.9	19.3	373.9
48	D	Tier I	265118	18.4	19.3	20.1	19.3	8363.1	3359.4	434.3	1061.7
			265134	18.9	17.9	19.8	18.8	8434.0	2284.5	620.1	1032.8
49	D	NLEV	174019	15.2	13.6	13.3	14.0	5125.5	1583.6	512.1	636.6
50	D	Tier II	146492	6.0	2.1	1.0	3.1	2767.9	12.5	520.4	796.4
51	D	Tier II	61271	11.7	9.4	8.9	10.0	487.2	846.3	89.2	592.9
52	D	Tier II	99046	4.9	2.0	0.9	2.6	70.5	174.3	205.4	445.5
53	D	Tier III	23547	12.63	4.64	3.78	7.02	58.68	6.54	44.32	677.71

The data shown in Table 7 also show that the on-road RDEs tests were repeated for the 2007 Dodge RAM 1500 LDT (Vehicle #15) and the 2006 Toyota Matrix gasoline PC (Vehicle #14). The observed variability in NH₃ emission rates of these duplicate tests is statistically insignificant at the 95% confidence level, which highlights good repeatability in the testing procedure. The p-value of the t-test (df = 2) that measured the difference in NH₃ rates of the 2007 Dodge tests was 0.24. This is larger than tail area probability of the 95% confidence level of $\alpha = 0.05$. Thus, ammonia emission rates of the two repeated tests are statistically considered as one group. The repeated tests of the 2006 Toyota Matrix were also treated as one group as the p-value of the t-test of 0.43 was also higher than 0.05. Insignificant difference in ammonia emissions over repeated tests was also reported by other researchers (Durbin et al., 2002; Livingston et al., 2009).

Repeatability of the testing procedure is also indicated by the exhaust emissions of NO_x, HC and CO₂ compounds. For instance, the NO_x, HC and CO₂ exhaust emission rates of the 2007 Dodge LDT repeated tests were within 3.8%, 0.21% and 0.81%, respectively.

However, the CO exhaust emission rates of the 2007 Dodge LDT repeated tests were within 21.9%. The difference in CO exhaust emission rates of the repeated tests could be due several reasons such as the driving conditions, the atmospheric temperature and the condition of the vehicle. The NO_x, HC and CO exhaust emission rates of the 2006 Toyota Matrix PC were not measured due to technical issues with the 5-Gas analyzer.

5.2. Descriptive analyses of NH₃ emissions rates of the entire vehicles test sample

A summary of averaged NH₃ emission rates from tested gasoline and diesel motor vehicles is shown in Table 8 and Figure 14. The data clearly show that diesel motor vehicles recorded significantly lower NH₃ emission rates than gasoline motor vehicles. This could be explained by the fact that diesel motor vehicles are not fitted with the TWC converters where over-reduction of NO usually occurs. The NH₃ emission rates of diesel motor vehicles had an average of 10.7 mg/mile and ranged between 2.6 and 19.3 mg/mile. On the other hand, the emission rates of NH₃ for the gasoline motor vehicles fleet averaged 62.0 mg/mile and ranged between 2.0 and 413.8 mg/mile. The current estimated EPA NH₃ emission rates for LD gasoline motor vehicles range from 1.6 mg/mile to 516.6 mg/mile, and have an average of 101.4 mg/mile. The fact that estimated EPA emission rates are based on earlier studies and are more representative of older technology vehicles, may explain the higher average emission rates as compared with the outcome of this study (Huai et al. 2003). The test sample of the current study mostly included Tier II and Tier III vehicles that have newer control technology and were associated with lower NH₃ emission rates than older vehicles due to better control of NH₃ precursors, CO and NO_x (Eq. 4-Eq. 8). Low emission rates of NH₃ from diesel motor

vehicles were also recorded by Mendoza-Villafuerte et al. (2017).

Table 8. Summary of ammonia emission rates of all the tests.

Tier	Unit	Gasoline	Diesel	Entire test fleet
No. vehicles	#	47	6	53
Total No. tests	#	145	21	166
Minimum NH ₃	mg/mile	2.0	2.6	2
25 th %	mg/mile	9.8	5	8.3
Median (50 th %)	mg/mile	26.6	10	19.4
75 th %	mg/mile	74.9	16.4	73.2
Maximum NH ₃	mg/mile	413.8	19.3	413.8
Mean	mg/mile	62.0	10.7	55.6
Standard deviation	mg/mile	87.9	6.9	83.9
95% confidence level	mg/mile	± 25.2	± 6.4	± 22.5

The mean NH₃ emission rates of the entire test fleet was 55.6 mg/mile. The standard deviation and the 95% confidence level of NH₃ emission rates for the entire fleet were 83.9 and ±22.5 mg/mile, respectively. The wide range (413.8 – 2 = 411.8 mg/mile) and the high standard deviation suggest high variability in NH₃ emission rates among the entire fleet. This is likely due to differences in vehicles characteristics and in NH₃ precursor concentrations as clearly illustrated in Table 7. For instance, the minimum NH₃ averaged emission rate of 2.0 mg/mile was recorded for a Tier III gasoline PC that had low overall mileage of 33,347 miles (vehicle #43), whereas the maximum NH₃ averaged emission rate of 413.8 mg/mile was measured for a Tier 0 gasoline LDT that had an

odometer reading of 284,117 miles (vehicle #1). Besides, the Tier III PC vehicle recorded low emission rates of CO and NO_x as compared with the Tier 0 LDT that had comparatively high CO and NO_x emission rates.

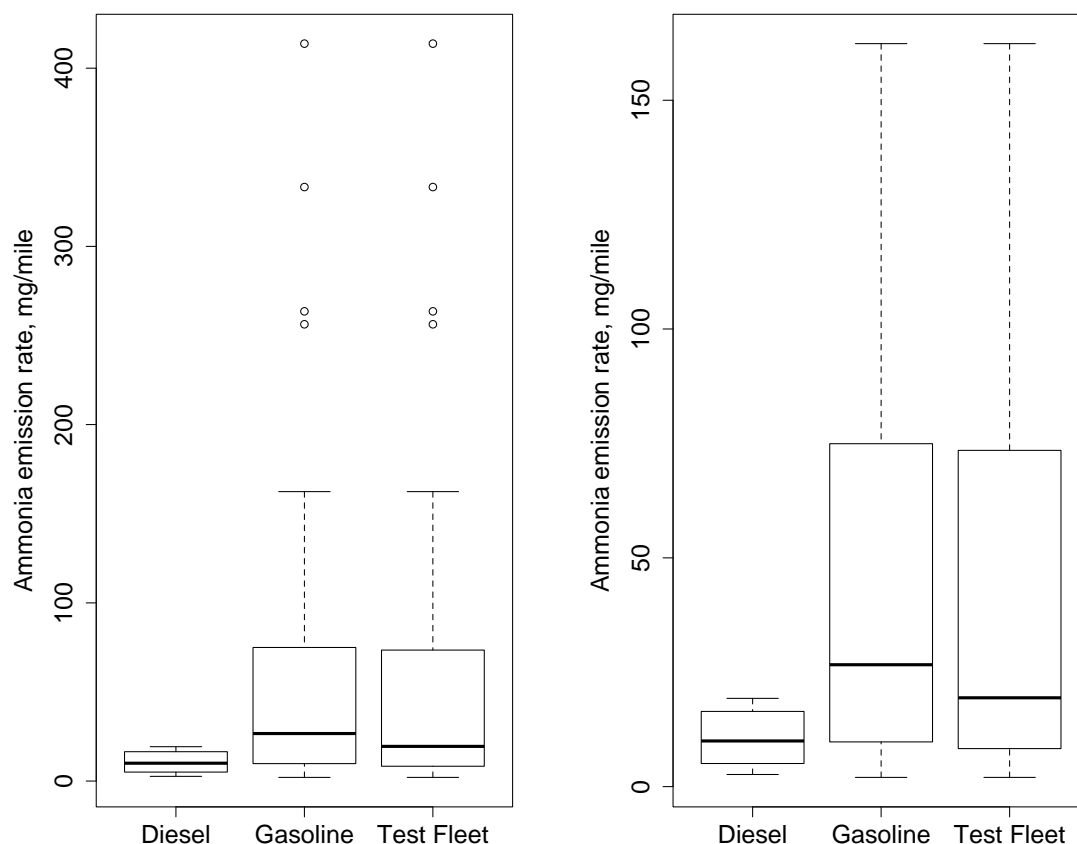


Figure 14. Boxplot of NH₃ emissions rates of tested motor vehicles in mg/mile with (left) and without (right) displaying the extreme values.

The data presented in Table 8 also showed that although the entire test fleet recorded a maximum NH₃ emission rate of 413.8 mg/mile, the 75th percentile was 73.2 mg/mile. Moreover, 89.3% of all the emission rates were within one standard deviation from the mean emission rate of 55.6 mg/mile. This indicates that most vehicles had comparatively small ammonia emission rates, and only a few vehicles recorded high

emissions rates. This is also shown in the right-skewed histogram drawn in Figure 15, where most NH_3 emission rates were below 100 mg/mile. Similar outcomes were reported by Durbin et al. (2002) who showed that 31 vehicles tested on a dynamometer had NH_3 emission rates of less than 100 mg/mile and only 8 vehicles had NH_3 emission rates higher than 100 mg/mile.

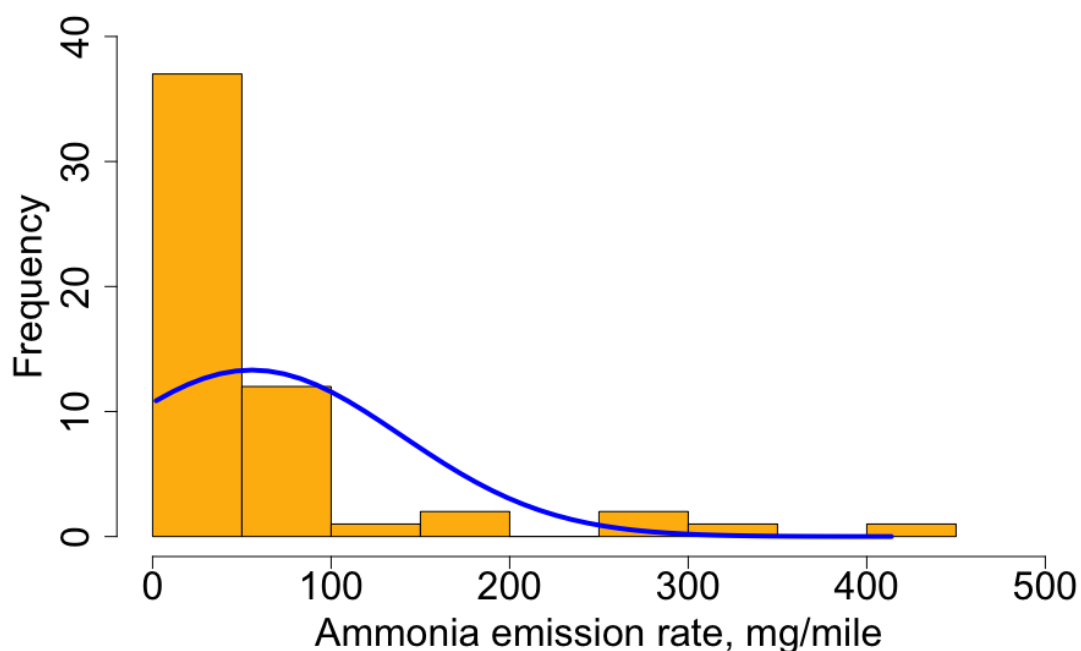


Figure 15. Histogram of NH_3 averaged emission rates for the gasoline and diesel vehicles fleet.

The boxplot presented in Figure 14 also shows that four extreme (very high) NH_3 averaged emission rates were recorded. The extreme NH_3 emission rates were larger than the upper whisker value that is calculated as 1.5 times the interquartile range (75th percentile– 25th percentile) above the 75th percentile. The lower whisker represented the minimum emission rate of NH_3 , whereas the bold line shown in the center of the box

represented the median (50th percentile) emission rate of NH₃. The bottom and top of the box represented the 25th percentile and 75th percentile, respectively. This description applies to all subsequent boxplot graphs shown in this study. The four extreme NH₃ emission rates of 256.3, 263.5, 333.3, and 413.8 mg/mile were measured for Tier I, NLEV, NLEV and Tier 0 gasoline motor vehicles, respectively. Similar outcomes obtained by Durbin et al. (2002), who also reported that the highest NH₃ emission rates were measured from Tier 0, Tier I and TLEV vehicles. This is also consistent with the outcomes of Durbin et al. (2004) and Huai et al. (2003) who reported that NH₃ emissions from vehicles with aged catalysts were higher than NH₃ from vehicles fitted with newer catalysts.

The four elevated NH₃ averaged emission rates were all reported for old vehicles with aged catalysts. The vehicles with the four highest NH₃ emission rates were made in 1993 (vehicle #1), 2002 (vehicle #8), 2003 (vehicle #10) and 1999 (vehicle #5). This supports the hypothesis that high-mileage old vehicles are responsible for higher emission rates of ammonia than newer vehicles. The vehicles with the highest three NH₃ emission rates had mileage readings greater than 200,000 miles, and the mileage reading from the vehicle with the fourth highest NH₃ emission rate was 160,714 miles. These four vehicles with the highest NH₃ emissions also recorded the highest emission rates of NO_x and CO. In fact, the four vehicles violated the U.S. EPA emission standard for CO (3400 mg/mile) and NO_x (1000, 400 and 200 mg/mile for Tier 0, Tier I and NLEV vehicles, respectively). It should be noted that the researchers don't know if these vehicles have a recent valid emission test. Therefore, it is likely that these vehicles were operating with aged catalysts or running most of the time at rich air-fuel conditions due to

malfunctioning oxygen sensors that no longer maintain the air-fuel ratio at stoichiometric conditions (Borsari and Assunção 2017; Cadle and Mulawa 1980; Dickson 1991).

Running vehicle engines under rich air/fuel conditions favors reducing processes on the surface of TWC converters and consequently causes significantly higher production of ammonia emissions. There was no way to determine if the TWC converters were replaced during the vehicle's lifetime. Original converters on motor vehicles are usually designed to last for the life of the vehicle only if they are properly used and well maintained (EPA 2000). However, TWC converters are expected to be replaced due to reduced performance after approximately 100,000 miles of service (Kidd and Kidd 2006). It should be noted that Tier II and Tier III vehicles would also emit high NH_3 emissions when their TWC converters age and stop working efficiently due to operating for long time of period.

Removing the four Tier 0, NLEV and Tier I vehicles that recorded the extreme emission rates from the entire test fleet would reduce the mean NH_3 emission rate by 36.2% from 55.6 mg/mile to 35.5 mg/mile. Together, Tier 0, NLEV and Tier I gasoline and diesel motor vehicles represent only 26.4% of the vehicle test fleet. This suggests that NH_3 emissions from the on-road vehicle fleet are largely produced by a small fraction of very high emitting aged-catalyst vehicles. Hence, limiting the number of on-road old vehicles would significantly lower the total NH_3 emissions from the Wasatch Front on-road vehicle fleet. This is because new vehicles are fitted with new exhaust emissions control devices that efficiently control exhaust emissions including ammonia precursors. Besides, the process of NO over-reduction rarely occurs on top of new TWC converters. The Vehicle Repair and Replacement Assistance Program (VRRAP) administered by the

local health departments in the counties of the State of Utah provides funding assistance to individuals whose vehicles are failing vehicle emission standards to either replace their failing vehicles with a newer, cleaner vehicle or to repair their vehicles to pass the test. This program is believed to reduce total exhaust emissions of the on-road fleets including ammonia as the number of old or/and broken vehicles would be small.

5.3. Variability of ammonia emission rate over triplicate laps

The data shown in Table 7 also illustrate that almost all tested gasoline and diesel motor vehicles recorded higher NH_3 emission rates in the first lap than in the second and third laps. This is also visually presented in Figure 16, where NH_3 emission rates of all gasoline and diesel motor vehicles for each lap were represented by a box plot. Ammonia emission rates for the first, second, and third laps from all of the vehicles had means of 78.4, 45.4 and 43.9 mg/mile, respectively. The mean NH_3 emission rate for the second and third runs was lower than the first run by 42.1% and 44.0%, respectively. This suggests that NH_3 emission rates from test gasoline and diesel motor vehicles decline after the first few miles of driving. Thus, higher emission rates for ammonia are anticipated during the first few miles until vehicles engine is warmed-up and the TWC converter's operation becomes optimal. Nevertheless, the difference in NH_3 among the three triplicates (laps) was not statistically significant at the 95% confidence interval as shown in an ANOVA test ($\text{Pr}(> F) = 0.067$). This $\text{Pr}(> F)$ value, however, indicates that the difference in NH_3 emission rates over the three runs was statistically significant at the 90% confidence level.

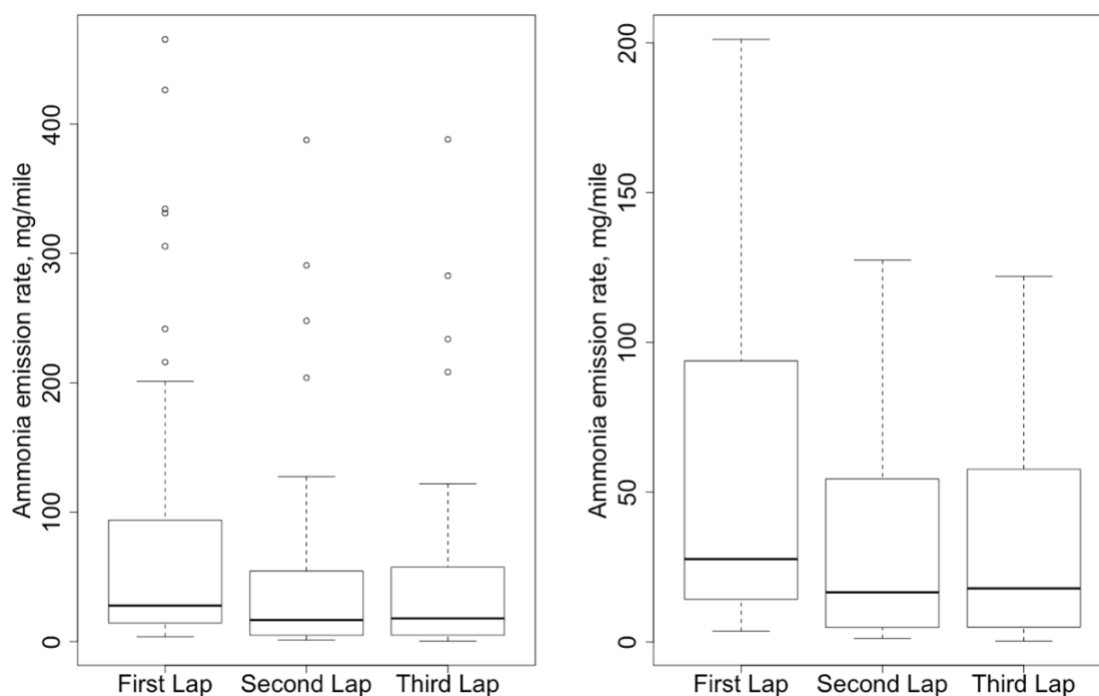


Figure 16. Boxplot of ammonia emissions rates from three runs with (left) and without (right) displaying the extreme values.

The difference in NH_3 emission rates over the three laps was also examined using the Tukey test (Figure 17). The outcomes of the Tukey test clearly show that the smallest difference (represented by the middle vertical line of each horizontal bar) in NH_3 emission rate of -1.5 was between the values of the third and second laps. The fact that the zero value was between the lower (-36.0) and upper (33.1) limits indicates that there is 90% chance that the difference in NH_3 emission rates of the second and third laps is zero, which highlights the fact that the difference in NH_3 emission rates of the third and second laps is statistically insignificant. Similarly, the zero value was between the lower (-67.4) and upper (1.4) limits of NH_3 emission rates of the second and first laps. This indicates that there is 90% chance that the difference in NH_3 emission rates of the second and first laps is zero. This suggests that the difference in NH_3 emission rates of the

second and first laps is statistically insignificant. Contrarily, the greatest difference in NH_3 emission rates of -34.5 was between the outcomes of the third and first laps. The fact that the zero value was not between the lower (-68.88) and upper (-0.02) limits indicates that there is 0% chance that the difference in NH_3 emission rates of the third and first laps is zero, which highlights the fact that the difference in NH_3 emission rates of the third and first laps are statistically insignificant.

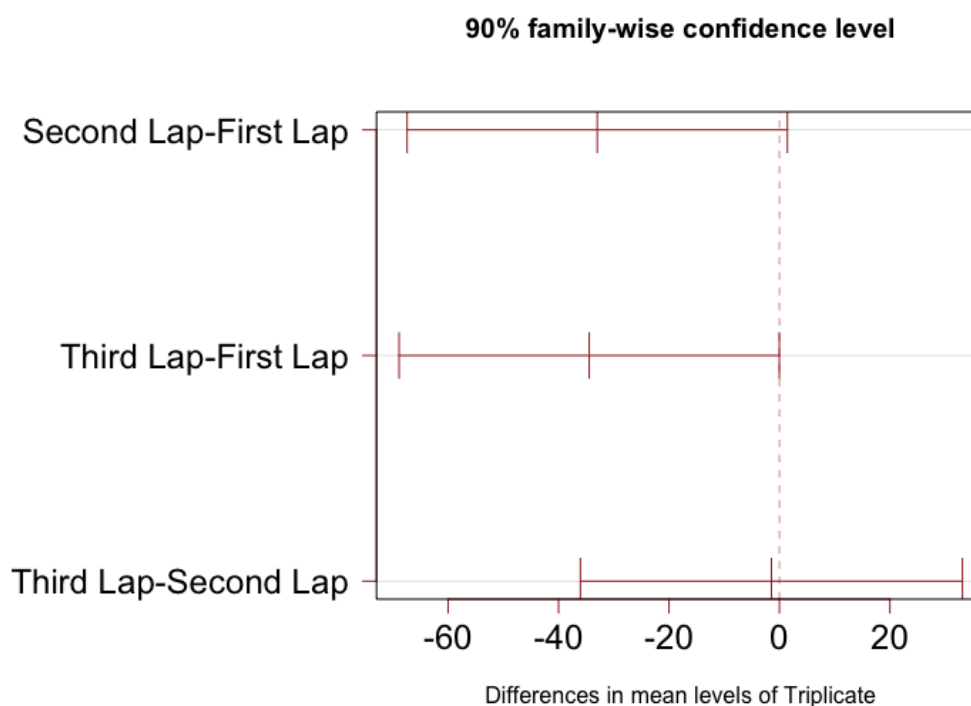


Figure 17. The results of the Tukey test for the difference in mean levels of the triplicate NH_3 emission rates

Having lower ammonia emission rates in the second and third laps than in the first lap is likely because the vehicle engine components (engine water, lubricating oil and pistons) of tested vehicles were still warming up in the first lap. This is indicated by the temperature readings of exhaust emissions of tested vehicles (Figure 18). The boxplots

presented in Figure 18 show that the temperature exhaust emissions of tested vehicles were lower during the first lap than in the second and third lap. The exhaust temperature of all tested vehicles of the first, second and third laps had a mean of 396.0 ± 33.1 , 435.1 ± 36.6 and 437 ± 36.0 K, respectively.

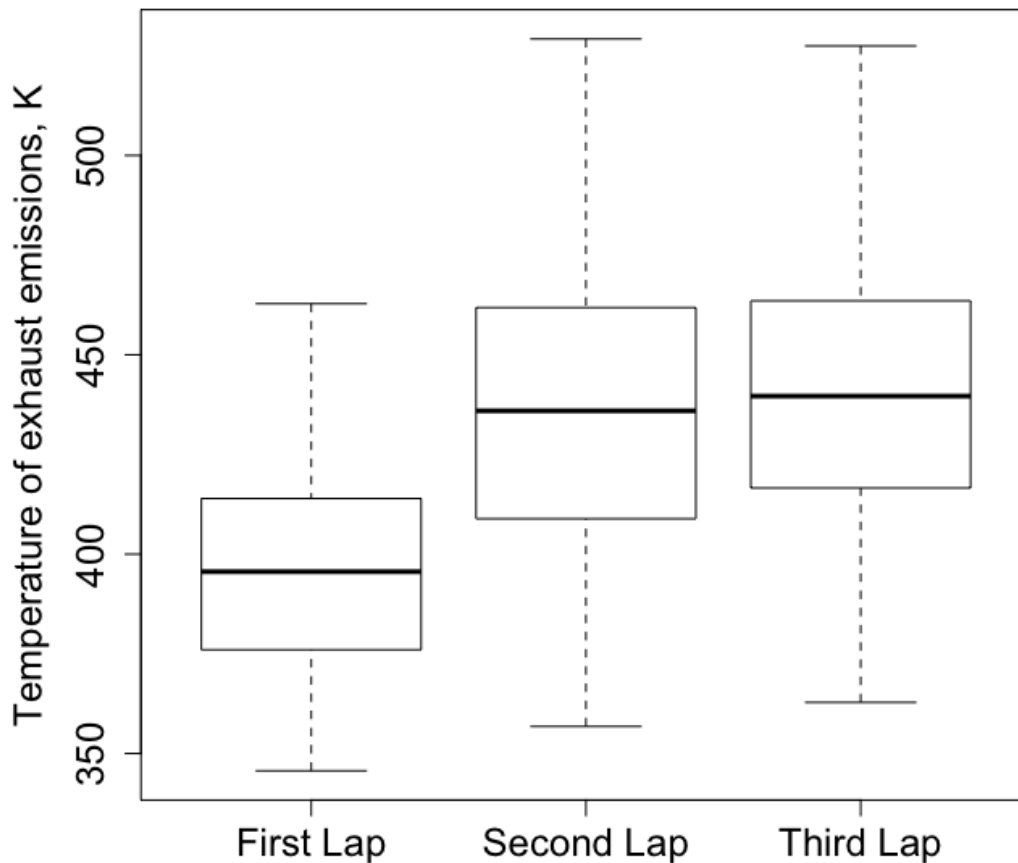


Figure 18. Boxplot of averaged exhaust temperature of the first, second and third laps of all tested vehicles

The data presented in Figure 19 also show that the temperature readings of the fitted TWC converters of tested vehicles reached higher levels in the second and third laps as compared with the first lap. The temperature of fitted TWC converters of all tested vehicles of the first, second and third laps had a mean of 844.5 ± 450.6 , 863.8 ± 428.3

and 865.5 ± 424.5 K, respectively. This could indicate that the TWC converters were working more efficiently during the second and third laps as compared with the first lap, which may have affected the concentrations of ammonia precursors.

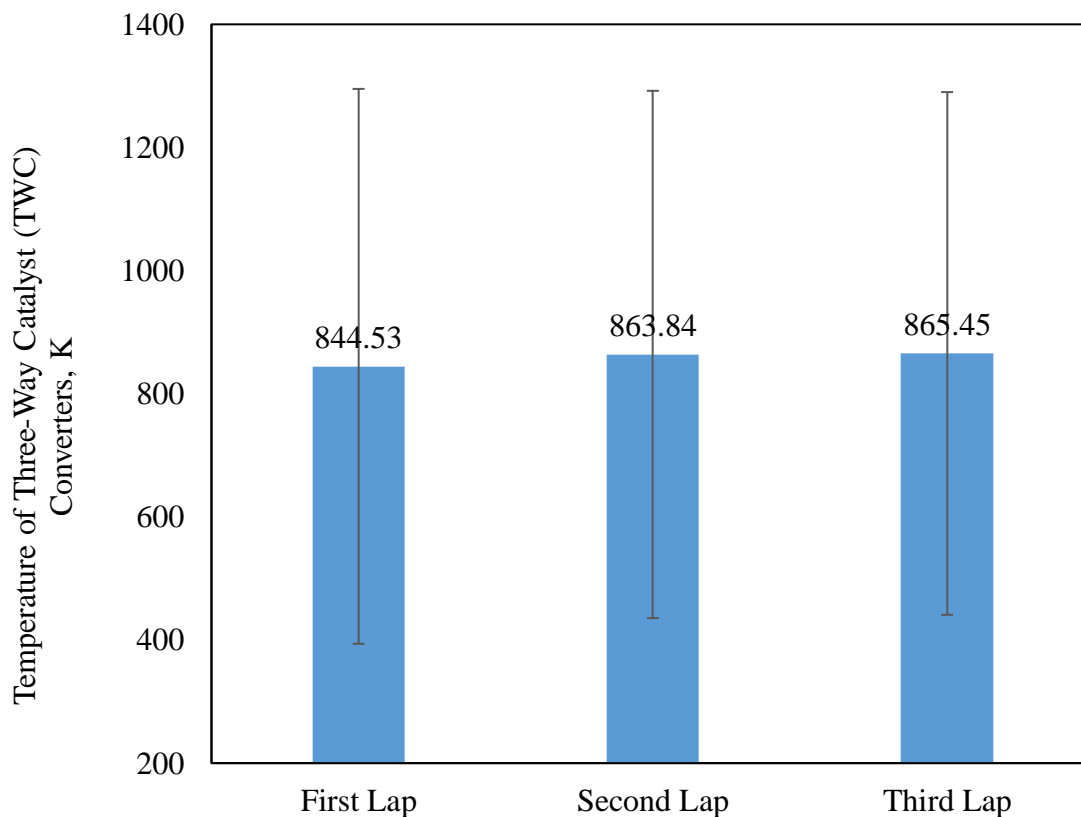


Figure 19. Bar chart of averaged temperature of fitted TWC converters of the first, second and third laps of the tested vehicles with available OBD II data.

Warming up of vehicles' engine components during the first lap may have resulted in better fuel combustion and lower percentages of ammonia precursors in the exhaust emissions in the subsequent laps (Cipollone et al. 2015). For instance, Andrews et al., (2004) showed upon quadruple testing of an Euro 1 spark engine car over a real-world test cycle (cycle length = 0.9 mile) that engine-out CO emissions were higher in the first three laps than in the fourth lap which represented a fully warmed up engine. The first lap

represented a cold start condition, whereas the second and third laps represented a slightly warmed up engine condition. The study of Andrews et al., (2004) further explained that engine combustion inefficiency reached lower percentages only after the third lap (travel distance = 2.70 miles). Similarly, the outcomes of this study show that post-catalyst concentrations of CO declined over the three laps as clearly shown in Figure 20. The data presented in Figure 20 also illustrate that post-catalyst concentrations of NO_x also declined over the three laps. This is likely due to warming up of vehicles' engine components and fitted TWC converters.

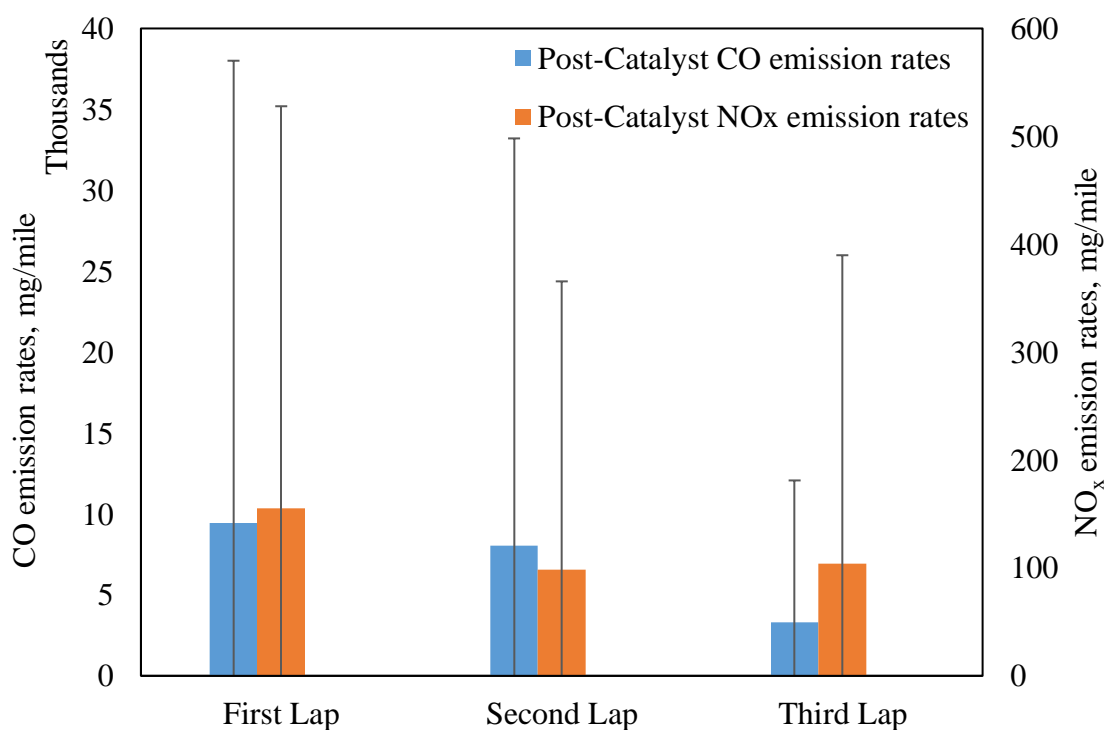


Figure 20. The mean of averaged CO and NO_x emission rates of all tested vehicles of the first, second and third laps (error bars represent the standard deviation).

Having higher ammonia emission rates in the first lap than in the second and third laps could be due to lower percentages of ammonia precursors in the exhaust emissions.

In addition to TWC converters' efficiency, this could also occur if vehicle engine components (engine water, lubricating oil and pistons) were still warming up in the first run, which could result in better fuel combustion (Cipollone et al. 2015).

5.4. Impact of vehicle speed and engine's RPM on NH₃ mass concentrations

The outcomes showed that NH₃ mass concentrations had a moderate correlation with engine's RPM reading. Contrarily, the NH₃ mass concentrations had no correlation with vehicle speed. The average Pearson's correlation coefficient (r) for the relationship between ammonia mass concentrations and engine's RPM and vehicle speed were 0.3 ± 0.2 and 0.0 ± 0.2 , respectively. However, the outcomes showed that ammonia mass concentrations spiked when engine's RPM suddenly increased due to stop-and-go driving condition as shown in Figure 21 that presents an example of ammonia emissions rates (mg/s) compared to engine RPM readings. Similar to the case of engine's RPM, ammonia mass concentrations spiked when the vehicle accelerated to reach higher speed limits as shown in Figure 22 that shows an example of ammonia emission rates compared to vehicle's speed. This could be explained by the fact that the mass concentrations of exhaust pollutants including NH₃ precursors, CO, and NO_x are influenced by the engine's RPM and vehicle speed. A vehicle speed and Engine's RPM usually indicate the volume of fuel being combusted inside vehicles engine as required by the engine load and driving conditions. This supports the suggestion that higher ammonia emissions are anticipated when a vehicle's engine is run at rich conditions.

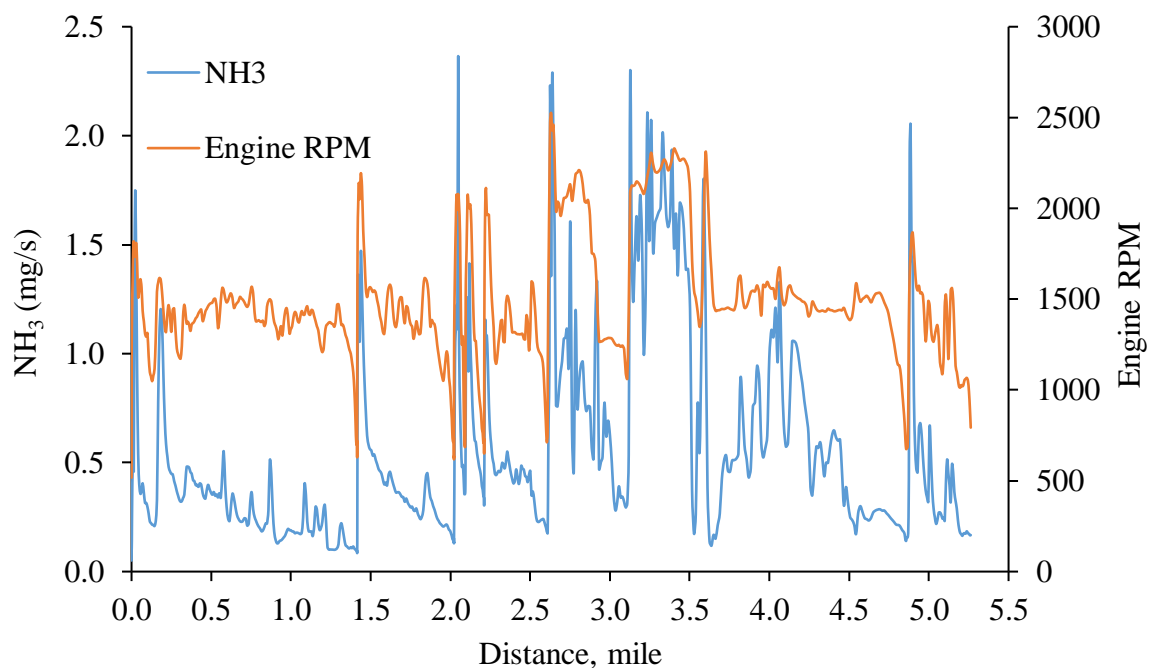


Figure 21. Ammonia emissions and vehicle's RPM of a 2007 gasoline Dodge light-duty truck (vehicle #15).

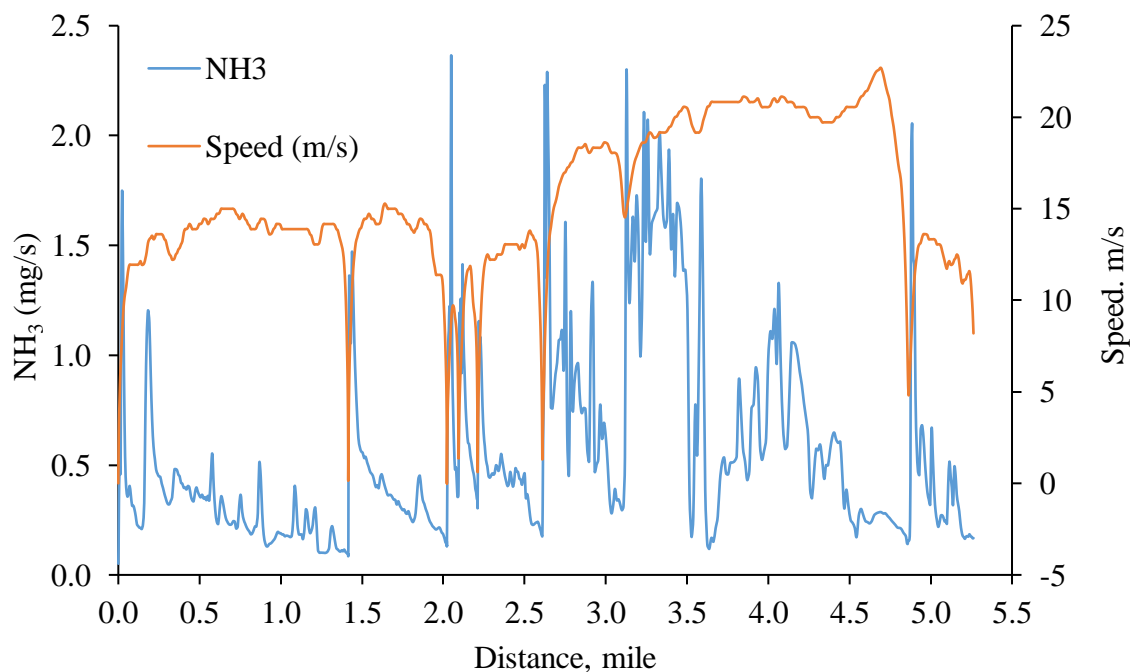


Figure 22. Ammonia emissions and vehicle speed of a 2007 gasoline Dodge light-duty truck (vehicle #15).

5.5. Vehicles Specific Power (VSP) impact on ammonia concentrations

The Vehicle Specific Power (VSP) histogram plots of the UWRL-UDTC cycle driven by all tested gasoline and diesel motor vehicles are shown in Figure 23 and Figure 24, respectively. The histogram plots are almost the same since all tested vehicles were driven on the same testing cycle and followed the same speed limits and traffic rules. The VSP histogram plots of gasoline and diesel are right-skewed histogram plots where most of the values were low. In fact, most of the VSP values of gasoline and diesel motor vehicles were less than 5 kW/ton, indicating low-level decelerating/accelerating or moderate load conditions. This is similar to the VSP histogram plot of the FTP-75 cycle that is used by the U.S. EPA for emission certification and fuel economy testing of light-duty vehicles in the United States (Khan and Frey 2016; Younglove et al. 2005).

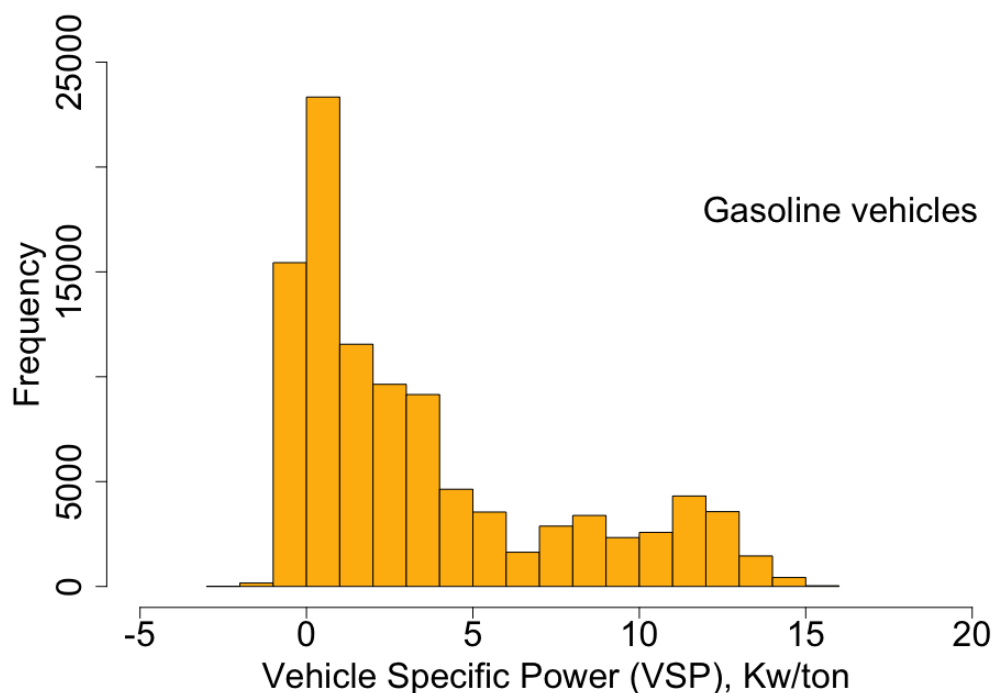


Figure 23. Histogram plots of Vehicle Specific Power (VSP) of gasoline motor vehicles.

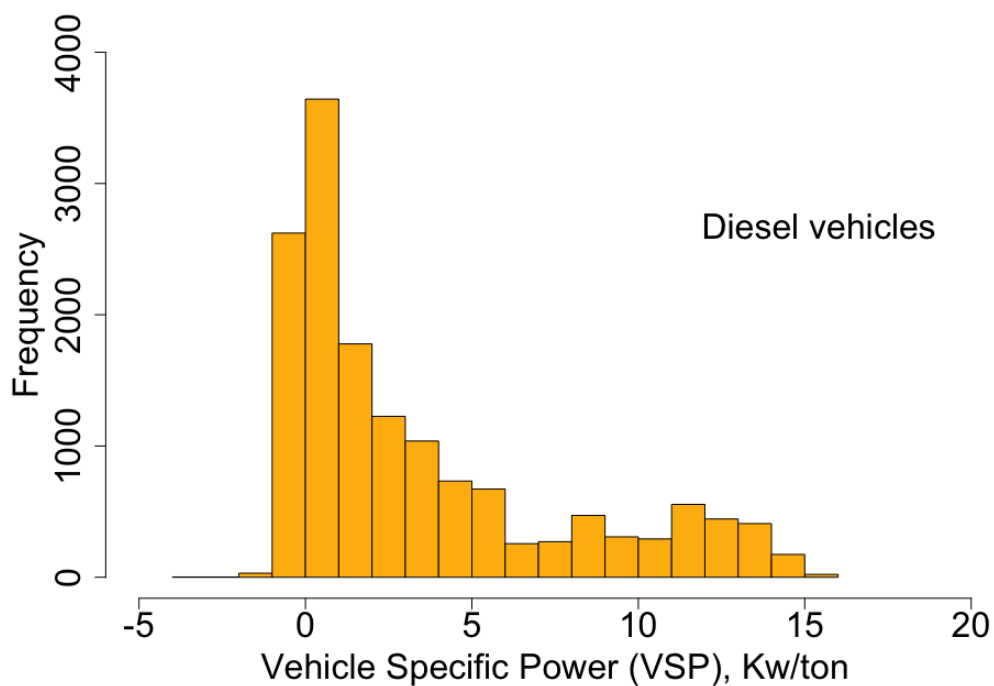


Figure 24. Histogram plots of Vehicle Specific Power (VSP) of diesel motor vehicles.

A typical example of the second-by-second VSP values is shown in Figure 25. The data shown in the plot are for the 1993 CK 1500 gasoline truck (vehicle #1). The plot shows that the mass concentration of NH_3 is positively correlated with the VSP values, which may support the relationship between the vehicle's specific power and NH_3 mass concentrations. The calculated second-by-second VSP for all gasoline motor vehicles were grouped based on their modes and then the corresponding NH_3 mass concentrations were averaged and are shown in Figure 26. The average NH_3 mass concentrations of gasoline motor vehicles had an increasing trend over the VSP modes. This could be explained by the fact that higher VSP modes mainly indicate higher vehicle speed. This could also indicate driving uphill (positive grade) and higher acceleration. High speed, uphill driving and rapid acceleration are driving condition known to cause fuel-rich driving conditions that result in higher concentrations of NH_3 precursors. The average

NH₃ mass concentrations, however, had large variability as the error bars shown in Figure 26 suggest.

The average VSP values and NH₃ mass concentrations of each VSP mode of gasoline and diesel vehicles were averaged and then fitted to a linear fitting line as shown in Figure 27 and Figure 28, respectively. The regression of diesel motor had lower R² than that of gasoline vehicles presumably due to small diesel vehicles testing sample. The data from gasoline and motor vehicles were could be separated into two sections based on the average VSP values of each mode. Negative VSP values including Mode 1 and Mode 2 mainly indicate deceleration or idling conditions, whereas positive VSP values (Mode 3-Mode 14) mainly suggest uphill and driving conditions at various speeds.

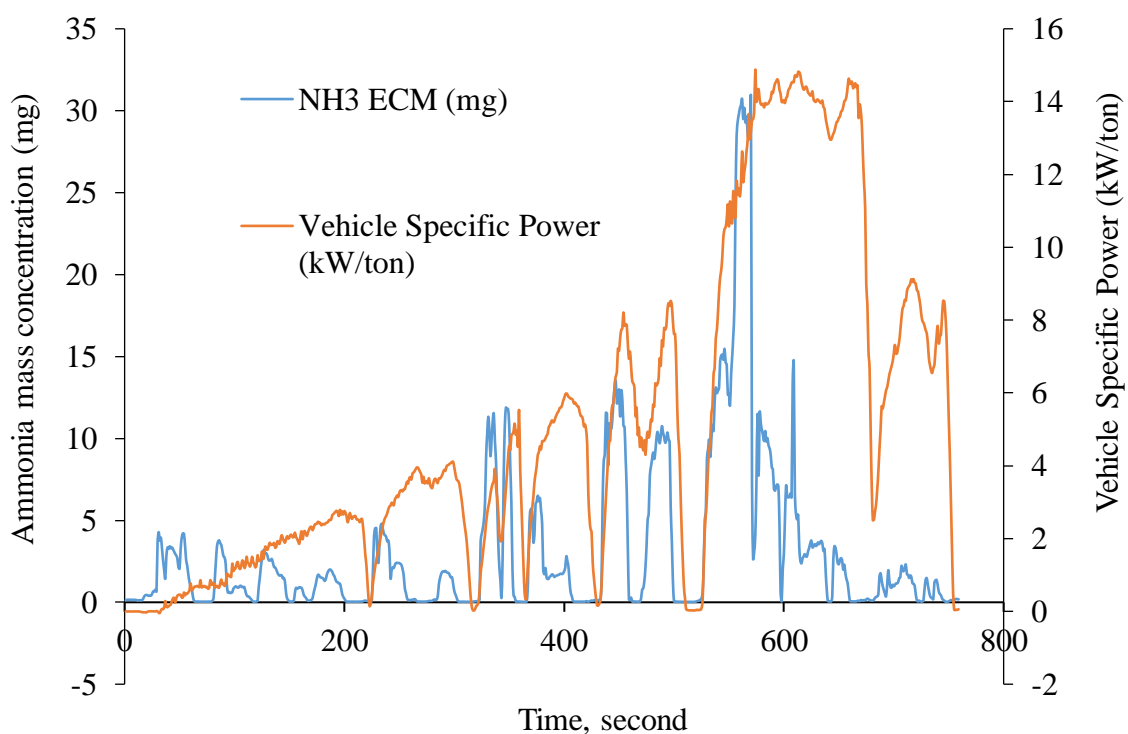


Figure 25. Vehicle specific power (kW/ton) and NH₃ mass concentration (mg) for the 1993 CK 1500 Chevrolet truck.

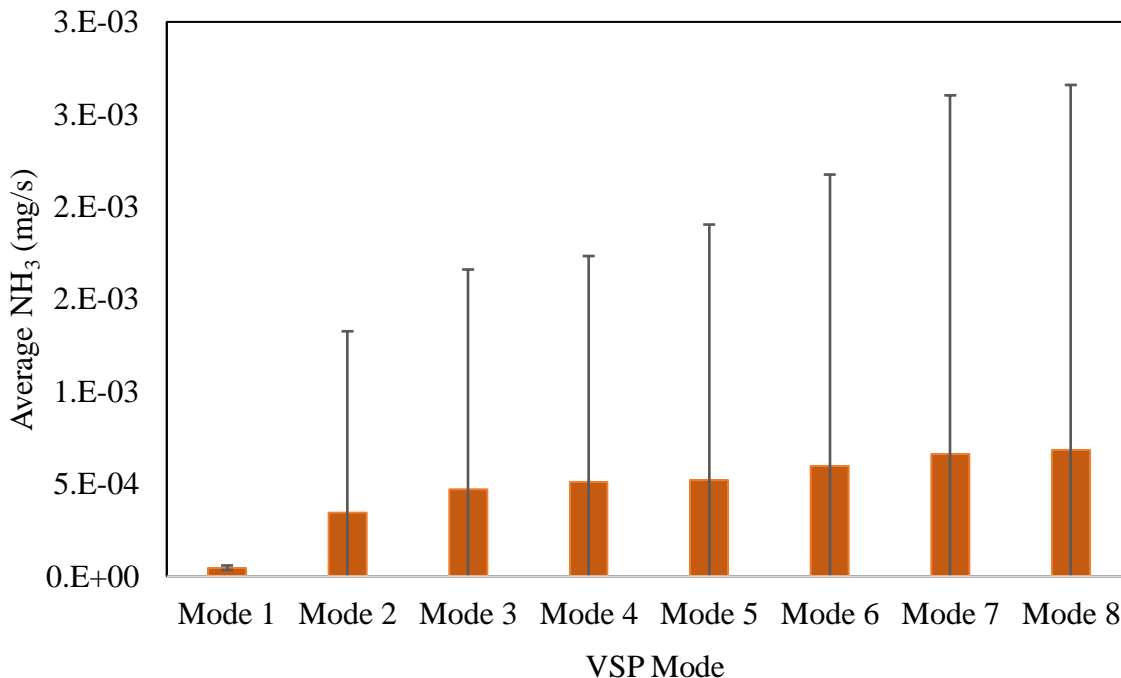


Figure 26. Average NH₃ mass concentration of each VSP mode (The error bars represent data standard deviation)

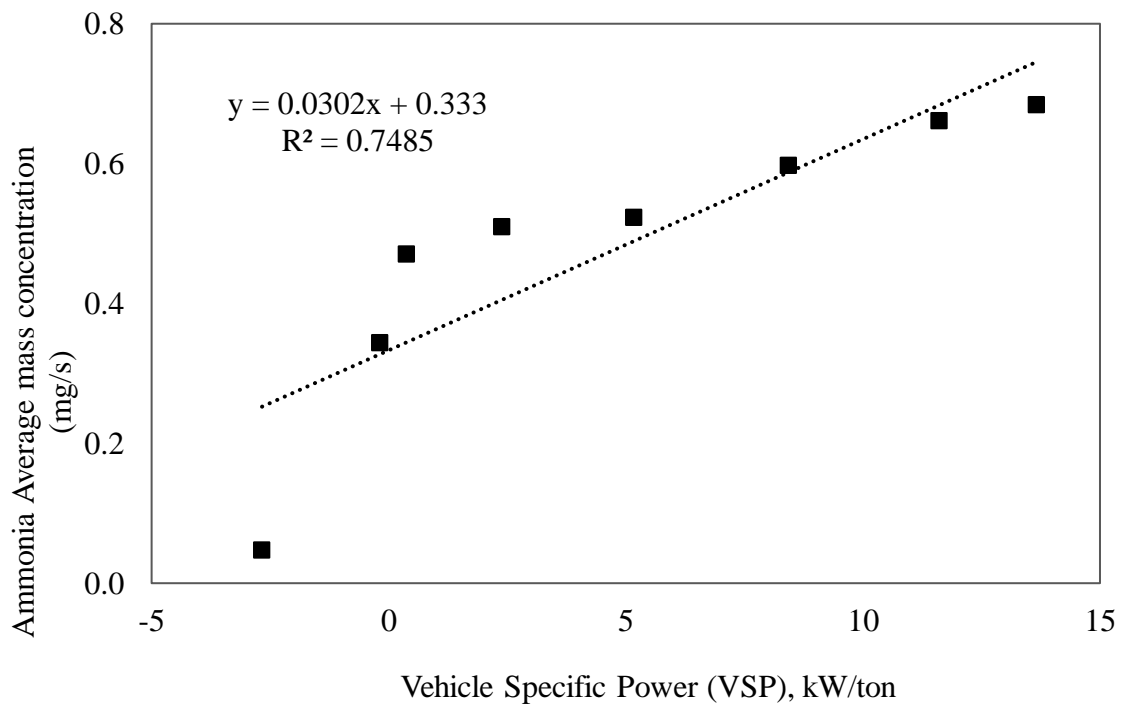


Figure 27. Correlation plot for NH₃ mass concentration and average power of each VSP mode for gasoline motor vehicles-overall regression.

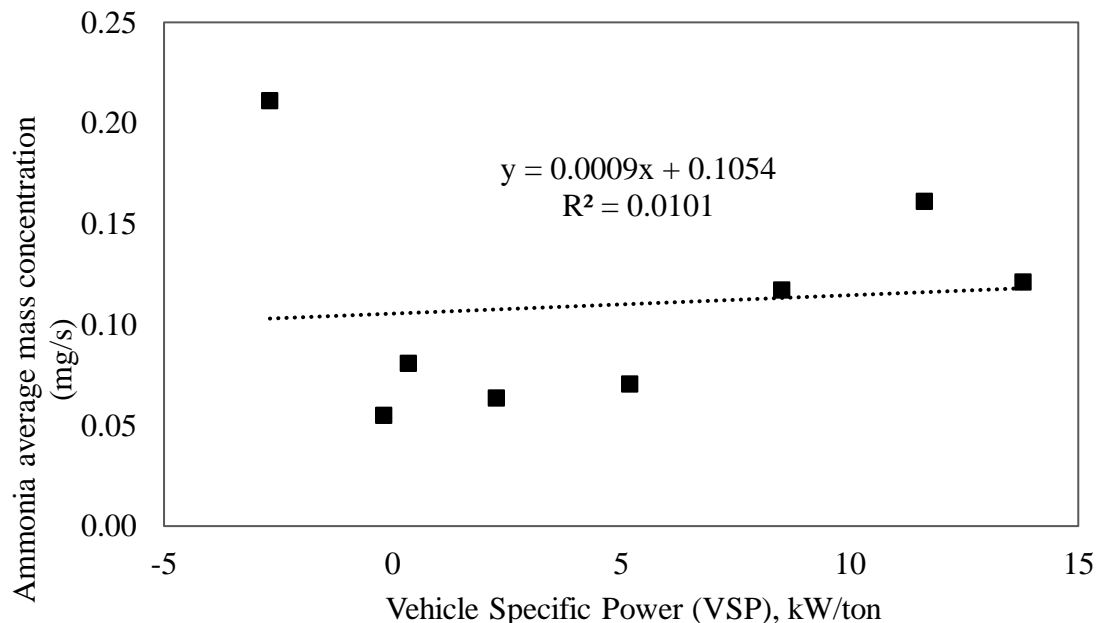


Figure 28. Correlation plot for NH₃ mass concentration and average power of each VSP mode for diesel motor vehicles-overall regression.

Ammonia mass concentrations had an increasing trend as the VSP value increases especially at positive VSP values. This could be explained by the fact that higher ammonia precursors would be generated at higher VSP values. A similar trend was also obtained by Huai et al. (2003) who showed over a dynamometer study that NH₃ mass concentrations from two different vehicles increased when the VSP values increased. The equations (Eq. 22 and Eq. 23) produced by Huai et al. (2003) for an 2001 Acura CL and 2001 Chevrolet Cavalier, respectively, were used to estimate NH₃ mass concentrations at various VSP values similar to these observed in this study and then were compared to the outcomes of this study (Table 9). The variable (Y) refers to NH₃ emission rates (mg/s) and the variable (x) refers to VSP value in kW/ton.

$$Y = 0.0061 x^2 + 0.0176 x - 0.0778 \quad \text{Eq. 22}$$

$$Y = 0.0112 x^2 + 0.1966 x - 0.5785 \quad \text{Eq. 23}$$

Table 9. Estimation of NH₃ mass concentration (mg/s) as a function of VPS parameter

VSP (kW/ton)	NH ₃ (mg/s)		
	This study	(Huai et al. 2003)	
		Eq. 22	Eq. 23
-2	0.3	< 0	< 0
2	0.4	0.0	< 0
5	0.5	0.2	0.7
10	0.6	0.7	2.5
15	0.8	1.6	4.9

The results show that the equation of this study estimated different NH₃ mass concentrations than the study of Huai et al. (2003) at the same VSP values. Nevertheless, the estimated NH₃ mass concentrations of this study were on the same order of magnitude of the outcomes obtained by Huai et al. (2003). This may suggest that there are more parameters affecting NH₃ mass concentrations. The outcomes of this study were obtained based on VSP data of >50 vehicles, whereas Huai et al. (2003) and his colleagues used VSP data of only two vehicles. It should be noted that the two equations Huai et al. (2003) also showed different mass concentrations at the same VSP values.

5.6. Effect of vehicle's driver on ammonia emission rates

Ammonia emission rates of the owner and researcher driver groups are summarized in Figure 29. The researcher drove 35 vehicles out of all 56 tested gasoline and diesel vehicles.

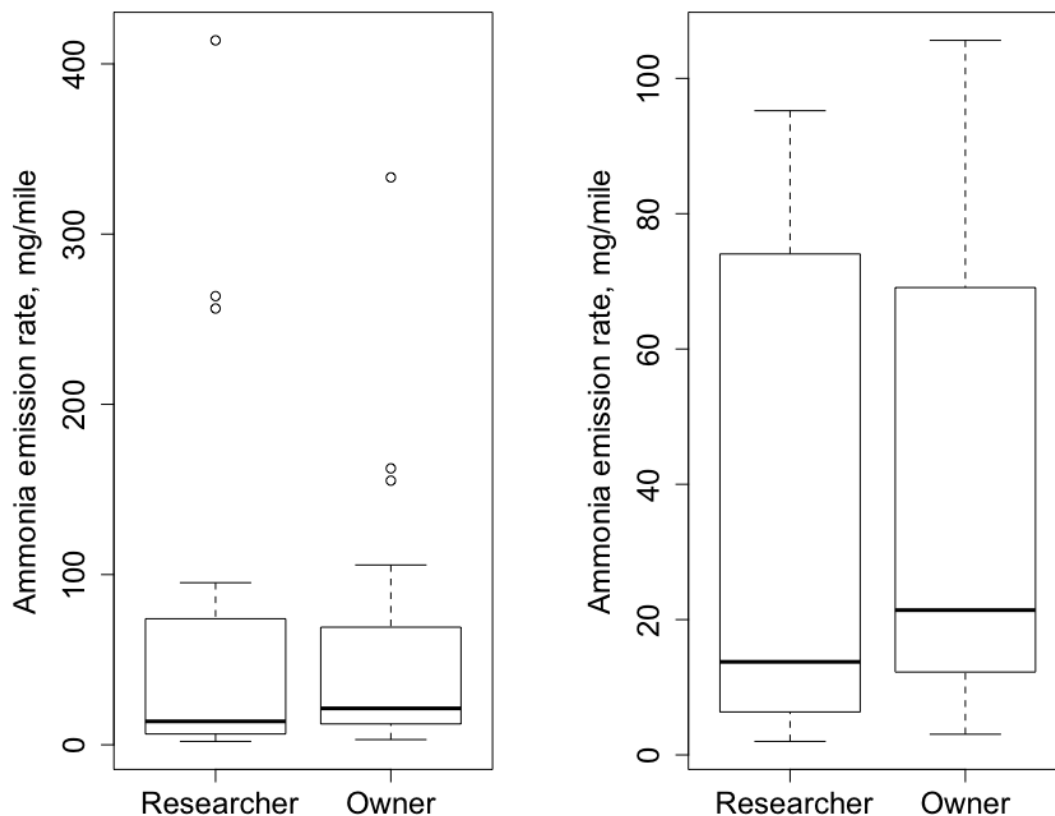


Figure 29. Boxplots of the owner and researcher groups with (left) and without (right) displaying the extreme values.

The “driver” factor had no statistical impact on measured ammonia emission rates as supported by the outcomes of the t-test that showed a p-value of 0.57. The p-value was larger than tail area probability of the 95% confidence level of $\alpha = 0.05$. This indicates that the two tested groups (owner driver VS researcher driver) had no statistically significant difference between them. The researcher and almost all vehicle owners who participated in the on-road tests were young male drivers with similar driving experience. This could be the reason behind having no statistically significant difference between the owner and researcher groups as no large driver variability existed between the groups. Drivers of similar ages and driving experience usually cause similar exhaust emissions including ammonia precursors such as CO and NO_x emissions (Khader and Martin 2019;

Zheng et al. 2017). It is also believed that having two instrument packages and a laptop computer carried on-board in the back seat and many cables coming out of the backseat's window to connect these instruments with their sensors made the researcher and vehicles owners drive with more caution and follow a similar smooth driving style to avoid having any troubles during the on-road testes.

5.7. Effect of fuel type on ammonia emission rates

The NH₃ emission rates of gasoline and diesel motor vehicles are summarized in Figure 14. Unlike the “driver” factor, the fuel factor has shown a significant impact on measured NH₃ rates as the statistics highlighted. The outcomes of the t-test showed a p-value of 0.0002, which is significantly smaller than tail area probability of the 95% confidence level of $\alpha = 0.05$. This indicates that the difference in NH₃ emission rates from tested gasoline and diesel motor vehicles is statistically significant.

As shown in Figure 14, gasoline motor vehicles were attributed to higher emission rates of ammonia than diesel vehicles. The average emission rates of ammonia from gasoline and diesel motor vehicles were 62 and 10.7 mg/miles, respectively. This is likely explained by the fact that gasoline motor vehicles are fitted with the TWC converter where NO over-reduction usually occurs and results in NH₃ formation. This could also indicate that no NH₃ slip occurred from the diesel vehicles fitted with the SCR converters. However, more diesel motor vehicles have to be tested to come up with a solid conclusion about ammonia slip due to the use SCR converters as only two vehicles were tested in this study.

5.8. Ammonia emission rates for gasoline vehicles of the same tier level

The NH₃ emission rates for gasoline vehicles of the similar, Tier-based emissions technology (emissions standards) are summarized in Figure 30. The variability of NH₃ emission rates within each tier level, especially Tier I and NLEV levels, could be due to unique vehicle characteristics and differences in ammonia precursor concentrations. The fact that NH₃ exhaust emission rates are not regulated as yet could also explain the variable emission rates of NH₃ for vehicles with similar emissions standards (Durbin et al. 2002). The tier levels are arranged in the plot in order of increasing stringency for tailpipe emissions of CO, NO_x, and unburned HC. Note that the emissions technology factor might be confounded with the mileage factor, as old vehicles (Tier 0, Tier I and NLEV) generally have higher mileage than newer vehicles (Tier II and Tier III). The mean NH₃ averaged emission rates as a function of vehicle tier level were as follows: 413.8 mg/mile for Tier 0 vehicles, 119.7 mg/mile for Tier I vehicles, 156.5 mg/mile for NLEV vehicles, 38.2 mg/mile for Tier II vehicles, and 9.5 mg/mile for Tier III vehicles. The variability in NH₃ emission rates among the vehicles of different tier level is likely due to the age of fitted TWC converters which is indicated by vehicles' mileage and/or model year.

In general, NH₃ emission rates had a decreasing trend as the standards increased in stringency towards limiting ammonia precursor compounds. A similar trend was also observed by Durbin et al. (2002). The results in Figure 30 show that Tier II and Tier III vehicles were linked with lower NH₃ emission rates than Tier 0 and Tier I vehicles. The NLEV vehicles, however, had higher average NH₃ emission rates than the Tier I vehicles. This may be explained by the fact that the NLEV tier emission standard extended only to

lighter motor vehicles and didn't include vehicles with a GVWR larger than 6,000 pounds. Based on that, the 2002 MPV Chevrolet Tahoe (GVWR > 6000 lbs.) (vehicle#8), which had the highest NH₃ emission rate among other NLEV vehicles, is subject to less stringent emission standards than other NLEV vehicles. Also, the NLEV and Tier I vehicles have the same CO emissions standard. A similar trend was also observed by Livingston et al. (2009), who showed that vehicles made between 2001 and 2003 (California classification: Transitional Low-Emission Vehicle (TLEV)) unexpectedly had higher NH₃ emission rates than Tier I vehicles. It is also possible that NLEV vehicles had higher averaged NH₃ emission rate than the Tier I due to the fact that only four NLEV vehicles were tested and that the 2002 MPV Chevrolet Tahoe vehicle (vehicle #8) which represented one fourth of the NLEV sample size skewed the data.

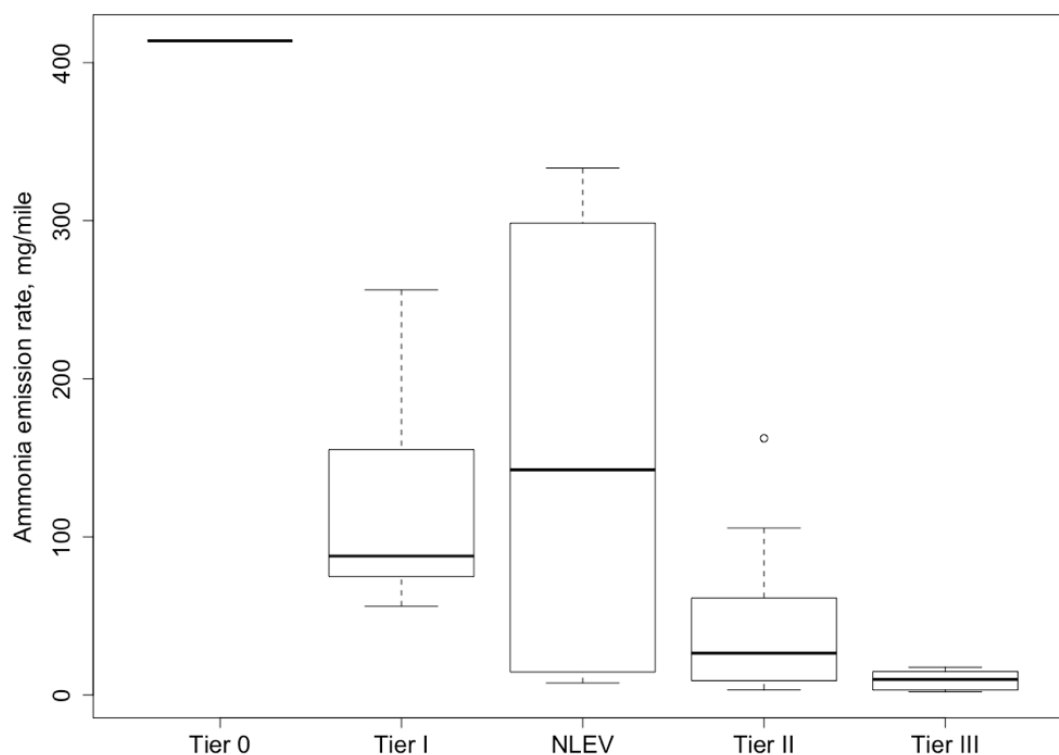


Figure 30. Boxplot of NH₃ emission rates of each tier level vehicles.

The outcomes of the ANOVA test (Table 10) show that the differences between the vehicles of different tier levels are statistically significant at the 95% confidence level. The $\text{Pr}(> F)$ of 7.9×10^{-8} was significantly smaller than the tail area probability of the 95% confidence level of $\alpha = 0.05$. This clearly suggests that gasoline vehicles of different tier standards have significantly different NH_3 emissions rates. This is likely due to differences in ammonia precursors, including NO_x and CO, vehicle characteristics, odometer readings, and vehicle model years.

Table 10. ANOVA results for the impact of emissions technology factor on NH_3 emission rate. (Significance code: ‘***’ $\alpha = 0.001$ (99.9%), ‘**’ $\alpha = 0.01$ (99%), ‘*’ $\alpha = 0.05$ (95%), ‘.’ $\alpha = 0.1$ (90%), ‘ ’ $\alpha = 1$ (0%))

	Df	Sum Sq	Mean Sq	F Value	Pr (>F)	Significance
Tier	4	214083	53521	15.1	7.9×10^{-8}	***
Residuals	44	156463	3556			

Figure 31 similarly shows that post-catalyst CO, NO_x , and CO_2 exhaust emission rates and mileage readings for each tier level had the same general trend as that of NH_3 emission rates. Specifically, the Tier II and Tier III vehicles had lower CO, NO_x , and CO_2 emission rates and mileage readings than Tier 0, Tier I, and NLEV vehicles. The post-catalyst CO_2 concentrations recorded by these vehicles may indicate the concentrations of pre-catalyst CO. The odometer reading is a good proxy of catalyst age and vehicle model year. Durbin et al. (2004) showed that bench-aged (at the lab) catalysts produced 12% higher CO ammonia precursor emissions than as-received catalysts. Lower NO emissions (g/kg fuel) were also measured for the newest vehicles in Tulsa, Oklahoma, and Denver, Colorado, in 2005 by Burgard et al. (2006). Higher NH_3 emission rates were measured

for bench-aged catalysts than as-received catalysts by Durbin et al. (2004) and Huai et al. (2003).

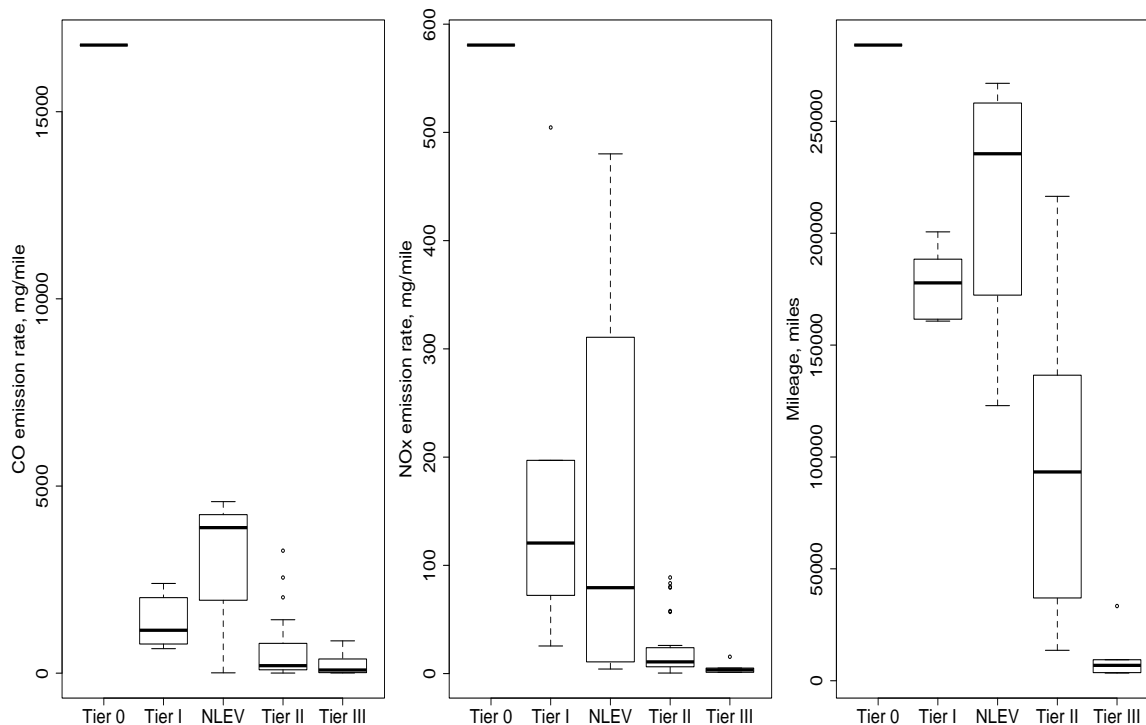


Figure 31. Boxplot of CO and NO_x emission rates and mileage for each vehicle tier level

5.9. The impact of exhaust control devices of diesel vehicles on NH₃ emission rates

Ammonia emission rates from diesel vehicles are grouped based on the same exhaust control device in the boxplot shown in Figure 32. It's shown in Figure 32 that pre-catalyst diesel vehicles had the highest emission rates of NH₃, while those fitted with both Diesel Oxidation Catalyst (DOC) and Selective Catalytic Reduction (SCR) converters recorded the lowest emission rates of NH₃. Pre-catalyst diesel vehicles, and those fitted with only oxidation DOC were linked with an average ammonia emission rates of 19.1 and 9.0 mg/mile, respectively, whereas those diesel motor vehicles fitted

with both DOC and SCR recorded an average ammonia emission rates of 4.8 mg/mile. Although pre-catalyst diesel vehicles were not fitted with catalytic converters, they were linked with an average ammonia emission rates of 19.2 mg/mile. This is due to limited number of NO over-reduction reactions inside their exhaust system. As mentioned before, this could indicate that no NH₃ slip occurred from the two tested diesel vehicles fitted with the SCR converters. However, more diesel motor vehicles have to be tested to come up with a solid conclusion about ammonia slip due to the use SCR converters.

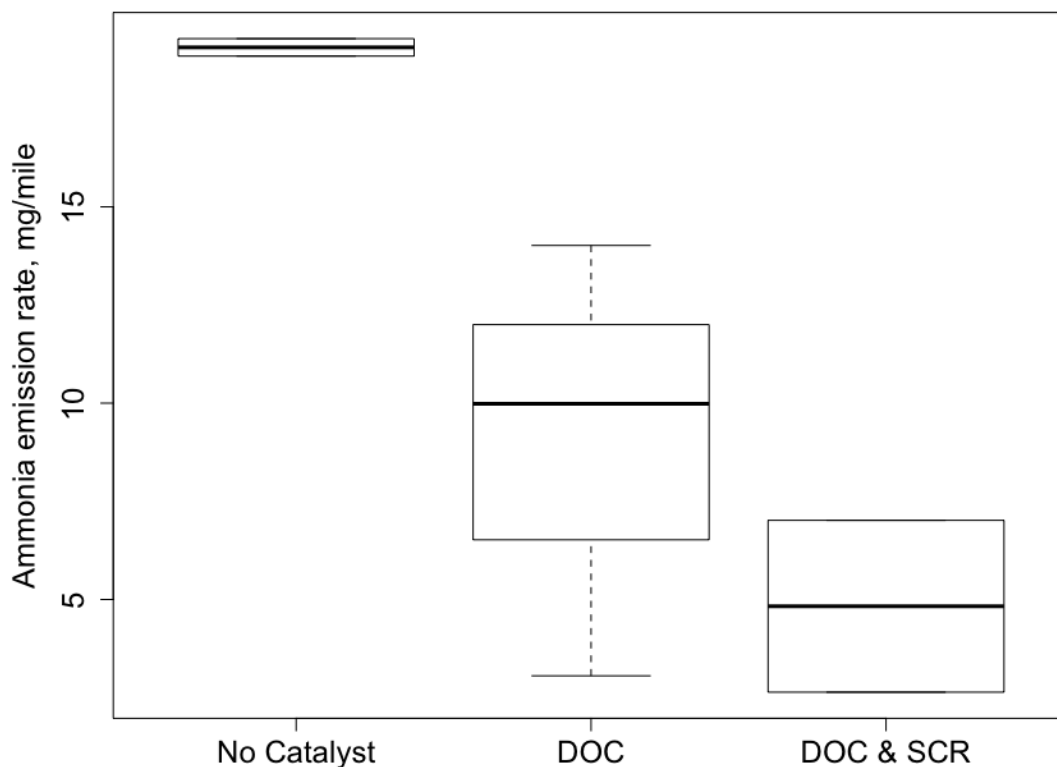


Figure 32. NH₃ emission rate from diesel vehicles based on catalytic converter.

The outcomes of the ANOVA test (Table 11) indicate that ammonia emission rates among the three groups were significantly different. The $\text{Pr}(>F)$ of 1.97×10^{-3} was significantly smaller than the tail area probability of the 95% confidence level of $\alpha =$

0.05. The pre-catalyst diesel vehicles had high odometer reading (265,118 miles) as compared with other diesel motor vehicles, whereas the odometer reading of diesel motor vehicles fitted with only DOC converters ranged between 61,271 and 174,019 miles. The diesel motor vehicles fitted with both DOC and SCR had comparatively small odometer reading (23,547 and 99,046 miles). The odometer reading and other vehicles unique characteristics could additionally explain the different NH₃ emission rates from diesel vehicles with different exhaust control devices. The small number of tested diesel motor vehicles within each group, however doesn't allow adequate statistical examination of the individual impact of diesel vehicles characteristics on NH₃ emission rates.

Table 11. ANOVA results for the impact of exhaust control devices on NH₃ emission rate. (Significance code: '***' $\alpha = 0.001$ (99.9%), '**' $\alpha = 0.01$ (99%), '*' $\alpha = 0.05$ (95%), '.' $\alpha = 0.1$ (90%), ' ' $\alpha = 1$ (0%))

	Df	Sum Sq	Mean Sq	F Value	Pr (>F)	Significance
Catalyst	2	5004	2502	8.507	1.97×10^{-3}	**
Residuals	21	6177	294.1			

5.10. Effect of vehicle's characteristics and post-catalyst exhaust gases

5.10.1. Gasoline vehicles fleet

The outcomes of the ANOVA tests showed that the "Type (Passenger Car (PC), Multi-purpose Vehicle (MPV) and Light-Duty Truck (LDT))" and "Make/manufacture" factors had no statistically significant impact on NH₃ exhaust emission rates for gasoline motor vehicles at the 95% confidence level. This could be explained by the fact that,

regardless of vehicle manufacturer, all were equipped with similar TWC converters that are the main implication of NH₃ exhaust emissions. As for vehicle type, gasoline motor vehicles are classified into PC, MPV, and LDT primarily based on their gross vehicle weight, which appeared to have little impact on NH₃ exhaust emissions ($r = 0.30$). The correlation coefficient (r) of 0.30 indicates a small correlation of gross vehicle weight with NH₃ emission rates.

Figure 33 shows that vehicle mileage, engine displacement, number of cylinders, and model year factors had a moderate to strong correlation with NH₃ emission rates, as the Pearson's correlation coefficient (r) indicates. The mileage factor had the strongest correlation with NH₃ emission rates, with a correlation coefficient value of 0.7. This seems to indicate that NH₃ emission rates increase with increased mileage for gasoline vehicles. These outcomes are consistent with Bishop and Stedman (2015), Bishop et al. (2010);, and Durbin et al. (2004), each of whom measured higher NH₃ emission rates from aged catalysts than from low-mileage catalysts. The negative strong correlation ($r = -0.6$) between the vehicle model year factor and NH₃ emission rates also supports the idea that gasoline motor vehicles with long-used TWC converters emit NH₃ at a higher rate than vehicles with well-operating TWC converters. The model year and odometer reading are good indications of catalyst's age.

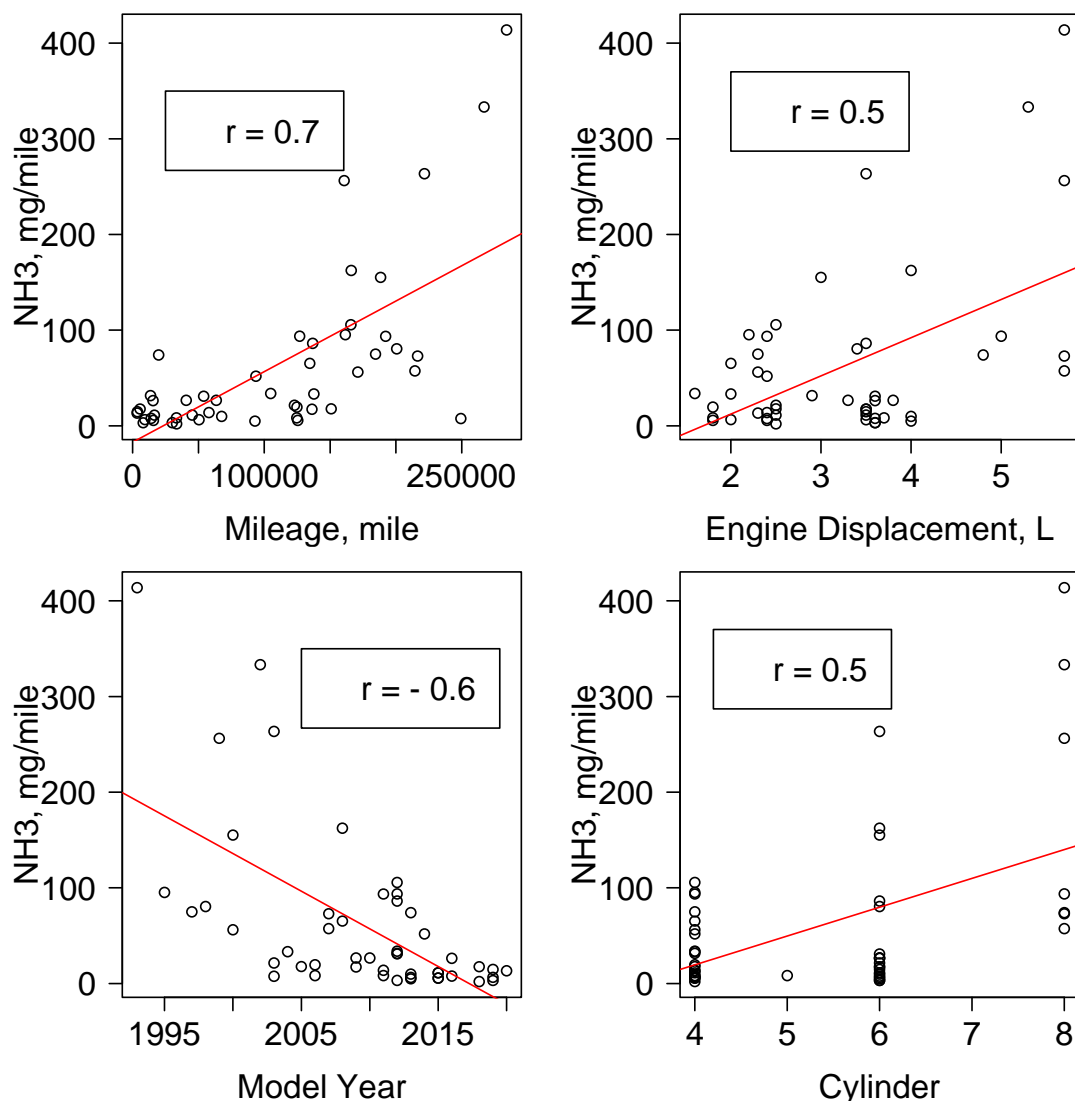


Figure 33. Correlation between NH₃ emission rates and gasoline vehicles characteristics

Similar to mileage and model year factors, engine displacement and number of cylinders also had a significant impact on NH₃ emission rates for gasoline motor vehicles ($r = 0.5$). The good correlation between NH₃ emission rates and both engine displacement and number of cylinders factors suggest that vehicles with comparatively high fuel combustion produce higher amounts of NH₃ exhaust due to higher concentrations of ammonia precursors. A strong linear correlation was measured between engine size and post-catalyst CO ($r = 0.5$) and NO_x ($r = 0.6$) emissions rates (Figure 34). Engine

displacement and cylinders' number are good indications of the fuel volume combusted inside vehicles' engine. Large engines with a large displacement volume usually produce larger volumes of total exhaust emissions than vehicle engines with smaller displacement. Similarly, the more cylinders in an engine, the more combustion occurs, and the more exhaust emissions production would occur. These larger volumes of exhaust emissions normally include NH_3 precursors that would result in higher NH_3 emissions.

The correlation plots presented in Figure 34 also demonstrate that NH_3 emission rates had a strong correlation with post-catalyst CO exhaust emissions, as indicated by the correlation coefficient of $r = 0.8$. This is consistent with many previous studies, including Kean et al. (2009), and Livingston et al. (2009). The scatter plots also show that a strong correlation was similarly measured between NH_3 and NO_x post-catalyst emissions ($r = 0.9$). The relationship between mean NH_3 emissions and NO_x emissions follow the trend reported in the literature (Bishop et al. 2010; Burgard et al. 2006; Andrew Kean et al. 2000). High post-catalyst concentrations of CO and NO_x indicate inefficient control of these pollutants by fitted TWC converters. This could indicate exhausted catalyst or/and faulty oxygen (Lambda) sensors that no longer control the air-fuel ratio to be running at near-stoichiometric conditions could also result in rich air-fuel ratio conditions. TWC converters works more efficiently near-stoichiometric conditions. The abundance of ammonia precursors (CO and NO_x) would increase the chances of ammonia formation on top of fitted TWC converters (Eq. 4-Eq. 8).

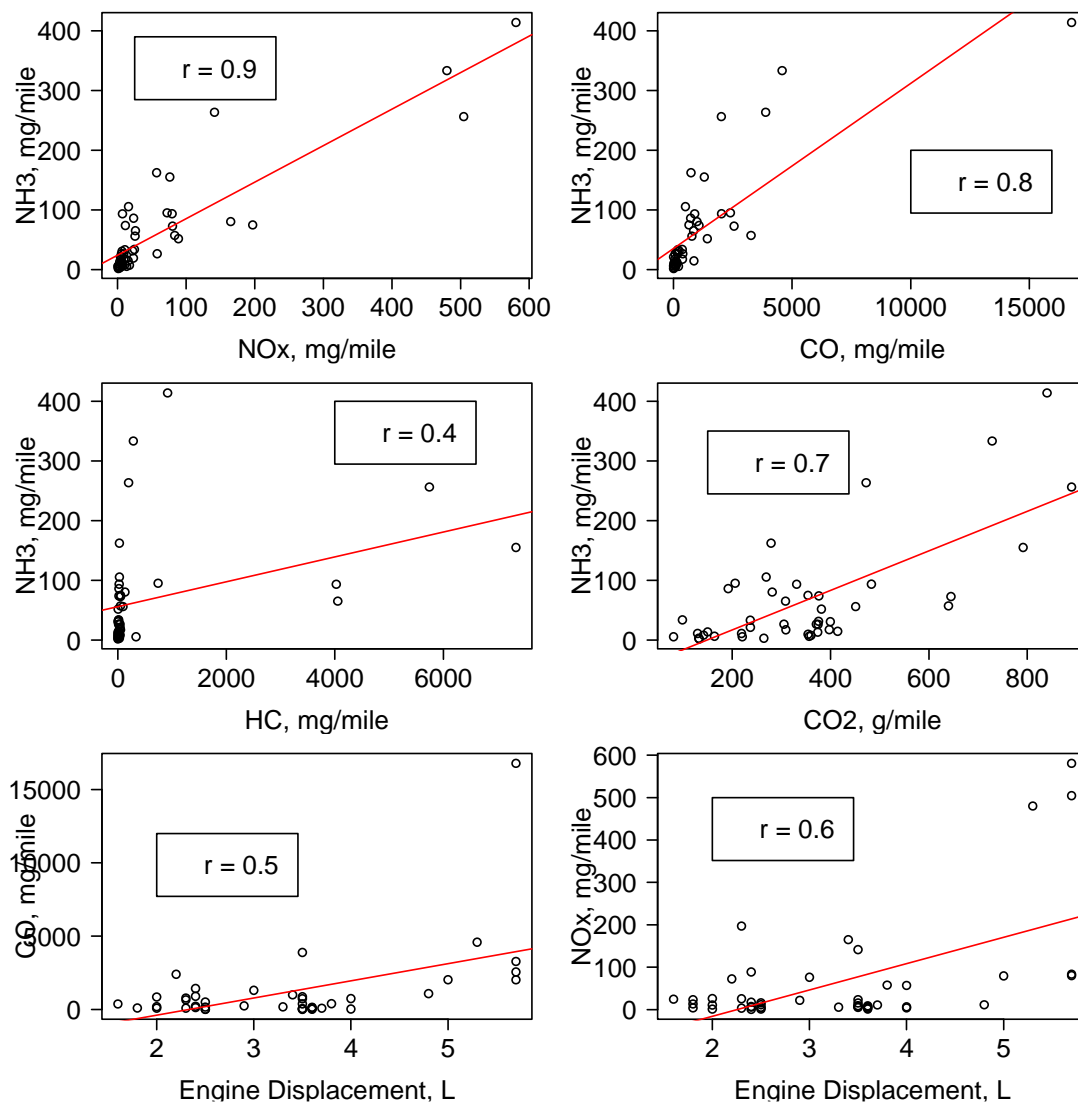


Figure 34. Correlation between NH_3 emission rates and post-catalyst exhaust gases

A stepwise regression analysis was used to build a prediction model for NH_3 from gasoline motor vehicles using the factors that showed good correlation with NH_3 emission rates including vehicles' mileage reading, model year, engine size (displacement), number of cylinder and post-catalyst concentration of NO_x , CO and CO_2 . The stepwise regression analysis steps are shown in Appendix D. The derived model is shown below.

$$\text{NH}_3 \text{ (mg/mile)} = 1.85 + 3.13 \times 10^{-4} \times \text{Mileage (miles)} + 3.61 \times 10^{-1} \times \text{NO}_x \text{ (mg/mile)} \\ + 8.13 \times 10^{-3} \times \text{CO (mg/mile)}$$

The model was then used to predict NH₃ emission rates from a Tier II gasoline vehicle that wasn't tested previously. The vehicle had the following characteristics; model year = 2012, mileage = 131,695 miles, displacement = 1.8 L and number of cylinders = 4. The emission rates of post-catalyst NO_x, CO and CO₂ were measured for the same vehicle using the Applus Autologic 5-Gas Portable Vehicle Gas Analyzer. The emission rates were 13.7 mg/mile, 65.6 mg/mile and 298.4 g/mile, respectively. As the stepwise regression showed, only mileage reading and post-catalyst emission rates of CO and NO_x will be used to predict NH₃ emission rate of the vehicle. Based on all these information, ammonia emission rate of this vehicle was calculated to 48.5 mg/mile. Model verification was impossible at this stage due to the fact that the ECM miniPEMS exhaust emission sensors had to be sent back to the manufacture for repair and calibration. Nevertheless, the estimated emission rate of 48.5 mg/mile was only 27.8% higher than NH₃ average emission rates of Tier II vehicles. The emission rates of NH₃ of tested Tier II vehicles in this study averaged at 38.2 mg/mile and ranged between 3.2 and 162 mg/mile.

5.10.2. Diesel vehicles fleet

The correlations between NH₃ emission rates of tested diesel vehicles and vehicle characteristics (mileage reading, model year, engine size, number of cylinders and vehicle gross weight), and post-catalyst emission rates of CO, NO_x, HC and CO₂ are shown in Figure 35 and Figure 36 , respectively.

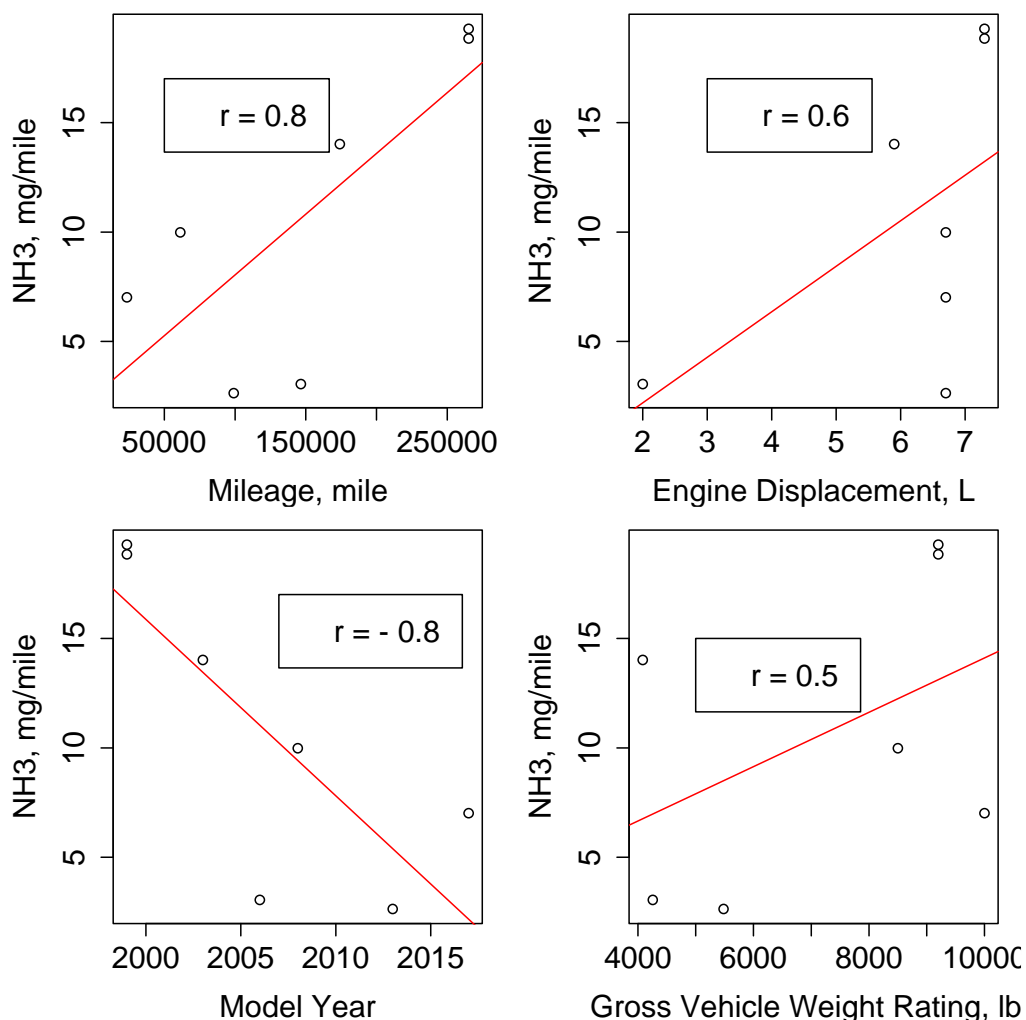


Figure 35. Correlation between NH₃ emission rates and diesel vehicles characteristics.

The correlation plot presented in Figure 35 show that the mileage, the engine displacement and model year factors are well correlated with NH₃ emission rates with a Person's correlation coefficient (r) greater than 0.5 or -0.5. This trend was also reported for gasoline motor vehicles. The cylinder factor of diesel vehicles also had strong correlation with NH₃ emission rates. The mileage and model year factors are good indicators of the age of diesel motor vehicles and their fitted catalytic converters. Similar to gasoline motor vehicles, old diesel vehicles tend to emit higher rates of NH₃ than newer vehicles. The strong correlation with engine displacement and number of cylinders

can be explained by the fact that diesel vehicles that consume larger volumes of fuel, normally result in higher emissions of NH_3 than those vehicles that consume smaller volumes of fuel due to their engine size and number of cylinders. The correlation plots also show that vehicles' GVWR factor had moderate correlation with NH_3 emission rates. Furthermore, ammonia emission rates of tested diesel motor vehicles were strongly correlated with NO_x ($r = 0.9$), CO ($r = 0.9$), CO_2 ($r = 0.7$) and moderately correlated with HC post-catalyst with $r = 0.5$ (Figure 36).

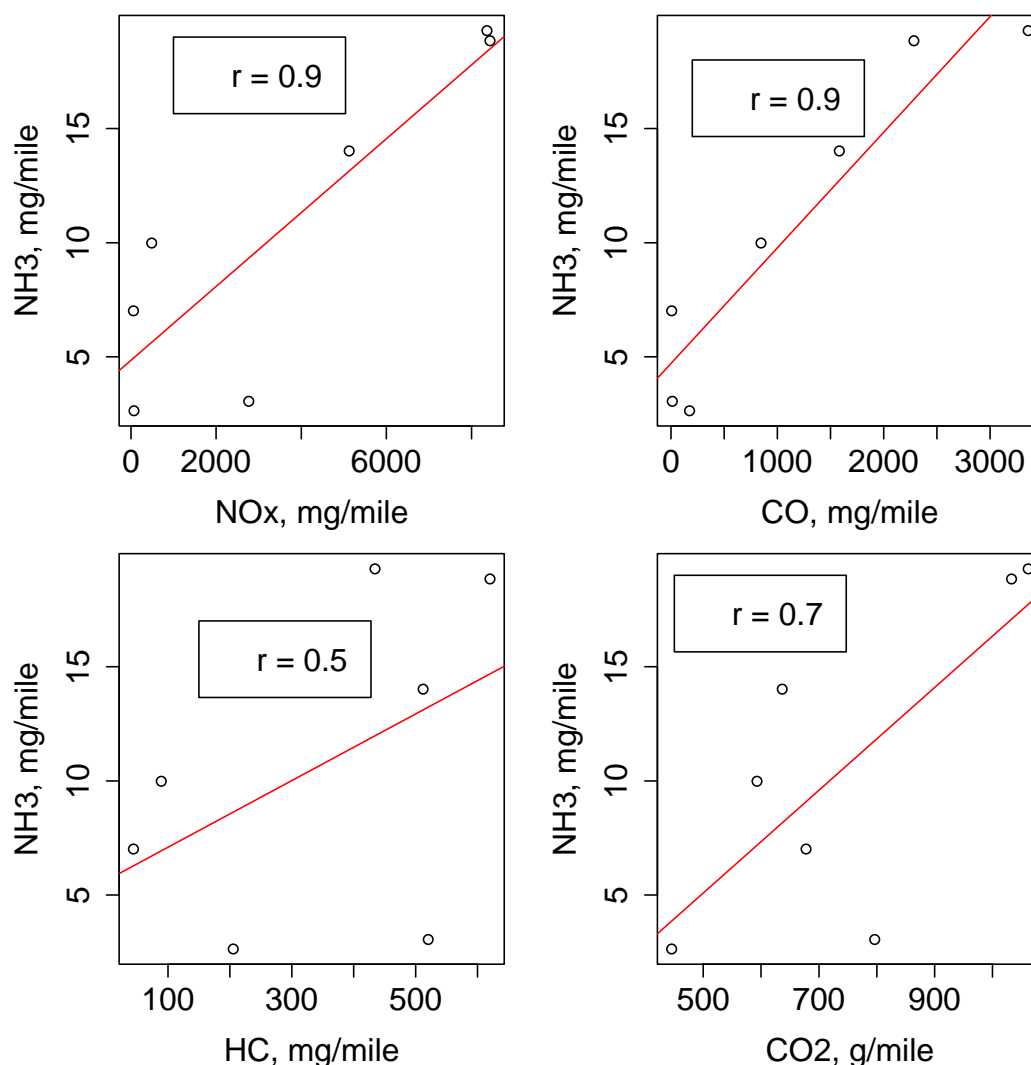


Figure 36. Correlation between NH_3 emission rates and diesel vehicle post-catalyst exhaust gases.

Similar to gasoline motor vehicles, a stepwise regression analysis was used to build a prediction model for NH₃ from diesel motor vehicles using all the factors since they show good correlation (> 0.5) with NH₃ emission rates. However, it should be highlighted that the data set used to build the model consisted only of the data of the six diesel vehicles tested in this study. The stepwise regression analysis steps are shown in Appendix D. The derived model is shown below.

$$\text{NH}_3 \text{ (mg/mile)} = 4.71 + 5.07 \times 10^{-3} \times \text{CO (mg/mile)}$$

5.11. Ammonia exhaust emissions from the Wasatch Front

The gasoline vehicles test sample for this study had the same tier-level distribution as the on-road gasoline motor vehicle fleet along the Wasatch Front in the State of Utah. The model years for the vehicles of the same tier level were not pre-defined. The research team randomly secured and tested motor vehicles until the total number of each tier level was complete. Additionally, the diesel vehicles test sample included pre-catalyst diesel vehicles and other diesel vehicles fitted with different exhaust control devices including the DOC and the SCR converter. As a result, NH₃ emission rates derived from this study are likely to be a good representation of NH₃ emissions for the Wasatch Front on-road gasoline motor vehicle fleet.

According to the Office of Highway Policy Information (OHPI) in the U.S. Department of Transportation Federal Highway Administration (FHWA), motor vehicles in the state of Utah are usually driven approximately 13,884 miles per year (OHPI 2018). Assuming that this applies to the on-road gasoline motor vehicles, the 1,932,113 on-road gasoline and diesel motor vehicles driven along the Wasatch Front drive for

approximately 2.68×10^{10} miles every year. This would yield a total NH_3 emission of 1,496.5 metric tons per year from the entire gasoline- and diesel-powered motor vehicles fleet. The contribution of diesel motor vehicles would be less than gasoline motor vehicles due to their small number and because they emit comparatively smaller rates of NH_3 than gasoline motor vehicles. Diesel vehicles would only yield a total NH_3 emission of 16.4 (1.2%) metric tons/year. Previous studies including ((Baum et al., 2001; Burgard et al., 2006; Thomas D Durbin et al., 2002; Emmenegger et al., 2004; Farren, et al., 2020; Karlsson, 2004) reported that NH_3 emission rates from the transport system seem to be greater than what emission inventories indicate. That assertion is also supported by the results of this study, which estimate that the Wasatch Front vehicles fleet emits nearly 4.1 tons of NH_3 every day (Figure 37). This is almost 41 % higher than estimates from the 2017 national emission inventory of 2.9 tons of NH_3 into the atmosphere every day.

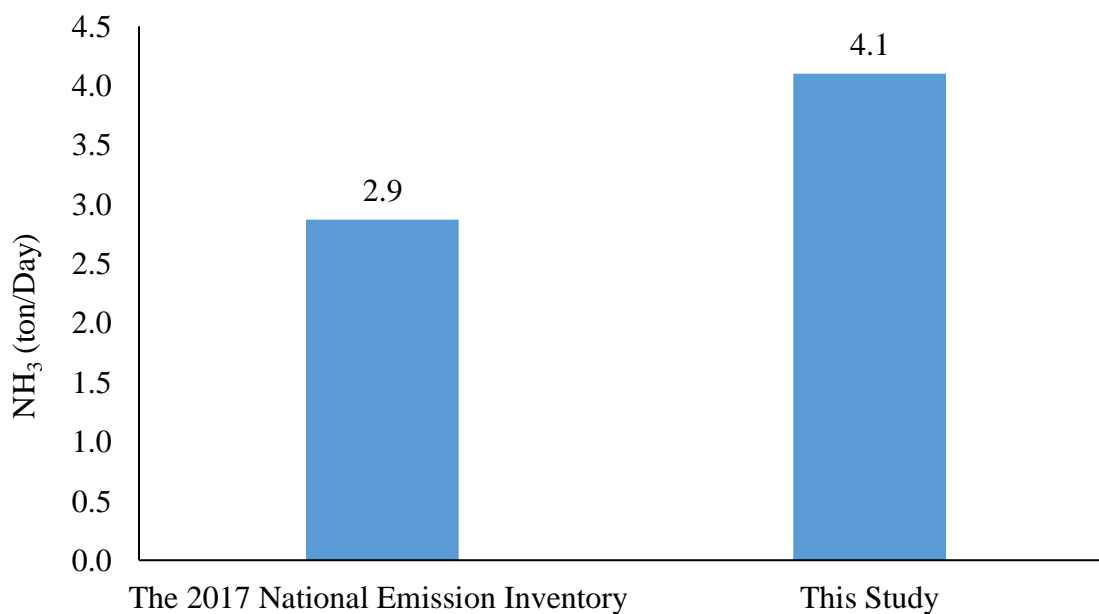


Figure 37. Estimation of the daily ammonia emission rates of on-road vehicle fleet in the State of Utah

The outcomes of this study and similar studies highlight the fact that in addition to exhaust emission models such as the MOVES model, the national emission inventory studies should also include the emission rates of ammonia reported by experimental studies as they normally report measured emission rates of ammonia based on actual measurement of ammonia from in-use motor vehicles. The data reported by experimental studies including this study could also be used to validate estimated emission rates of ammonia from exhaust emission models.

Compared with other sources, the Wasatch Front gasoline and diesel motor vehicle fleet would emit the third highest amount of NH_3 after stationary sources and fire sources. The 2017 national emission inventory showed that stationary sources constitute the largest fraction of NH_3 emissions at approximately 99 tons per day, whereas fire sources (mainly wildfires) constitute the second largest fraction of NH_3 emissions at approximately 15.2 tons per day (Baasandorj et al. 2018). The main sectors included in the stationary sources are agriculture, dust from roads and construction sites and fuel combustion processes.

5.12. Comparison with previous studies

As compared with previous studies as shown in Figure 38 and Figure 39, the mean emission rate for exhaust NH_3 measured in the present study was qualitatively consistent with previously measured NH_3 emission rates for gasoline and diesel motor vehicles. The outcomes of the t-test (p -value = 0.94) suggests that the difference between the mean NH_3 emission rate in this study and those reported by previous studies is statistically insignificant at the 95% confidence level. The p -value of 0.94 is larger than

the tail area probability of the 95% confidence level of $\alpha = 0.05$. This indicates that the Null Hypothesis (H_0) which assumes that expected difference between tested groups is insignificant can't be rejected as it was supported by the data.

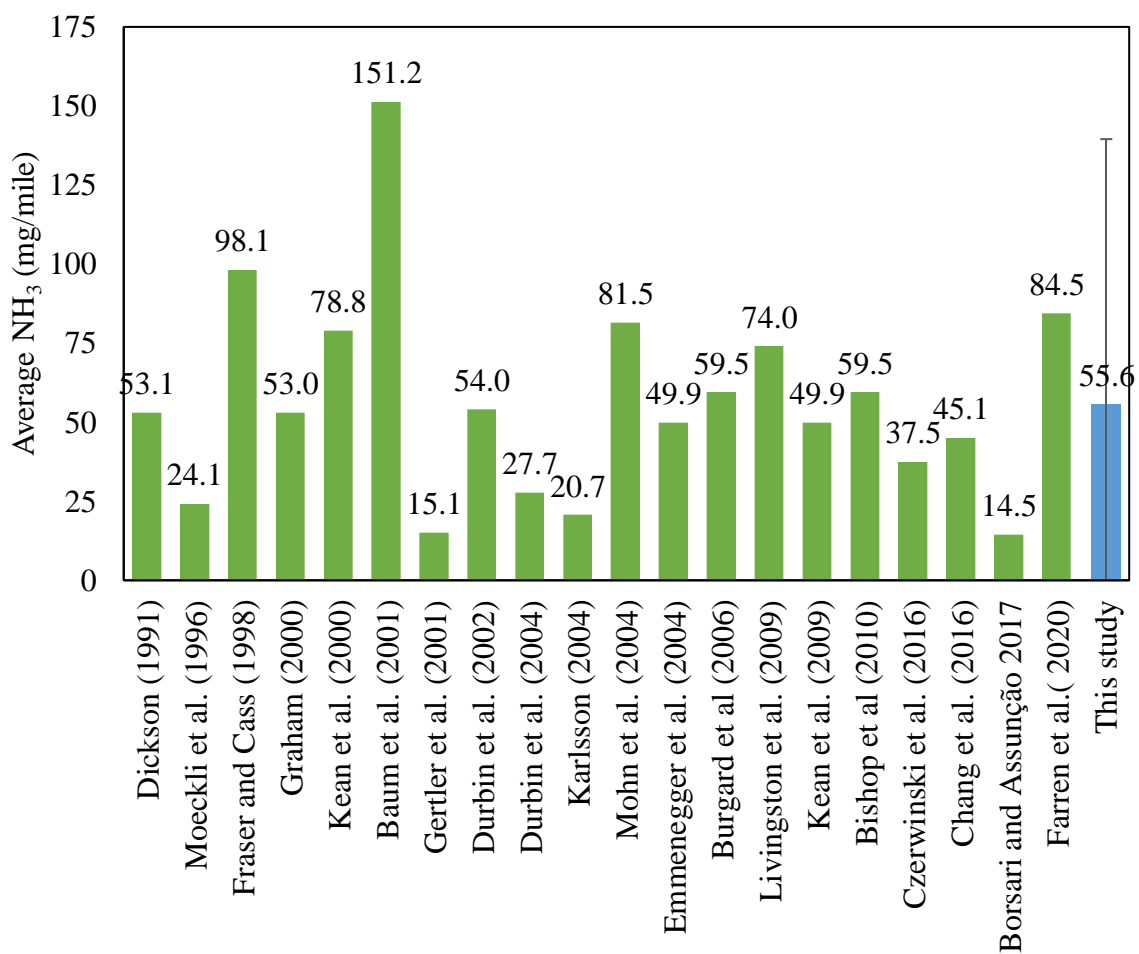


Figure 38. Comparison of NH₃ emission rates from previous studies and current study. (The error bar on our data represents one standard deviation)

Ammonia emission rates of previous studies were estimated using vehicle test samples that contained gasoline vehicles fitted with aged and new TWC converters. However, the differences in ammonia emission rates among the different studies presented in Figure 38 are likely due to differences in testing methodologies, vehicle fleet

characteristics, catalyst age of tested vehicles, fuel type and composition, evolving emission control technology, vehicle state of operation, and driving patterns (Livingston et al. 2009).

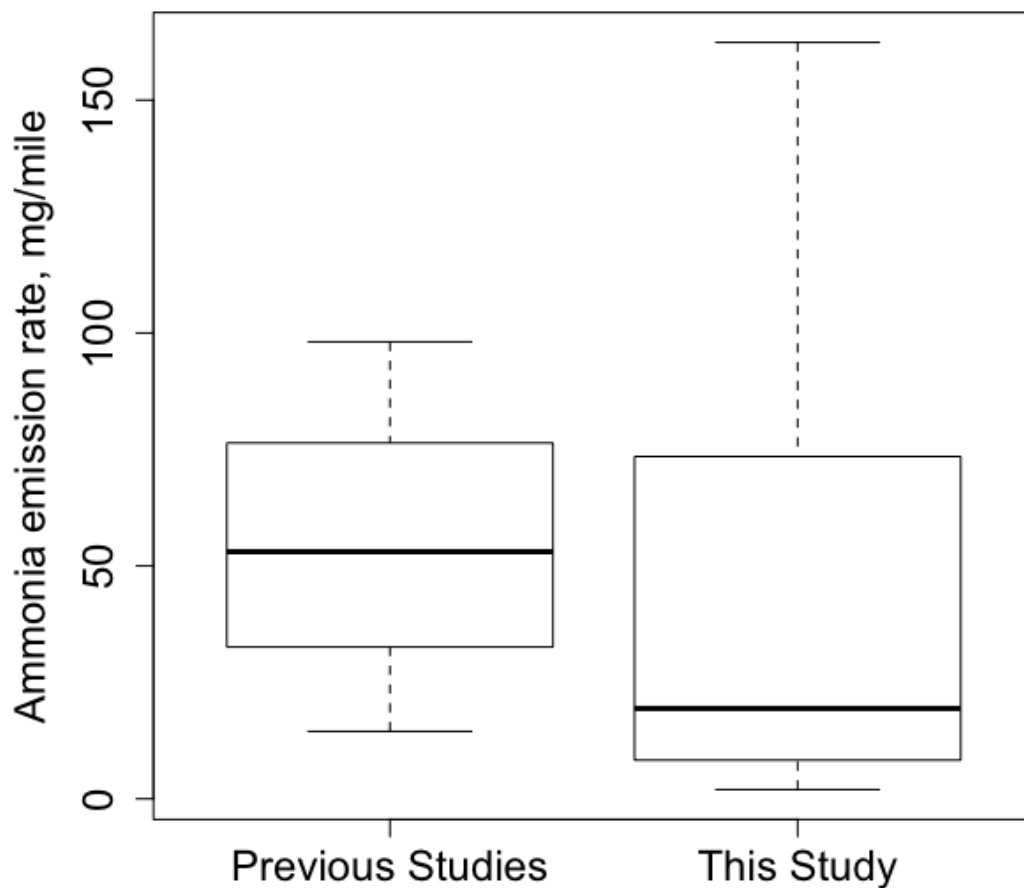


Figure 39. Boxplot of NH_3 emission rates from previous studies and current study.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

A total of 166 on-road RDEs tests were carried out to estimate the emission rates of exhaust NH_3 from the on-road light-duty gasoline and diesel motor vehicles fleet representative of the Wasatch Front. Ammonia exhaust emission rates of 47 light-duty gasoline motor vehicles and 6 light-duty diesel motor vehicles were quantified using the portable ECM miniPEMS over real on-road Real Driving Emissions (RDEs) tests. The ECM miniPEMS also reported the post-catalyst NO_x concentrations. Besides the ECM miniPEMS, a portable Applus Autologic 5-Gas Portable Vehicle Gas Analyzer (model 310-0220) was used to measure the concentration of post-catalyst CO , CO_2 and unburned HC. Both instruments were carried onboard the tested vehicles during the tests. The gasoline test vehicle sample of 47 light-duty motor vehicles were chosen to have the same tier level distribution of the on-road gasoline vehicles fleet of the Wasatch Front. The diesel motor vehicles sample were selected to have vehicles with different exhaust control devices including the Diesel Oxidation Catalyst (DOC) and the Selective Catalytic Reduction (SCR) catalyst. The RDEs testes were carried out on a predefined urban-driving test cycle designed using the local road network in the city of Logan, Utah. The on-road RDE tests were conducted on an urban-driving test cycle that included residential and highway roads, various speed limit zones, uphill and downhill road segments, stop signs, traffic lights, and a school zone with a reduced speed limit. The data obtained from the RDEs tests were analyzed using the Microsoft Excel, MATLAB and RStudio software packages.

Unlike early studies that expected that NH_3 exhaust emissions from motor vehicles will remain insignificant even if all gasoline motor vehicles were equipped with the TWC converters, the outcomes of this study showed that exhaust-originated ammonia emissions might be significant especially in big cities and urban areas where motor vehicles are predominant. For instance, the outcomes of this study showed that ammonia average emission rates of gasoline and diesel motor vehicles were 62.0 and 10.7 mg/mile, respectively. The entire vehicle test sample had an average ammonia emission rate of 55.6 mg/mile. This would yield an estimated 4.1 metric tons per day of NH_3 emissions from the Wasatch fleet of on-road gasoline and diesel motor vehicles. This is 41 % higher than the estimate from the 2017 national emission inventory, which estimated that the Wasatch Front gasoline motor vehicles fleet emits 2.9 tons of NH_3 into the atmosphere every day. This suggests that ammonia emission rates from the transport system seem to be greater than what emission inventories usually indicate.

The outcomes also showed that NH_3 emission rates from tested gasoline and diesel motor vehicles with different characteristics were statistically different. For instance, tested Tier 0, Tier I, NLEV, Tier II and Tier III gasoline motor vehicles had average NH_3 emission rates of 413.8, 119.7, 156.5, 38.2 and 9.5 mg/mile, respectively. Similarly, pre-catalyst diesel vehicles, and those fitted with only oxidation DOC were linked with an average NH_3 emission rates of 19.1 and 9.0 mg/mile, respectively, whereas those diesel motor vehicles fitted with both DOC and SCR recorded an average NH_3 emission rates of 4.8 mg/mile. Further, the research results highlighted that NH_3 emission rates from most tested vehicles were higher in the first lap than in the second and third laps. This could be due to optimized catalyst converter performance or better

fuel combustion inside vehicles engine after the engine warmed up during the first lap.

Ammonia emission rates were also impacted by vehicles' characteristics and other post-catalyst exhaust gases including CO, NO_x and CO₂. The results illustrated that the ammonia precursors, CO and NO_x had strong correlations to ammonia emission rates from gasoline and diesel motor vehicles with a Pearson correlation coefficient (r) greater than 0.5. Similarly, post-catalyst exhaust emissions of CO₂ also strong correlation to NH₃ exhaust emission rates of gasoline and diesel motor vehicles. Contrarily, post-catalyst exhaust emissions of unburned HC had only a moderate correlation ($r = 0.4$) to ammonia exhaust emissions of gasoline motor vehicles. Ammonia exhaust emission rates of gasoline and diesel motor vehicles were also influenced by vehicle physical characteristics. For instance, ammonia exhaust emissions of both gasoline and diesel motor vehicles were strongly correlated ($r > 0.5$) to vehicles' odometer reading, model year and engine displacement, and moderately to vehicles gross vehicle weight rating (GVWR). Lastly, the vehicle specific power (VSP) parameter was strongly correlated ($r > 0.5$) with NH₃ mass emission rates from gasoline motor vehicles and poorly correlated ($r < 0.3$) with NH₃ mass emission rates from the tested diesel motor vehicles.

CHAPTER VII

ENGINEERING SIGNIFICANCE

Direct quantification of raw exhaust ammonia emissions using appropriate reliable portable instrumentation mounted on vehicles tailpipes over on-road driving conditions will result in better understanding of vehicles' real-world contribution to total anthropogenic ammonia emissions. This gives a better idea of the influence of gasoline and diesel vehicles on the air quality of Utah, as well as within similar regions, in terms of direct emissions of exhaust ammonia into the atmosphere and in terms of the potential formation of secondary particulate matter such as ammonium nitrate and sulfate.

This study produced accurate estimations of NH_3 emissions from mobile sources, which in return should aid in better quantifying and understanding of vehicle contribution to the atmospheric NH_3 inventory. This should help regulators in planning, facilitating and implementing effective reduction strategies for particulate matter especially in areas where PM occurs at elevated concentrations and violates the applicable standards. For instance, the Vehicle Repair and Replacement Assistance Program (VRRAP) that provides funding assistance to individuals whose vehicles are failing vehicle emission standards to either replace their failing vehicles with a newer, cleaner vehicle or to repair their vehicles to pass the test would help in better control of NH_3 emissions from gasoline and motor vehicles fleet as CO, NO_x and HC exhaust emissions would be minimized. Additionally, precise estimations of NH_3 from mobile sources could help the manufacturers in improving the exhaust systems of motor vehicles.

Furthermore, the outcomes of this study, particularly NH_3 emission rates would be beneficial when carrying out inventory studies and in case of using modeling tools such as the MOtor Vehicle Emission Simulator (MOVES) model which is used by the U.S. EPA to estimate emissions from on-road and off-road vehicles in the United States. The outcomes of this study showed that Tier II (2004-2016) gasoline motor vehicles would produce an average NH_3 emission rate of 38.2 mg/mile, whereas the MOVES model estimates as average NH_3 emission rate of 20.1 mg/mile for the same category of gasoline vehicles. The outcomes of this study and other experimental studies would help in validating the estimated emission rates of ammonia using the exhaust emission models. Besides, these studies might also help exhaust emission models in selecting the factors (e.g., vehicle characteristics) that significantly impact ammonia emission rates from motor vehicles.

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APPENDICES

Appendix A. The ECM MiniPEMS Data Reduction Code

```

%%
tic
format long
clear all
clc

%-----
%-----
% Gasoline Vehicles- ECM
%-----
%-----
% DATA INPUT
% This section for inputting variable inputs that will be used for further
% calculations

tic

MDL_f      =0.05299;           % The minimum detection limit (MDL) for the NOxCANf
MDL_t      =0.71829;           % The minimum detection limit (MDL) for the NOxCANt
MDL_NH3    =0.6716;           % The minimum detection limit (MDL) for the NH3
lag_i      =100;               % How many steps the NOxCANf is behind (Initial)
lag_f      =10;                % How many steps the NOxCANf is behind (selected after trying
different initial values)
up         =0;

ECM_Input = readtable('ECM_178.xlsx');           % Read the data from the EXCEL file
Rows_count = numel(ECM_Input(:,1));             % Count the # of Rows
ECM=ECM_Input(7:Rows_count,:);                 % Import only valid cells with numbers
Rows_count = numel(ECM(:,1));                   % Re-Count the # of Rows of the variable (ECM)

ECM_NOxf_in = ECM(:,5);                         % Take column # 5 as NOx concentrations (PPM)
ECM_NOxt_in = ECM(:,24);                       % Take column # 27 as NOx+NH3 concentrations
(PPM)
ECM_Temp = ECM(:,18);                           % Take column # 18 as Temperature concentrations
(PPM)
ECM_RPM = ECM(:,45);                            % Take column # 47 as Engine RPM concentrations
(PPM)
ECM_Time = ECM(:,3);                            % Take column # 3 as the Time (second)
ECM_speed = ECM(:,35);                          % Take column # 50 as the vehicle speed (km/hr)
ECM_Cat_Temp_celsius = ECM(:,52);              % Take column # 51 as the Catalyst
Temperature

% Error codes
Err1_NOxf= ECM(:,12);                           % Take column # 12 as ECM_ErrCode1_0x10
Err2_NOxf= ECM(:,14);                           % Take column # 14 as ECM_ErrCode2_0x10
Err1_4tc= ECM(:,21);                            % Take column # 23 as ECM_ErrCode1_0x11
Err2_4tc= ECM(:,22);                            % Take column # 25 as ECM_ErrCode2_0x11
Err1_NOxt= ECM(:,31);                           % Take column # 34 as ECM_ErrCode1_0x12
Err2_NOxt= ECM(:,33);                           % Take column # 36 as ECM_ErrCode2_0x12

ECM_NOxf_in = str2double(table2array(ECM_NOxf_in)); % Convert the (NOx) table to
array and then double
ECM_NOxt_in = str2double(table2array(ECM_NOxt_in)); % Convert the (NOx+NH3)
table to array and then double

```

```

ECM_Temp = str2double(table2array(ECM_Temp));           % Convert the (Temp) table to
array and then double
ECM_RPM = str2double(table2array(ECM_RPM));           % Convert the (Engine RPM)
table to array and then double
ECM_Time = str2double(table2array(ECM_Time));         % Convert the (Time) table to
array and then double
ECM_speed = str2double(table2array(ECM_speed));       % Convert the (Vehicle Speed)
table to array and then double
ECM_Cal_Temp_celsius = str2double(table2array(ECM_Cal_Temp_celsius)); % Convert the
(Catalyst temperature) table to array and then double

Err1_NOxf = str2double(table2array(Err1_NOxf));       % Convert the
(ECM_ErrCode1_0x10) table to array and then double
Err2_NOxf = str2double(table2array(Err2_NOxf));       % Convert the
(ECM_ErrCode2_0x10) table to array and then double
Err1_4tc = str2double(table2array(Err1_4tc));         % Convert the (ECM_ErrCode1_0x11)
table to array and then double
Err2_4tc = str2double(table2array(Err2_4tc));         % Convert the (ECM_ErrCode2_0x11)
table to array and then double
Err1_NOxt = str2double(table2array(Err1_NOxt));       % Convert the
(ECM_ErrCode1_0x12) table to array and then double
Err2_NOxt = str2double(table2array(Err2_NOxt));       % Convert the
(ECM_ErrCode2_0x12) table to array and then double
toc

%%
tic
%-----
%-----
% DATA INPUT
% This section for inputting Grade data that will be used for furthur
% calculations

Grade_Input = readtable('Grade_10_meters.xlsx');
Grade_count = Grade_Input(:,1);
Grade = Grade_Input(:,8);

Grade_count = table2array(Grade_count);
Grade = table2array(Grade);

toc

%%
%-----
%-----
% Minimum Detection Limit (MDL)
% This section will take the NOxCANt and NOxCANf and repalce all the readings
% of NOxCANf that have the values of less than 0.05299 with <MDL and the
% values of NOxCANt that have the value of less than 0.71829 with <MDL.
% This section also show if there were any error codes

tic

%-----

```

```

%-----
% NOxCANf and NOxCANt

ECM_NOxf_i = ECM_NOxf_in;
ECM_NOxt_i = ECM_NOxt_in;

s=1;
e(s,1)="Run1 ECM(102)";
e(s,2)="NOxCANf";
e(s,3)="NOxCANt";
e(s,4)="4tcCAN (Temperature)";

s=s+1;
e(s,1)="Count (Total)";
e(s,2)=numel(ECM_NOxf_i);
e(s,3)=numel(ECM_NOxt_i);
e(s,4)=numel(ECM_Temp);

s=s+1;
e(s,1)="Minimum";
e(s,2)=min(ECM_NOxf_i);
e(s,3)=min(ECM_NOxt_i);
e(s,4)=min(ECM_Temp);

NOxf_NEG=0;
NOxt_NEG=0;

for m=1:Rows_count

    if ECM_NOxf_i(m) < MDL_f
        ECM_NOxf(m,1) = (MDL_f/2);
        NOxf_NEG=NOxf_NEG+1;
    else
        ECM_NOxf(m,1) = ECM_NOxf_i(m);
    end

    if ECM_NOxt_i(m) < MDL_t
        ECM_NOxt(m,1) = (MDL_t/2);
        NOxt_NEG=NOxt_NEG+1;
    else
        ECM_NOxt(m,1) = ECM_NOxt_i(m);
    end
end

s=s+1;
e(s,1)="Minimum Detection Limit (MDL) ";
e(s,2)=MDL_f;
e(s,3)=MDL_t;
e(s,4)="NA";

s=s+1;
e(s,1)="Count (<MDL)";
e(s,2)=NOxf_NEG;
e(s,3)=NOxt_NEG;

```



```

e(s,4)="NA";

s=s+1;
e(s,1)="Percentage (%)(<MDL)";
e(s,2)=NOxf_NEG/numel(ECM_NOxf_i)*100;
e(s,3)=NOxt_NEG/numel(ECM_NOxt_i)*100;
e(s,4)="NA";

E1_NOxf = 0; % Take column # 12 as ECM_ErrCode1_0x10
E2_NOxf = 0; % Take column # 14 as ECM_ErrCode2_0x10
E1_4tc = 0; % Take column # 23 as ECM_ErrCode1_0x11
E2_4tc = 0; % Take column # 25 as ECM_ErrCode2_0x11
E1_NOxt = 0; % Take column # 34 as ECM_ErrCode1_0x12
E2_NOxt = 0; % Take column # 36 as ECM_ErrCode2_0x12

for m=1:Rows_count

    if Err1_NOxf(m) > 0
        E1_NOxf = E1_NOxf+1;
    end

    if Err2_NOxf(m) > 0
        E2_NOxf = E2_NOxf+1;
    end

    if Err1_4tc(m) > 0
        E1_4tc = E1_4tc+1;
    end

    if Err2_4tc(m) > 0
        E2_4tc = E2_4tc+1;
    end

    if Err1_NOxt(m) > 0
        E1_NOxt = E1_NOxt+1;
    end

    if Err2_NOxt(m) > 0
        E2_NOxt = E2_NOxt+1;
    end
end

s=s+1;
e(s,1)="ECM_ErrCode1-Count";
e(s,2)=E1_NOxf;
e(s,3)=E1_NOxt;
e(s,4)=E1_4tc;

s=s+1;
e(s,1)="ECM_ErrCode2-Count";
e(s,2)=E2_NOxf;
e(s,3)=E2_NOxt;
e(s,4)=E2_4tc;
s=0;

```

```

toc

%%
tic
%-----
%-----
% NOxCANt and NOxCANf Data Alignment

s=1;
ee(s,1)="Lag steps";
ee(s,2)="Lag Time";
ee(s,3)="Count NH3";
ee(s,4)="Minimum NH3";
ee(s,5)="Count < Zero";
ee(s,6)="Percentage < Zero";

for lag = 0:1:lag_i
    start=lag+1;
    End = Rows_count-lag;
    ECM_NOxf_al = ECM_NOxf(start:Rows_count,1);
    ECM_NOxt_al = ECM_NOxt(1:End,1);
    ECM_NH3 = ECM_NOxt_al-ECM_NOxf_al;

    s=s+1;
    ee(s,1)=lag;
    ee(s,2)=ECM_Time(start);
    ee(s,3)=numel(ECM_NH3);
    ee(s,4)=min(ECM_NH3);
    ee(s,5)=sum(ECM_NH3(:) < 0);
    ee(s,6)=(sum(ECM_NH3(:) < 0))/(numel(ECM_NH3))*100;
end

toc
%%
%-----
%-----
% Take the values of parameters based on alignemnt
tic

Count = Rows_count;

start = lag_f+1;
End = Count-lag_f;
ECM_NOx_aligned = ECM_NOxf(start:Count,1);
ECM_NOxt_aligned = ECM_NOxt(1:End,1);

Count = Count-lag_f;
x_plot=[1:1:Count];
y1_plot=ECM_NOx_aligned+up;
y2_plot=ECM_NOxt_aligned;

plot (x_plot,y1_plot,x_plot,y2_plot)

```

```

ECM_NOx = ECM_NOx_aligned;
ECM_NH3 = ECM_NOxt_aligned-ECM_NOx;
ECM_RPM = ECM_RPM(1:End,1);
ECM_Time = ECM_Time(1:End,1);
ECM_Temp_c = ECM_Temp(1:End,1);
ECM_Temp_k = ECM_Temp_c+273.15;
ECM_speed_kmh = ECM_speed(1:End,1);
ECM_speed_ms = ECM_speed_kmh*0.277778;
ECM_Cal_Temp_celsius = ECM_Cal_Temp_celsius(1:End,1);

```

```

for cu=1:1:Count

```

```

    if ECM_NH3(cu) < MDL_NH3
        ECM_NH3(cu) = MDL_NH3/2;
    end
end

```

```

Time_Steps (1,1)=0;

```

```

for p=2:1:Count
    Time_Steps(p,1) = ECM_Time(p,1) - ECM_Time(p-1,1);
end

```

```

Distance = ECM_speed_ms.*Time_Steps;
first_value = Distance (1,1);
Distance_cum (1,1)= first_value;

```

```

for p=2:1:Count
    Distance_cum(p,1) = Distance(p,1) + first_value;

```

```

    first_value = Distance_cum(p,1);
end

```

```

for cu=1:1:Count

```

```

    if Distance_cum(cu) < 0.01
        Distance_cumulative(cu) = 0.01;
    else
        Distance_cumulative (cu) = Distance_cum (cu);
    end
end
Distance_cumulative=Distance_cumulative';

```

```

for a=1:1:Count
    g = ceil(Distance_cumulative (a)/10);
    cal_Grade(a)=Grade(g);
end

```

```

cal_Grade=cal_Grade';

```

```

r=1;
Result(r,r) = "#";
Result(r,r+1)= "Time (Second)";
Result(r,r+2)= "NH3 (ppm)";
Result(r,r+3)= "NOx (ppm)";
Result(r,r+4)= "Engine RPM";
Result(r,r+5)= "Temperature (Kelvin)";
Result(r,r+6)= "Vehicle Speed (m/s)";
Result(r,r+7)= "Time Steps (s)";
Result(r,r+8)= "Distance (m)";
Result(r,r+9)= "Distance Cumulative (m)";
Result(r,r+10)= "Grade (%)";
Result(r,r+11)= "Catalyst Temperature (Celsius)";

```

```

r=1;
Result(2:Count+1,r) =[1:1:Count];
Result(2:Count+1,r+1) =ECM_Time;
Result(2:Count+1,r+2) =ECM_NH3;
Result(2:Count+1,r+3) =ECM_NOx;
Result(2:Count+1,r+4) =ECM_RPM;
Result(2:Count+1,r+5) =ECM_Temp_k;
Result(2:Count+1,r+6) =ECM_speed_ms;
Result(2:Count+1,r+7) =Time_Steps;
Result(2:Count+1,r+8) =Distance;
Result(2:Count+1,r+9) =Distance_cum;
Result(2:Count+1,r+10) =cal_Grade;
Result(2:Count+1,r+11) =ECM_Cal_Temp_celsius;

```

```

toc
%%
% Averaging
tic

```

```

n=1;
k=0;

```

```

sum_NOx=0;
sum_NH3=0;
sum_RPM=0;
sum_Temp=0;
sum_Speed=0;
sum_grade=0;
sum_Cal_Temp=0;

```

```

u=1;
Results_Averaged(u,u)="Time (Second)";
Results_Averaged(u,u+1)="Cumulative distance";
Results_Averaged(u,u+2)="ECM NOx (ppm)";
Results_Averaged(u,u+3)="NH3 PPM (ppm)";
Results_Averaged(u,u+4)="Engine RPM";
Results_Averaged(u,u+5)="Temperature (K)";
Results_Averaged(u,u+6)="Speed (m/s)";
Results_Averaged(u,u+7)="Grade (%)";
Results_Averaged(u,u+8)="Catalyst Temperature (Celsius)";

```

```

for cc=1:Count
  if ECM_Time(cc) < n

    k=k+1;

    sum_NOx      = sum_NOx+ECM_NOx(cc);
    sum_NH3      = sum_NH3+ECM_NH3(cc);
    sum_RPM      = sum_RPM+ECM_RPM(cc);
    sum_Temp     = sum_Temp+ECM_Temp_k(cc);
    sum_Speed    = sum_Speed+ECM_speed_ms(cc);
    sum_grade    = sum_grade+cal_Grade(cc);
    sum_Cal_Temp = sum_Cal_Temp+ECM_Cal_Temp_celsius(cc);
    Cum_Dis      = Distance_cum(cc);

    ave_NOx      = sum_NOx/k;
    ave_NH3      = sum_NH3/k;
    ave_RPM      = sum_RPM/k;
    ave_Temp     = sum_Temp/k;
    ave_speed    = sum_Speed/k;
    ave_grade    = sum_grade/k;
    ave_Cal_Temp = sum_Cal_Temp/k;

    Results_Averaged(n+1,1) =n;
    Results_Averaged(n+1,2) =Cum_Dis;
    Results_Averaged(n+1,3) =ave_NOx;
    Results_Averaged(n+1,4) =ave_NH3;
    Results_Averaged(n+1,5) =ave_RPM;
    Results_Averaged(n+1,6) =ave_Temp;
    Results_Averaged(n+1,7) =ave_speed;
    Results_Averaged(n+1,8) =ave_grade;
    Results_Averaged(n+1,9) =ave_Cal_Temp;

  else
    n=n+1;
    k=1;

    sum_NOx      = ECM_NOx(cc);
    sum_NH3      = ECM_NH3(cc);
    sum_RPM      = ECM_RPM(cc);
    sum_Temp     = ECM_Temp_k(cc);
    sum_Speed    = ECM_speed_ms(cc);
    sum_grade    = cal_Grade(cc);
    sum_Cal_Temp = ECM_Cal_Temp_celsius(cc);

  end
end

toc

Route=Distance_cum (Count)
lag_f

```


Appendix B. The Data Analysis RStudio Code

```
library(readxl)
require(DescTools)
require(nlstools)
require(circlize)
require(MASS)
require(NADA)
require(dplyr)
require(pls)
require(carx)

##### Import file
setwd("~/Dropbox/Thesis/R")
dataset <- read_excel('Data.xlsx')
View(dataset)

options("scipen"=10, "digits"=2)

data.all <- dataset
data.g <- dataset[1:49,]
data.d <- dataset[50:56,]

R1 <- as.numeric(data.all$NH3_1)
R2 <- as.numeric(data.all$NH3_2)
R3 <- as.numeric(data.all$NH3_3)
NH3 <- data$NH3

##### Remove NA values from the R1, R2 and R3
R1.NA <-R1[!is.na(R1)]
R2.NA <-R2[!is.na(R2)]
R3.NA <-R3[!is.na(R3)]

##### total number of tests
Tests <- c(R1.NA,R2.NA,R3.NA)
Tests.count <- length(Tests)
print(Tests.count)

### Dodge and Matrix

dd.1 <- data.all$NH3_1[16]
dd.2 <- data.all$NH3_2[16]
dd.3 <- data.all$NH3_3[16]
dd1 <- c(dd.1,dd.2,dd.3)
dd1 <- as.numeric(dd1)
```



```
dd.1 <- data.all$NH3_1[17]
dd.2 <- data.all$NH3_2[17]
dd.3 <- data.all$NH3_3[17]
dd2 <- c(dd.1,dd.2,dd.3)
dd2 <- as.numeric(dd2)
```

```
T.test <- t.test (dd1, y=dd2, alternative = 'two.sided', paired = TRUE)
T.test$p.value
```

```
mx.1 <- data.all$NH3_1[14]
mx.2 <- data.all$NH3_2[14]
mx.3 <- data.all$NH3_3[14]
mx1 <- c(mx.1,mx.2,mx.3)
mx1 <- as.numeric(mx1)
```

```
mx.1 <- data.all$NH3_1[15]
mx.2 <- data.all$NH3_2[15]
mx.3 <- data.all$NH3_3[15]
mx2 <- c(mx.1,mx.2,mx.3)
mx2 <- as.numeric(mx2)
```

```
T.test <- t.test (mx1, y=mx2, alternative = 'two.sided', paired = TRUE)
T.test$p.value
```

```
options("scipen"=10, "digits"=3)
```

```
dd.CO1 <- data.all$CO[16]
dd.CO2 <- data.all$CO[17]
```

```
dd.NOx1 <- data.all$NOx[16]
dd.NOx2 <- data.all$NOx[17]
```

```
dd.HC1 <- data.all$HC[16]
dd.HC2 <- data.all$HC[17]
```

```
dd.CO21 <- data.all$CO2[16]
dd.CO22 <- data.all$CO2[17]
```

```
(dd.CO1-dd.CO2)*100/dd.CO1
(dd.NOx1-dd.NOx2)*100/dd.NOx1
(dd.HC1-dd.HC2)*100/dd.HC1
(dd.CO21-dd.CO22)*100/dd.CO21
```

```
#####
```

```
#####
##### Entier test fleet #####
#####
#####

##### Descriptive statistics
#### Gasoline

data <- data.g

R1 <- as.numeric(data$NH3_1)
R2 <- as.numeric(data$NH3_2)
R3 <- as.numeric(data$NH3_3)
NH3 <- data$NH3
##### Remove NA values from the R1, R2 and R3
R1.NA <- R1[!is.na(R1)]
R2.NA <- R2[!is.na(R2)]
R3.NA <- R3[!is.na(R3)]
##### total number of tests
Tests <- c(R1.NA,R2.NA,R3.NA)
Tests.count <- length(Tests)
print(Tests.count)

NH3.min <- min(NH3)
Q.25th <- quantile(NH3, 0.25)
Q.50th <- quantile(NH3, 0.50)
Q.75th <- quantile(NH3, 0.75)
NH3.max <- max(NH3)
NH3.ave <- mean(NH3)
NH3.sd <- sd(NH3)

No.NH3 <- length(NH3)
sy.NH3 <- NH3.sd/sqrt(No.NH3)
t.NH3 <- qt (0.975,No.NH3-1)

NH3.95CL<-t.NH3*sy.NH3

Upper.NH3.95 <- NH3.ave + t.NH3*sy.NH3
Lower.NH3.95 <- NH3.ave - t.NH3*sy.NH3
Lower.NH3.95
Upper.NH3.95

m <- matrix(nrow = 12, ncol = 1)
rownames(m) <- c("No. Vehicles", "Total NO. Tests", "Min NH3 rate ", "25th % NH3
rate", "Median (50th %) NH3 rate ", "75th % NH3 rate", "Max NH3 rate", "Average NH3
```

```
rate", "Standard Deviation", "95 % C.L", "Lower 95%","Upper 95%")
colnames(m) <- c("Value")
```

```
NO.vehicles <- 47
m[1,1] <-NO.vehicles
m[2,1] <-as.numeric(Tests.count)
m[3,1] <-NH3.min
m[4,1] <-Q.25th
m[5,1] <-Q.50th
m[6,1] <-Q.75th
m[7,1] <-NH3.max
m[8,1] <-NH3.ave
m[9,1] <-NH3.sd
m[10,1] <-NH3.95CL
m[11,1] <-Lower.NH3.95
m[12,1] <-Upper.NH3.95
```

```
options("scipen"=10, "digits"=2)
m
```

```
options("scipen"=10, "digits"=3)
```

```
#### Diesel
```

```
data <- data.d
```

```
R1 <- as.numeric(data$NH3_1)
R2 <- as.numeric(data$NH3_2)
R3 <- as.numeric(data$NH3_3)
NH3 <- data$NH3
##### Remove NA values from the R1, R2 and R3
R1.NA <-R1[!is.na(R1)]
R2.NA <-R2[!is.na(R2)]
R3.NA <-R3[!is.na(R3)]
##### total number of tests
Tests <- c(R1.NA,R2.NA,R3.NA)
Tests.count <- length(Tests)
print(Tests.count)
```

```
NH3.min <-min(NH3)
Q.25th <- quantile(NH3, 0.25)
Q.50th <- quantile(NH3, 0.50)
Q.75th <- quantile(NH3, 0.75)
NH3.max <-max(NH3)
NH3.ave <-mean(NH3)
```

```

NH3.sd <-sd(NH3)

No.NH3 <- length(NH3)
sy.NH3 <- NH3.sd/sqrt(No.NH3)
t.NH3 <- qt (0.975,No.NH3-1)

NH3.95CL<-t.NH3*sy.NH3

Upper.NH3.95 <- NH3.ave + t.NH3*sy.NH3
Lower.NH3.95 <- NH3.ave - t.NH3*sy.NH3
Lower.NH3.95
Upper.NH3.95

m <-matrix(nrow = 12, ncol = 1)
rownames(m) <- c("No. Vehicles","Total NO. Tests", "Min NH3 rate ", "25th % NH3
rate", "Median (50th %) NH3 rate ", "75th % NH3 rate", "Max NH3 rate", "Average NH3
rate", "Standard Deviation", "95 % C.L", "Lower 95%", "Upper 95%")
colnames(m) <- c("Value")

NO.vehicles <- 6
m[1,1] <-NO.vehicles
m[2,1] <-as.numeric(Tests.count)
m[3,1] <-NH3.min
m[4,1] <-Q.25th
m[5,1] <-Q.50th
m[6,1] <-Q.75th
m[7,1] <-NH3.max
m[8,1] <-NH3.ave
m[9,1] <-NH3.sd
m[10,1] <-NH3.95CL
m[11,1] <-Lower.NH3.95
m[12,1] <-Upper.NH3.95

options("scipen"=10, "digits"=2)
m

options("scipen"=10, "digits"=3)

#### Entire test fleet

data <- data.all

R1 <- as.numeric(data$NH3_1)
R2 <- as.numeric(data$NH3_2)
R3 <- as.numeric(data$NH3_3)

```

```

NH3 <- data$NH3
##### Remove NA values from the R1, R2 and R3
R1.NA <-R1[!is.na(R1)]
R2.NA <-R2[!is.na(R2)]
R3.NA <-R3[!is.na(R3)]
##### total number of tests
Tests <- c(R1.NA,R2.NA,R3.NA)
Tests.count <- length(Tests)
print(Tests.count)

NH3.min <-min(NH3)
Q.25th <- quantile(NH3, 0.25)
Q.50th <- quantile(NH3, 0.50)
Q.75th <- quantile(NH3, 0.75)
NH3.max <-max(NH3)
NH3.ave <-mean(NH3)
NH3.sd <-sd(NH3)

No.NH3 <- length(NH3)
sy.NH3 <- NH3.sd/sqrt(No.NH3)
t.NH3 <- qt (0.975,No.NH3-1)

NH3.95CL<-t.NH3*sy.NH3

Upper.NH3.95 <- NH3.ave + t.NH3*sy.NH3
Lower.NH3.95 <- NH3.ave - t.NH3*sy.NH3
Lower.NH3.95
Upper.NH3.95

m <-matrix(nrow = 12, ncol = 1)
rownames(m) <- c("No. Vehicles", "Total NO. Tests", "Min NH3 rate ", "25th % NH3
rate", "Median (50th %) NH3 rate ", "75th % NH3 rate", "Max NH3 rate", "Average NH3
rate", "Standard Deviation", "95 % C.L", "Lower 95%", "Upper 95%")
colnames(m) <- c("Value")

NO.vehicles <- 53
m[1,1] <-NO.vehicles
m[2,1] <-as.numeric(Tests.count)
m[3,1] <-NH3.min
m[4,1] <-Q.25th
m[5,1] <-Q.50th
m[6,1] <-Q.75th
m[7,1] <-NH3.max
m[8,1] <-NH3.ave
m[9,1] <-NH3.sd
m[10,1] <-NH3.95CL

```

```

m[11,1] <-Lower.NH3.95
m[12,1] <-Upper.NH3.95

options("scipen"=10, "digits"=2)
m

options("scipen"=10, "digits"=3)

#Box plot

NH3.f <- data.all$NH3
NH3.g <- data.g$NH3
NH3.d <- data.d$NH3

vehicles <- rep(c('Diesel','Gasoline','Test Fleet'), times =
c(length(NH3.d),length(NH3.g),length(NH3.f)))
Ammonia.v <- c(NH3.d,NH3.g,NH3.f)
ammonia <- data.frame(vehicles,Ammonia.v)

par(mfrow = c(1,2))
par(mar = c(2,5,2,1)+1)

ammonia$vehicles <- factor(ammonia$vehicles , levels=c("Diesel", "Gasoline", "Test
Fleet"))
boxplot(ammonia$Ammonia~ammonia$vehicles ,ylab = 'Ammonia emission rate,
mg/mile', xlab= "",cex.lab = 1.5, cex.axis =1.5, outline = TRUE)
boxplot(ammonia$Ammonia~ammonia$vehicles ,ylab = 'Ammonia emission rate,
mg/mile', xlab= "",cex.lab = 1.5, cex.axis =1.5, outline = FALSE)

##### min and max NH3 emissiion rates

NH3.min <-min(NH3.f)
NH3.max <-max(NH3.f)
NH3.ave <-mean(NH3.f)
NH3.sd <-sd(NH3.f)
No.NH3 <- length(NH3.f)

min<- c(data.all$Type[data.all$NH3 == NH3.min],data.all$Technology[data.all$NH3 ==
NH3.min],data.all$Mileage[data.all$NH3 == NH3.min])
max<- c(data.all$Type[data.all$NH3 == NH3.max],data.all$Technology[data.all$NH3
== NH3.max],data.all$Mileage[data.all$NH3 == NH3.max])
min
max

```

```

options("scipen"=10, "digits"=3)

NH3.w.sd <- NH3.f[NH3.f < (NH3.ave+NH3.sd)]
NH3.wo.sd <- NH3.f[NH3.f > (NH3.ave+NH3.sd)]

length(NH3.w.sd)/No.NH3*100
length(NH3.wo.sd)/No.NH3*100

NH3.ave+NH3.sd

##### Histogram NH3 averaged emission rates
par(mfrow = c(1,1))
par(mar = c(4,5,2,1)+1)

h <-hist(NH3.f, breaks = 4, ylim = c(0,50), xlim = c(0,600),main = "", xlab = 'Ammonia
emission rate, mg/mile', cex.lab = 2, cex.axis =2, col = 'darkgoldenrod1')
xfit <-seq(min(NH3.f), max(NH3.f), length = 47)
yfit<-dnorm(xfit,mean=mean(NH3.f),sd=sd(NH3.f))
yfit <- yfit*diff(h$mids[1:2])*length(NH3.f)
lines(xfit, yfit, col="blue", lwd=4)

##### NH3 emission rates without extreme values
options("scipen"=10, "digits"=4)

Q.25th <- quantile(NH3.f, 0.25)
Q.50th <- quantile(NH3.f, 0.50)
Q.75th <- quantile(NH3.f, 0.75)

IQR <- c(Q.75th-Q.25th)
edge <- Q.75th+1.5*IQR
print(edge)

NH3.extr <- NH3.f[NH3.f > edge]
NH3.extr
NH3.extr.removed <- NH3.f[NH3.f < edge]
NH3.extr.removed
length(NH3.extr.removed)
NH3.ave_Er <- mean(NH3.extr.removed)
print(NH3.ave_Er)
reduction <- (NH3.ave-NH3.ave_Er)/NH3.ave*100
print(reduction)

NH3.tier0 <- data.all$NH3[data.all$Technology == 'Tier 0']

```

```

NH3.NLEV <- data.all$NH3[data.all$Technology == 'NLEV']
NH3.tierI <- data.all$NH3[data.all$Technology == 'Tier I']
n <- length(NH3.tier0) + length(NH3.NLEV)+length(NH3.tierI)

n/NO.vehicles *100

#####
##### Variability of NH3 emission rate over the three triplicates

R1 <- as.numeric(data.all$NH3_1)
R2 <- as.numeric(data.all$NH3_2)
R3 <- as.numeric(data.all$NH3_3)

##### Remove NA values from the R1, R2 and R3
R1.NA <-R1[!is.na(R1)]
R2.NA <-R2[!is.na(R2)]
R3.NA <-R3[!is.na(R3)]

options("scipen"=10, "digits"=4)
mean(R1.NA)
mean(R2.NA)
mean(R3.NA)

(mean(R1.NA)-mean(R2.NA))*100/mean(R1.NA)
(mean(R1.NA)-mean(R3.NA))*100/mean(R1.NA)

par(mfrow = c(1,2))

TriPLICATE <- rep(c('First Lap','Second Lap','Third Lap'), times =
c(length(R1.NA),length(R2.NA),length(R3.NA)))
NH3.value <- c(R1.NA,R2.NA,R3.NA)

boxplot(NH3.value~TriPLICATE,ylab = 'Ammonia emission rate, mg/mile', xlab= "",cex.lab
= 2, cex.axis =2)
boxplot(NH3.value~TriPLICATE,ylab = 'Ammonia emission rate, mg/mile', xlab= "",cex.lab
= 2, cex.axis =2, outline = FALSE)
par(mfrow = c(1,1))

ANOVA.triplicate <- aov(NH3.value~TriPLICATE)
summary(ANOVA.triplicate)
PostHocTest(ANOVA.triplicate,method='bonf', conf.level = 0.95)

par(mar = c(2,10,2,2)+1)
TUKEY <- TukeyHSD(x=ANOVA.triplicate,conf.level=0.95)
TUKEY

```



```

plot(TUKEY , las=1 , col="brown")

t.test (R1.NA, y=R2.NA, alternative = 'two.sided', paired = FALSE)
t.test (R1.NA, y=R3.NA, alternative = 'two.sided', paired = FALSE)
t.test (R2.NA, y=R3.NA, alternative = 'two.sided', paired = FALSE)

##### Comparison with other studies

This_Study <- NH3.f
Previous_Studies <-
c(53.1,24.1,98.1,53.0,78.8,151.2,15.1,54.0,27.7,20.7,81.5,49.9,59.5,74.0,49.9,59.5,37.5,4
5.1,14.5,84.5)

Study <- rep(c("This Study", "Previous Studies"), times
=c(length(NH3),length(Previous_Studies)))
Rates <- c(This_Study,Previous_Studies)
ANOVA.Comp <- aov(Rates~Study)
summary(ANOVA.Comp)
PostHocTest(ANOVA.Comp,method='bonf')

boxplot(Rates~Study,ylab = 'Ammonia emission rate, mg/mile', xlab= "",cex.lab = 1.5,
cex.axis =1.5, outline =FALSE)

T.test<-t.test (This_Study, y=Previous_Studies, alternative = 'two.sided', paired =
FALSE)
T.test$p.value

ave.Pstd<-mean (Previous_Studies)
n.Pstd <- length(Previous_Studies)
sd.Pstd <- sd(Previous_Studies)
sy.Pstd <- sd.Pstd/sqrt(n.Pstd)
t.Pstd <- (ave.Pstd-mean(This_Study))/sy.Pstd

level.95.lower <- ave.Pstd - (qt (0.975,n.Pstd-1) * sy.Pstd)
level.95.up <- ave.Pstd + (qt (0.975,n.Pstd-1) * sy.Pstd)

level.95.lower
level.95.up

##### Driver
par(mfrow = c(1,1))

ow <- data.all$NH3[data.all$Driver== 'O']
res <- data.all$NH3[data.all$Driver == 'R']

```

```
length(ow)
length(res)
length(ow)+length(res)
```

```
t.test (ow, y=res, alternative = 'two.sided', paired = FALSE)
dri <- rep(c("Owner", " Researcher"), times =c(length(ow),length(res)))
```

```
par(mfrow = c(1,2))
NH3.driver <- c(ow, res)
boxplot(NH3.driver~dri,ylab = 'Ammonia emission rate, mg/mile', xlab= ",cex.lab = 1.5,
cex.axis =1.5, outline =TRUE)
boxplot(NH3.driver~dri,ylab = 'Ammonia emission rate, mg/mile', xlab= ",cex.lab = 1.5,
cex.axis =1.5, outline =FALSE)
```

```
##### Fuel
```

```
par(mfrow = c(1,1))
```

```
Gas <- data.all$NH3[data.all$Fuel== 'G']
Dis <- data.all$NH3[data.all$Fuel == 'D']
```

```
length(Gas)
length(Dis)
length(Gas)+length(Dis)
```

```
t.test (Gas, y=Dis, alternative = 'two.sided', paired = FALSE)
```

```
par(mfrow = c(1,2))
fuel <- rep(c("Gasoline", " Diesel"), times =c(length(Gas),length(Dis)))
NH3.fuel <- c(Gas, Dis)
boxplot(NH3.fuel~fuel,ylab = 'Ammonia emission rate, mg/mile', xlab= ",cex.lab = 1.5,
cex.axis =1.5, outline =TRUE)
boxplot(NH3.fuel~fuel,ylab = 'Ammonia emission rate, mg/mile', xlab= ",cex.lab = 1.5,
cex.axis =1.5, outline =FALSE)
```

```
#####
#####
##### Gasoline Motor Vehicles#####
#####
#####
##### Tier
```

```

par(mfrow = c(1,1))

Tier0 <- data.g$NH3[data.g$Technology == 'Tier 0']
Tier1 <- data.g$NH3[data.g$Technology == 'Tier I']
NLEV <- data.g$NH3[data.g$Technology == 'NLEV']
Tier2 <- data.g$NH3[data.g$Technology == 'Tier II']
Tier3 <- data.g$NH3[data.g$Technology == 'Tier III']

Tier0
Tier1
NLEV
Tier2
Tier3

par(mar = c(2,5,2,1)+1)
Tier <- rep(c('Tier 0','Tier I','NLEV','Tier II','Tier III'), times =
c(length(Tier0),length(Tier1),length(NLEV),length(Tier2),length(Tier3)))
Ammonia <- c(Tier0,Tier1,NLEV,Tier2,Tier3)

da <- data.frame(Tier,Ammonia)
da$Tier <- factor(da$Tier , levels=c("Tier 0", "Tier I", "NLEV", "Tier II", "Tier III"))
boxplot(da$Ammonia~da$Tier ,ylab = 'Ammonia emission rate, mg/mile', xlab=
",cex.lab = 1.5, cex.axis =1.5, data=da)

options("scipen"=10, "digits"=5)

mean(Tier0)
mean(Tier1)
mean(NLEV)
mean(Tier2)
mean(Tier3)

ANOVA.Ammonia <- aov(da$Ammonia~da$Tier)
summary(ANOVA.Ammonia)
PostHocTest(ANOVA.Ammonia,method='bonf')

TUKEY <- TukeyHSD(x=ANOVA.Ammonia,conf.level=0.95)
TUKEY
plot(TUKEY , las=1 , col="black")

### CO
par(mfrow = c(1,1))

Tier0.CO <- data.g$CO[data.g$Technology == 'Tier 0']
Tier1.CO <- data.g$CO[data.g$Technology == 'Tier I']

```

```

NLEV.CO <- data.g$CO[data.g$Technology == 'NLEV']
Tier2.CO <- data.g$CO[data.g$Technology == 'Tier II']
Tier3.CO <- data.g$CO[data.g$Technology == 'Tier III']

par(mar = c(2,5,2,1)+1)
Tier.CO <- rep(c('Tier 0','Tier I','NLEV','Tier II','Tier III'), times =
c(length(Tier0.CO),length(Tier1.CO),length(NLEV.CO),length(Tier2.CO),length(Tier3.
CO)))
con.CO <- c(Tier0.CO,Tier1.CO,NLEV.CO,Tier2.CO,Tier3.CO)

da.CO <- data.frame(Tier.CO,con.CO)
da.CO$Tier.CO <- factor(da.CO$Tier.CO , levels=c("Tier 0","Tier I","NLEV","Tier
II","Tier III"))
boxplot(da.CO$con.CO~da.CO$Tier.CO ,ylab = 'CO emission rate, mg/mile', xlab=
",cex.lab = 1.5, cex.axis =1.5, data=da)

```

NOX

```

Tier0.NOx <- data.g$NOx[data.g$Technology == 'Tier 0']
Tier1.NOx <- data.g$NOx[data.g$Technology == 'Tier I']
NLEV.NOx <- data.g$NOx[data.g$Technology == 'NLEV']
Tier2.NOx <- data.g$NOx[data.g$Technology == 'Tier II']
Tier3.NOx <- data.g$NOx[data.g$Technology == 'Tier III']

par(mar = c(2,5,2,1)+1)
Tier.NOx <- rep(c('Tier 0','Tier I','NLEV','Tier II','Tier III'), times =
c(length(Tier0.NOx),length(Tier1.NOx),length(NLEV.NOx),length(Tier2.NOx),length(T
ier3.NOx)))
con.NOx <- c(Tier0.NOx,Tier1.NOx,NLEV.NOx,Tier2.NOx,Tier3.NOx)

da.NOX <- data.frame(Tier.NOx,con.NOx)
da.NOX$Tier.NOx <- factor(da.NOX$Tier.NOx , levels=c("Tier 0","Tier
I","NLEV","Tier II","Tier III"))
boxplot(da.NOX$con.NOx~da.NOX$Tier.NOx ,ylab = 'NOx emission rate, mg/mile',
xlab= ",cex.lab = 1.5, cex.axis =1.5, data=da)

```

Mileage

```

Tier0.mi <- data.g$Mileage[data.g$Technology == 'Tier 0']
Tier1.mi <- data.g$Mileage[data.g$Technology == 'Tier I']
NLEV.mi <- data.g$Mileage[data.g$Technology == 'NLEV']
Tier2.mi <- data.g$Mileage[data.g$Technology == 'Tier II']
Tier3.mi <- data.g$Mileage[data.g$Technology == 'Tier III']

par(mar = c(2,5,2,1)+1)
Tier.mi <- rep(c('Tier 0','Tier I','NLEV','Tier II','Tier III'), times =

```

```
c(length(Tier0.mi),length(Tier1.mi),length(NLEV.mi),length(Tier2.mi),length(Tier3.mi))
)
mi <- c(Tier0.mi,Tier1.mi,NLEV.mi,Tier2.mi,Tier3.mi)
```

```
da.mi <- data.frame(Tier.mi,mi)
da.mi$Tier.mi <- factor(da.mi$Tier.mi , levels=c("Tier 0","Tier I","NLEV","Tier
II","Tier III"))
boxplot(da.mi$mi~da.mi$Tier.mi ,ylab = 'Mileage, miles', xlab= ",cex.lab = 1.5, cex.axis
=1.5, data=da)
```

```
### CO2
```

```
Tier0.CO2 <- data.g$CO2[data.g$Technology == 'Tier 0']
Tier1.CO2 <- data.g$CO2[data.g$Technology == 'Tier I']
NLEV.CO2 <- data.g$CO2[data.g$Technology == 'NLEV']
Tier2.CO2 <- data.g$CO2[data.g$Technology == 'Tier II']
Tier3.CO2 <- data.g$CO2[data.g$Technology == 'Tier III']
```

```
par(mar = c(2,5,2,1)+1)
Tier.CO2 <- rep(c('Tier 0','Tier I','NLEV','Tier II','Tier III'), times =
c(length(Tier0.CO2),length(Tier1.CO2),length(NLEV.CO2),length(Tier2.CO2),length(Ti
er3.CO2)))
con.CO2 <- c(Tier0.CO2,Tier1.CO2,NLEV.CO2,Tier2.CO2,Tier3.CO2)
```

```
da.CO2 <- data.frame(Tier.CO2,con.CO2)
da.CO2$Tier.CO2 <- factor(da.CO2$Tier.CO2 , levels=c("Tier 0","Tier I","NLEV","Tier
II","Tier III"))
boxplot(da.CO2$con.CO2~da.CO2$Tier.CO2 ,ylab = 'CO2 emission rate, g/mile', xlab=
",cex.lab = 1.5, cex.axis =1.5, data=da)
```

```
### HC
```

```
Tier0.HC <- data.g$HC[data.g$Technology == 'Tier 0']
Tier1.HC <- data.g$HC[data.g$Technology == 'Tier I']
NLEV.HC <- data.g$HC[data.g$Technology == 'NLEV']
Tier2.HC <- data.g$HC[data.g$Technology == 'Tier II']
Tier3.HC <- data.g$HC[data.g$Technology == 'Tier III']
```

```
par(mar = c(2,5,2,1)+1)
Tier.HC<- rep(c('Tier 0','Tier I','NLEV','Tier II','Tier III'), times =
c(length(Tier0.HC),length(Tier1.HC),length(NLEV.HC),length(Tier2.HC),length(Tier3.
HC)))
con.HC <- c(Tier0.HC,Tier1.HC,NLEV.HC,Tier2.HC,Tier3.HC)
```

```
da.HC <- data.frame(Tier.HC,con.HC)
```

```
da.HC$Tier.HC <- factor(da.HC$Tier.HC , levels=c("Tier 0", "Tier I", "NLEV", "Tier
II", "Tier III"))
boxplot(da.HC$con.HC~da.HC$Tier.HC ,ylab = 'HC emission rate, g/mile', xlab=
",cex.lab = 1.5, cex.axis =1.5, data=da)
```

```
dev.new ()
par(mfrow = c(1,4))
par(mar = c(2,3.5,2,0.0)+1)
n=1.7
boxplot(da.CO$con.CO~da.CO$Tier.CO ,ylab = 'CO emission rate, mg/mile', xlab=
",cex.lab =n , cex.axis =n, data=da)
boxplot(da.NOX$con.NOx~da.NOX$Tier.NOx ,ylab = 'NOx emission rate, mg/mile',
xlab= ",cex.lab = n, cex.axis =n, data=da)
boxplot(da.CO2$con.CO2~da.CO2$Tier.CO2 ,ylab = 'CO2 emission rate, g/mile', xlab=
",cex.lab = n, cex.axis =n, data=da)
boxplot(da.mi$mi~da.mi$Tier.mi ,ylab = 'Mileage, miles', xlab= ",cex.lab = n, cex.axis
=n, data=da)
```

```
dev.off ()
```

```
##### Type
```

```
par(mfrow = c(1,1))
PC <- data.g$NH3[data.g$Type == 'PC']
MPV <- data.g$NH3[data.g$Type == 'MPV']
LDT <- data.g$NH3[data.g$Type == 'LDT']
```

```
PC
MPV
LDT
```

```
mean(PC, na.rm= TRUE)
mean(MPV)
mean(LDT)
```

```
Type <- rep(c("PC", "MPV", "LDT"), times =c(length(PC),length(MPV),length(LDT)))
NH3.Type <- c( PC,MPV, LDT)
ANOVA.comp <- aov(NH3.Type~Type)
summary(ANOVA.comp)
```

```
PostHocTest(ANOVA.comp,method='bonf')
```

```
boxplot(NH3.Type~Type,ylab = 'Ammonia emission rate, mg/mile', xlab= ",cex.lab =
1.5, cex.axis =1.5, outline =FALSE)
```

```
TUKEY <- TukeyHSD(x=ANOVA.comp,conf.level=0.95)
TUKEY
```

```
plot(TUKEY , las=1 , col="black")
```

```
PC.m <- data$CO2[data$Type == 'PC']
MPV.m <- data$CO2[data$Type == 'MPV']
LDT.m <- data$CO2[data$Type == 'LDT']
NH3.m <- c( PC.m,MPV.m, LDT.m)
boxplot(NH3.m~Type,ylab = 'Ammonia emission rate, mg/mile', xlab= ",cex.lab = 1.5,
cex.axis =1.5, outline =FALSE)
```

```
##### Make
```

```
par(mfrow = c(1,1))
```

```
BMW <- data$NH3[data$Make == 'BMW']
Chevrolet <- data$NH3[data$Make == 'Chevrolet']
Chrysler <- data$NH3[data$Make == 'Chrysler']
Dodge<- data$NH3[data$Make == 'Dodge']
Ford<- data$NH3[data$Make == 'Ford']
GMC<- data$NH3[data$Make == 'GMC']
Honda<- data$NH3[data$Make == 'Honda']
Hyundai<- data$NH3[data$Make == 'Hyundai']
Jeep<- data$NH3[data$Make == 'Jeep']
Kia<- data$NH3[data$Make == 'Kia']
Mercedes_Benz <- data$NH3[data$Make == 'Mercedes Benz']
Nissan<- data$NH3[data$Make == 'Nissan']
Pontiac<- data$NH3[data$Make == 'Pontiac']
Subaru<- data$NH3[data$Make == 'Subaru']
Toyota<- data$NH3[data$Make == 'Toyota']
```

```
Make <- rep(c("BMW", "Chevrolet","Chrysler","Dodge", "Ford","GMC","Honda",
"Hyundai","Jeep","Kia",
"Mercedes_Benz","Nissan", "Pontiac","Subaru","Toyota"),
times
=c(length(BMW),length(Chevrolet),length(Chrysler),length(Dodge),length(Ford),length(
GMC),
length(Honda),length(Hyundai),length(Jeep),length(Kia),length(Mercedes_Benz),length(
Nissan),
length(Pontiac),length(Subaru),length(Toyota)))
NH3.Make <- c(BMW,Chevrolet,
Chrysler,Dodge,Ford,GMC,Honda,Hyundai,Jeep,Kia,Mercedes_Benz,Nissan,Pontiac,Su
baru,Toyota)
```

```

ANOVA.comp <- aov(NH3.Make~(Make))
summary(ANOVA.comp)

PostHocTest(ANOVA.comp,method='bonf')

boxplot(NH3.Make~Make,ylab = 'Ammonia emission rate, mg/mile', xlab= '',cex.lab =
1.5, cex.axis =1.5, outline =FALSE)

##### corrolation With mileage

par(mfrow = c(1,1))
par(mar = c(5,5,0,4)+1)

cor.test(data$Mileage,NH3)
plot(data$Mileage,NH3, xlab= 'Mileage', ylab = 'NH3, mg/mile',cex.lab = 1.5, cex.axis
=1.5)
lm.mi <-lm(NH3 ~ data$Mileage)
abline(lm.mi, col='red')
Cls <-predict(lm.mi, interval ='confidence', level = 0.95)
Cls <- data.frame(Cls)
Cls$mi <- data$Mileage

lines (Cls$mi)#, Cls$lwr, lty = 2)
lines (Cls$mi, Cls$upr, lty = 1)

legend(x=25000,y=350, legend = c("r = 0.67 "),cex=1.5)

cor.test(data$Engine,NH3)
plot(data$Engine,NH3,xlab= 'Engine Displacement, L', ylab = 'NH3, mg/mile',cex.lab =
1.5, cex.axis =1.5)
abline(lm(NH3 ~ data$Engine), col='red')
legend(x=2,y=380, legend = c("r = 0.51 "),cex=1.5)

cor.test(data$Year,NH3)
plot(data$Year,NH3,xlab= 'Model Year', ylab = 'NH3, mg/mile',cex.lab = 1.5, cex.axis
=1.5)
abline(lm(NH3 ~ data$Year), col='red')
legend(x=2006,y=320, legend = c("r = - 0.61 "),cex=1.5)

cor.test(data$GVWR,NH3)
plot(data$GVWR, NH3,xlab= 'Gross Vehicle Weight Rating, lbs', ylab = 'NH3,
mg/mile',cex.lab = 1.5, cex.axis =1.5)
abline(lm(NH3 ~ data$GVWR), col='red')
legend(x=2800,y=380, legend = c("r = 0.30 "),cex=1.5)

```



```

cor.test(data$Cylinder,NH3)
plot(data$Cylinder,NH3,xlab= 'Cylinder', ylab = 'NH3, mg/mile',cex.lab = 1.5, cex.axis
=1.5)
abline(lm(NH3 ~ data$Cylinder), col='red')
legend(x=4.2,y=350, legend = c("r = 0.49 "),cex=1.5)

```

```

par(mfrow = c(1,1))

```

```

##### corrolation Gases

```

```

dev.new ()
par(mfrow = c(3,3))
par(mar = c(3,4,0,0)+1)

```

```

cor.test(data$Mileage,NH3)
plot(data$Mileage,NH3, xlab= 'Mileage, mile', ylab = 'NH3, mg/mile',cex.lab = 1.5,
cex.axis =1.5)
abline(lm(NH3 ~ data$Mileage), col='red')
legend(x=25000,y=350, legend = c("r = 0.67 "),cex=1.5)

```

```

cor.test(data$Engine ,NH3)
plot(data$Engine,NH3,xlab= 'Engine Displacement, L', ylab = 'NH3, mg/mile',cex.lab =
1.5, cex.axis =1.5)
abline(lm(NH3 ~ data$Engine ), col='red')
legend(x=2,y=350, legend = c("r = 0.51 "),cex=1.5)

```

```

cor.test(data$Year,NH3)
plot(data$Year,NH3,xlab= 'Model Year', ylab = 'NH3, mg/mile',cex.lab = 1.5, cex.axis
=1.5)
abline(lm(NH3 ~ data$Year), col='red')
legend(x=2013,y=350, legend = c("r = - 0.61 "),cex=1.5)

```

```

cor.test(data$GVWR,NH3)
plot(data$GVWR,NH3,xlab= 'Gross Vehicle Weight Rating, lbs', ylab = 'NH3,
mg/mile',cex.lab = 1.5, cex.axis =1.5)
abline(lm(NH3 ~ data$GVWR), col='red')
legend(x=3300,y=400, legend = c("r = 0.30 "),cex=1.5)

```

```

cor.test(data$Cylinder,NH3)
plot(data$Cylinder,NH3,xlab= 'Cylinder', ylab = 'NH3, mg/mile',cex.lab = 1.5, cex.axis
=1.5)
abline(lm(NH3 ~ data$Cylinder), col='red')
legend(x=4.2,y=350, legend = c("r = 0.49 "),cex=1.5)

```

```

cor.test(data$NOx,NH3)
plot(data$NOx,NH3, xlab= 'NOx, mg/mile', ylab = 'NH3, mg/mile',cex.lab = 1.5, cex.axis
=1.5)
abline(lm(NH3 ~ data$NOx), col='red')
legend(x=25,y=380, legend = c("r = 0.88 "),cex=1.5)

```

```

cor.test(data$CO,NH3)
plot(data$`CO`,NH3,xlab= 'CO, mg/mile', ylab = 'NH3, mg/mile',cex.lab = 1.5, cex.axis
=1.5)
abline(lm(NH3 ~ data$`CO`), col='red')
legend(x=250,y=400, legend = c("r = 0.80 "),cex=1.5)

```

```

cor.test(data$HC,NH3)
plot(data$HC,NH3,xlab= 'HC, mg/mile', ylab = 'NH3, mg/mile',cex.lab = 1.5, cex.axis
=1.5)
abline(lm(NH3 ~ data$HC), col='red')
legend(x=5000,y=350, legend = c("r = 0.36 "),cex=1.5)

```

```

cor.test(data$CO2,NH3)
plot(data$CO2,NH3,xlab= 'CO2, g/mile', ylab = 'NH3, mg/mile',cex.lab = 1.5, cex.axis
=1.5)
abline(lm(NH3 ~ data$CO2), col='red')
legend(x=150,y=350, legend = c("r = 0.71 "),cex=1.5)

```

```
dev.off()
```

```
##### Diesel
```

```

NH3.d
No.cat <- NH3.d[1:2]
DOC <- NH3.d[3:5]
DOC_SCR <- NH3.d[6:7]

```

```

cat <- rep(c("No Catalyst", "DOC", "DOC & SCR"), times
=c(length(No.cat),length(DOC), length(DOC_SCR)))
NH3.cat <- c(No.cat, DOC,DOC_SCR)
ammonia.cat <- data.frame(cat,NH3.cat)
ammonia.cat$cat <- factor(ammonia.cat$cat, levels=c("No Catalyst", "DOC", "DOC &
SCR"))

```

```

boxplot(ammonia.cat$NH3.cat~ammonia.cat$cat,ylab = 'Ammonia emission rate,
mg/mile', xlab= "",cex.lab = 1.5, cex.axis =1.5, outline =FALSE)

```

```
##### corrolation -- diesel
```

```
dev.new ()
par(mfrow = c(3,3))
par(mar = c(3,4,0,0)+1)
data <- data.d
View(data)
NH3 = NH3.d
```

```
cor.test(data$Mileage,NH3)
plot(data$Mileage,NH3, xlab= 'Mileage, mile', ylab = 'NH3, mg/mile',cex.lab = 1.5,
cex.axis =1.5)
abline(lm(NH3 ~ data$Mileage), col='red')
legend(x=50000,y=15, legend = c("r = 0.76 "),cex=1.5)
```

```
cor.test(data$Displacement,NH3)
plot(data$Displacement,NH3,xlab= 'Engine Displacement, L', ylab = 'NH3,
mg/mile',cex.lab = 1.5, cex.axis =1.5)
abline(lm(NH3 ~ data$Displacement ), col='red')
legend(x=3,y=17, legend = c("r = 0.0.56 "),cex=1.5)
```

```
cor.test(data$Year,NH3)
plot(data$Year,NH3,xlab= 'Model Year', ylab = 'NH3, mg/mile',cex.lab = 1.5, cex.axis
=1.5)
abline(lm(NH3 ~ data$Year), col='red')
legend(x=2010,y=15, legend = c("r = - 0.79 "),cex=1.5)
```

```
cor.test(data$GVWR,NH3)
plot(data$GVWR,NH3,xlab= 'Gross Vehicle Weight Rating, lbs', ylab = 'NH3,
mg/mile',cex.lab = 1.5, cex.axis =1.5)
abline(lm(NH3 ~ data$GVWR), col='red')
legend(x=5000,y=15, legend = c("r = 0.46 "),cex=1.5)
```

```
cor.test(data$Cylinder,NH3)
plot(data$Cylinder,NH3,xlab= 'Cylinder', ylab = 'NH3, mg/mile',cex.lab = 1.5, cex.axis
=1.5)
abline(lm(NH3 ~ data$Cylinder), col='red')
legend(x=4.5,y=15, legend = c("r = 0.85 "),cex=1.5)
```

```
cor.test(data$NOx,NH3)
plot(data$NOx,NH3, xlab= 'NOx, mg/mile', ylab = 'NH3, mg/mile',cex.lab = 1.5, cex.axis
=1.5)
abline(lm(NH3 ~ data$NOx), col='red')
legend(x=1000,y=15, legend = c("r = 0.87 "),cex=1.5)
```

```
cor.test(data$CO,NH3)
plot(data$`CO`,NH3,xlab= 'CO, mg/mile', ylab = 'NH3, mg/mile',cex.lab = 1.5, cex.axis
=1.5)
abline(lm(NH3 ~ data$`CO`), col='red')
legend(x=500,y=15, legend = c("r = 0.94 "),cex=1.5)

cor.test(data$HC,NH3)
plot(data$HC,NH3,xlab= 'HC, mg/mile', ylab = 'NH3, mg/mile',cex.lab = 1.5, cex.axis
=1.5)
abline(lm(NH3 ~ data$HC), col='red')
legend(x=150,y=15, legend = c("r = 0.48 "),cex=1.5)

cor.test(data$CO2,NH3)
plot(data$CO2,NH3,xlab= 'CO2, g/mile', ylab = 'NH3, mg/mile',cex.lab = 1.5, cex.axis
=1.5)
abline(lm(NH3 ~ data$CO2), col='red')
legend(x=450,y=15, legend = c("r = 0.74 "),cex=1.5)

dev.off()
```

Appendix C. Detailed Vehicles Specific Information

Driver	Type	Make	Model	Year	Emission Standard Tier	Engine Displacement (L)	Cylinder	GVWR (lbs.)
R	LDT	Chevrolet	CK 1500	1993	Tier 0	5.7	8	6400
R	PC	Subaru	Legacy	1995	Tier I	2.2	4	4245
O	LDT	Ford	Ranger XLT	1997	Tier I	2.3	4	4740
R	MPV	Pontiac	Trans Sport	1998	Tier I	3.4	6	5357
R	MPV	GMC	Suburban	1999	Tier I	5.7	8	7300
O	PC	Honda	Accord	2000	Tier I	3	6	4235
O	PC	Mercedes Benz	SLK 230	2000	Tier I	2.3	4	3485
O	MPV	Chevrolet	Tahoe	2002	NLEV	5.3	8	6900
O	MPV	Honda	CR-V	2003	NLEV	2.4	4	4320
R	PC	Nissan	Maxima	2003	NLEV	3.5	6	4295
O	PC	BMW	325i	2003	NLEV	2.5	6	4365
O	PC	Hyundai	Elantra	2004	Tier II	2	4	3880
O	PC	Subaru	Forester	2005	Tier II	2.5	4	4150
O	PC	Toyota	Matrix XR	2006	Tier II	1.8	4	3845
O								
O	LDT	Dodge	RAM 1500	2007	Tier II	5.7	8	6700
O								
O	MPV	Nissan	Pathfinder	2008	Tier II	4	6	6113
O	PC	Nissan	Sentra	2008	Tier II	2	4	3920
O	MPV	Chrysler	Grand Caravan	2009	Tier II	3.3	6	6050
O	MPV	Honda	Odyssey	2009	Tier II	3.5	6	5941
R	MPV	Chrysler	Town & Country	2010	Tier II	3.8	6	6050
R	PC	Hyundai	Sonata	2011	Tier II	2.4	4	4299
R	LDT	Chevrolet	Colorado LT	2011	Tier II	3.7	5	5300
O	PC	Chevrolet	Malibu Lt	2011	Tier II	2.4	4	4419
O	PC	Subaru	Legacy	2012	Tier II	2.5	4	4435
O	PC	Nissan	Versa	2012	Tier II	1.6	4	3388
O	MPV	Kia	Sedona	2012	Tier II	3.5	6	5853
O	LDT	Ford	F 150	2012	Tier II	5	8	7350
R	PC	Chevrolet	Impala	2012	Tier II	3.6	6	4564

Driver	Type	Make	Model	Year	Emission Standard Tier	Engine Displacement (L)	Cylinder	GVWR (lbs.)
R	MPV	Chevrolet	Traverse	2012	Tier II	3.6	6	6459
R	LDT	Chevrolet	Colorado LT	2012	Tier II	2.9	4	5000
R	MPV	Toyota	Highlander	2013	Tier II	3.5	6	6000
R	LDT	Toyota	Tacoma	2013	Tier II	4	6	5500
R	LDT	Chevrolet	Silverado	2013	Tier II	4.8	8	6400
R	MPV	Toyota	FJ Cruiser	2013	Tier II	4	6	5570
O	PC	Chrysler	200 S	2014	Tier II	2.4	4	4600
O	MPV	Nissan	Quest	2015	Tier II	3.5	6	5818
R	LDT	Chevrolet	Colorado	2015	Tier II	2.5	4	5400
O	PC	Toyota	Corolla	2015	Tier II	1.8	4	3820
R	MPV	Chevrolet	Equinox	2015	Tier II	2.4	4	5070
O	MPV	Jeep	Wrangler	2016	Tier II	3.6	6	4900
O	LDT	Chevrolet	Colorado	2016	Tier II	3.6	6	6000
O	LDT	Toyota	Tacoma	2018	Tier III	3.5	6	5600
R	PC	Subaru	Legacy	2018	Tier III	2.5	4	4519
O	MPV	Subaru	Cross Trek	2019	Tier III	2	4	4343
O	LDT	Toyota	Tacoma	2019	Tier III	3.5	6	5600
O	MPV	Chrysler	Pacifica	2019	Tier III	3.6	6	6055
O	LDT	Ford	Ranger	2020	Tier III	2.3	4	6050
O	LDT	Ford	F5300-Stock	1999	Tier I	7.3	8	9200
O	LDT	Ford	F5300-Fuel Economy	1999	Tier I	7.3	8	9200
R	LDT	Dodge	RAM 2500	2003	NLEV	5.9	6	4083
O	PC	Volkswagen	Jetta	2006	Tier II	2	4	4256
R	LDT	Dodge	RAM 2500	2008	Tier II	6.7	6	8500
R	LDT	Dodge	RAM 2500	2013	Tier II	6.7	6	5482

Appendix D. Step-Wise Regression Analysis

- Gasoline Motor vehicles:

Start: AIC=397.96

NH3 ~ 1

	Df	Sum of Sq	RSS	AIC
+ NOx	1	277255	78984	333.68
+ CO	1	229866	126373	354.36
+ Mileage	1	199116	157123	363.95
+ CO ₂	1	178318	177921	369.42
+ Year	1	154574	201665	374.93
+ Engine	1	91827	264412	386.85
+ Cylinder	1	78824	277415	388.96
none>			356239	397.96

Step: AIC=333.68

NH3 ~ NOx

	Df	Sum of Sq	RSS	AIC
+ Mileage	1	21917.5	57067	321.38
+ CO	1	13868.5	65116	327.19
+ Year	1	5286.7	73697	332.64
+ CO ₂	1	3789.2	75195	333.52
<none>			78984	333.68
+ Cylinder	1	614.2	78370	335.34
+ Engine	1	121.2	78863	335.62

Step: AIC=321.38

NH3 ~ NOx + Mileage

	Df	Sum of Sq	RSS	AIC
+ CO	1	7783.3	49283	316.93
<none>			57067	321.38
+ Year	1	1317.6	55749	322.35
+ CO ₂	1	1263.3	55803	322.4
+ Cylinder	1	782.1	56284	322.78
+ Engine	1	463.7	56603	323.02

Step: AIC=316.93

NH3 ~ NOx + Mileage + CO

	Df	Sum of Sq	RSS	AIC
<none>			49283	316.93
+ CO ₂	1	886.67	48397	318.13
+ Year	1	838.7	48445	318.18
+ Cylinder	1	313.61	48970	318.65
+ Engine	1	65.12	49218	318.87

Call:

lm(formula = NH3 ~ NOx + Mileage + CO, data = dataset)

Coefficients:

(Intercept)	NOx	Mileage	CO
1.852423	0.360875	0.000313	0.008126

- **Diesel Motor vehicles:**

Start: AIC=28

NH3 ~ 1

	Df	Sum of Sq	RSS	AIC
+ CO	1	256.441183	31.973979	14.633086
+ NOx	1	218.79528	69.619882	20.07998
+ Cylinder	1	207.9625	80.452662	21.092312
+ Year	1	181.575084	106.840078	23.077961
+ Mileage	1	164.985612	123.429551	24.088323
+ CO ₂	1	159.233324	129.181838	24.407176
+ Displacement	1	89.962427	198.452735	27.412486
+ <none>			288.415162	28.029436
+ HC	1	67.636068	220.779094	28.158767
+ GVWR	1	59.838642	228.57652	28.401726

Step: AIC=15

NH3 ~ CO

	Df	Sum of Sq	RSS	AIC
<none>			31.973979	14.633086
+ GVWR	1	5.7179137	26.256065	15.253908
+ Cylinder	1	3.8408356	28.133143	15.737267
+ Displacement	1	3.2136946	28.760284	15.891597
+ Mileage	1	2.0360569	29.937922	16.172511
+ NOx	1	0.7389953	31.234984	16.4694
+ CO ₂	1	0.7346	31.239379	16.470385
+ HC	1	0.0674282	31.906551	16.618308
+ Year	1	0.0340192	31.93996	16.625634

Call:

lm(formula = NH3 ~ CO, data = dataset.model)

Coefficients:

(Intercept) CO
4.70851 0.00507