ABSTRACT

Title of Thesis:	ANALYSIS OF TEMPERATURE AND SPECIFIC
	HUMIDITY DEPENDENCE OF MOVES OUTPUT
	FOR MOTOR VEHICLE EMISSIONS
	Sai Sreedhar Varada, Master of Science, 2017
Thesis directed by:	Professor Sheryl Ehrman
	Department of Chemical and Biomolecular
	Engineering

Air pollution and climate change are some of the important consequences of modern industrialization. In a large developed country like the United States of America, these changes have a greater impact due to the country's high energy demands. This project focuses on air pollution caused by emissions released by combustion of fuels in automobile engines. The mobile emissions inventory for the National Emissions Inventory (NEI) is based on the estimates from MOtor Vehicle Emissions Simulator (MOVES), which is a software program used to model automobile emissions. Analysis of in-situ roadside monitor observations shows that emissions from automobile sources, especially CO and NOx emissions are correlated with ambient temperature and humidity. In this research, I compared the MOVES model output dependence on ambient temperature and specific humidity to observations from an Air Quality Monitoring Site which is located in Maryland on Interstate-95 (I-95) and adjusted the model output to nearly match the observations. The adjusted model was used to obtain emissions estimates of another month (here, Nov 2014) and these estimated ratios nearly matched with the observations.

ANALYSIS OF TEMPERATURE AND SPECIFIC HUMIDITY DEPENDENCE OF MOVES OUTPUT FOR MOTOR VEHICLE EMISSIONS

by

Sai Sreedhar Varada

Thesis submitted to the Faculty of the Graduate School of the University of Maryland, College Park in partial fulfillment of the requirements for the degree of *Master of Science* 2017

Advisory Committee: Professor Sheryl Ehrman, Chair/Advisor Professor Michael Zachariah Doctor Akua A. Asa-Awuku Professor Russell Dickerson © Copyright by Sai Sreedhar Varada 2017

Dedication

To my mother Bhagya Lakshmi and my brother Sai Sree Harsha.

Acknowledgments

First of all, I would like to thank my advisor, Sheryl Ehrman for her continuous support as a mentor throughout my Master's program.

I would like to thank other mentors, especially Russell Dickerson, Timothy Canty, Hao He and Ross Salawitch.

I would like to thank Dolly Hall, for the observational data analysis and help with understanding MOVES and Matlab.

Thank you to Maryland Department of Environment for their financial assistance and Mohamed Khan from MDE for MOVES input data.

Finally, I would like to thank my family and friends for their constant support. Especially, Kanishka Macherla for helping me understand few statistical concepts and Sreenivas Reddy for helping with MySQL.

Table of Contents

Dedication				
Ac	know	ledgem	ents	iii
1	Intro	duction	1	1
	1.1	US and	d Mid-Atlantic air quality	3
	1.2	Emissi	on control in automobiles	7
		1.2.1	Catalytic converters:	7
		1.2.2	Air-fuel ratio:	8
		1.2.3	Oxygen-sensor:	9
	1.3	Past re	esearch on measurements and modeling data of mobile emissions	10
2	MOV	VES sof	tware	14
	2.1	Descri	ption	14
	2.2	Count	y data manager	15
	2.3	MOVE	ES technical reports	16
		2.3.1	Temperature adjustments for gasoline start emissions:	16
		2.3.2	Temperature adjustments for gasoline running emissions:	17
		2.3.3	Temperature adjustments for diesel fueled automobile vehicles:	17
		2.3.4	Temperature effects in Compressed Natural Gas (CNG) emissions: .	18
		2.3.5	Humidity adjustments in MOVES:	18
	2.4	Metho	ds used in MOVES	18
		2.4.1	Temperature dependence:	18
		2.4.2	Specific humidity dependence:	19
3	MOV	VES out	put results and discussion	21
	3.1	MOVE	ES temperature dependence	21
	3.2	MOVE	ES specific humidity dependence	24

4	MOV	/ES output comparison to observations and adjustments in MOVES	28		
	4.1	I-95 observations measuring site			
	4.2	Observational emissions vs ambient temperature			
	4.3	Observational emissions vs specific humidity			
	Comparisons of measured and modeled data	31			
		4.4.1 Temperature dependence	32		
		4.4.2 Specific humidity	33		
	4.5	Plotting observations and MOVES output	33		
	4.6	Disagreement between MOVES and observations	35		
	4.7	MOVES adjustments and comparisons to observations	36		
	4.8	Adjusted MOVES model applied to November, 2014	38		
	4.9	Observed vs MOVES vehicle distribution	40		
5	Cond	clusions and future work	43		
	5.1	Conclusions	43		
	5.2	Future work	43		
A Appendix		endix	45		
	A.1	Adjustments in the MOVES default code	45		
Bił	Bibliography				

Chapter 1: Introduction

Keeping the levels of pollutants below the standards that affect human health and cause danger to ecosystems has always been a major concern to the governments which make laws to protect the people and environment. Harmful pollutants that cause air pollution are mainly emitted from powerplants, automobile vehicles and natural causes like wildfires and volcanoes. Automobiles are one of the important sources for CO, NO_x, particulate emissions and volatile organic carbons (VOCs) that are released into air. Due to the increase in use of automobiles in modern day, fuel consumption is increased by various motor vehicles like motorcycles, cars, buses, and trucks. The emissions from these automobiles depend on various processes inside the engine including air-fuel ratios, as well as sulfur content in the fuel, tire-wear, type of fuel and ambient temperature.

To accurately measure the observations of emissions from automobile sources, the US Environmental Protection Agency (EPA) has been maintaining near-road and far-road air quality sites next to freeways and other local roads. This kind of monitoring is important because each year additional number of vehicles are being added on-road in millions [3]. But the monitoring sites can only provide measurements for present and an archive of past conditions. Being able to predict for future years is also important. So, EPA has designed a software program for modeling the mobile emissions and has been improving it over the years. As of now MOVES 2014a [9] is the latest version. All the mobile emissions that are prepared in the National Emissions Inventory (NEI) are from MOVES 2014a output. The NEI is prepared once every three years by EPA by including the data collected from State, Local and Tribal agencies which consists of criteria and hazardous pollutant emissions estimates and their precursors from various sources. So, it is important for MOVES to have a more realistic approach towards estimations.

The main focus in this study is the investigation of temperature and humidity dependence for CO and NO_x in MOVES output. It is important to get temperature dependence of emissions in the MOVES output correct. The reason why NO_x emissions are important because long term exposure to NO_x emissions can cause respiratory problems which can lead to decrease in the lung functions and NO_x also acts as a precursor for the formation of O_3 , one of the criteria pollutants that has a national standard of 70 ppb [12] and has adverse human health effects especially in summer. O3 being a highly unstable compound tends to react immediately after its formation, but O3 concentration increases when the formation rate is higher than reacting rate. This phenomena is favorable in warmer temperatures, like temperatures above 70 °F and we observe O3 exceedances especially during afternoons in the months of May-September. CO is a toxic pollutant and used as a tracer gas for mobile emissions. Exposure to high amounts of CO can cause decrease of the oxygen levels in blood stream which may lead to problems in brain like dizziness, unconsciousness, confusion and problems in heart like chest pain and sometimes even can lead to death. Research on observational data collected from a road side monitor on I-95 shows that NO_x decreases with the increase of ambient temperature and specific humidity in the atmosphere while CO is relatively constant for these changes. The next section gives a brief review of air quality in the USA and previous work on CO and NO_x measured and modeled emissions from automobiles.

1.1 US and Mid-Atlantic air quality

Air quality in the USA has been a serious concern from 1940s in the state of Pennsylvania, where burning coal caused severe smoke pollution [18]. A new law called the Clean Air Act [2] was implemented in 1970 by the Environmental Protection Agency (EPA) which sets the National Ambient Air Quality Standards (NAAQS) for pollutants that have adverse effects on human health. These pollutants are called criteria pollutants and they are CO, NO₂, SO₂, PM_{2.5},O₃, CO and lead (Pb). Bernard et al., (2001) [16] did a detailed study on the role of climate change on air pollution caused by the criteria pollutants and their health impacts in the US. Since the implementation of Clean Air Act, the pollution levels in the US were decreased by 31% as of 1997, although the population was increased by 31%, vehicle miles traveled increased 127% and gross domestic production increased 114%. Some of the criteria pollutants like lead emissions decreased by almost 98%. The significant decrease in lead was possible because of setting early reduction standards in fuel starting from 1973 and completely abandoning the sale of leaded fuel from 1996 by law under the Clean Air Act [8]. More recent results show CO has decreased by 85%, 8-hour average O_3 has decreased by 31% and annual NO₂ has decreased by 62% from 1990 to 2016 [13] in the US.

Pennsylvania, D.C, Maryland, Delaware, Virginia and West Virginia and parts of New York, New Jersey and North Carolina are together called the Mid-Atlantic region. The Mid-Atlantic region of the USA is one of the important regions in the US where air pollution is a major concern due to its urbanization, and its location downwind of the states that produce huge amount of emissions because of the presence of large power plants. The increased air pollution in this can also be accounted due to increase in population and various climate conditions [30]. Many research studies have been done to investigate various pollutants in this region. Often there is an exceedance of O₃ in summer due to local and remotely transported VOCs and NO2. Studies like Lewis et al., (2007) [24], Hains et al., (2007) [20] and He et al., (2014) [22] studied the mid-Atlantic region using aircraft measurements. They discussed pollution caused by long range transport of pollutants from various upwind sources. Lewis et al., (2007) [24] did a cluster analysis by placing observations in 6 clusters and found that 'only marine and upper tropospheric clusters as clean' and rest of the remote locations in Mid-Atlantic as polluted. Hains et al., (2007) [20] also did a clustering analysis for O_3 sources and found one cluster profile from the Canadian forest fires and the other five were directly related to NO_x emissions from point sources. They also found that NO_x emissions from both mobile and point sources affect O₃. An overall study of Mid-Atlantic air pollution due to climate change in the region was done by Ryan et al., (1999) [32] and Rogers et al., (2000) [31]. Ryan et al., (1999) [32] used multiple regression analysis for ground level O₃ and made accurate forecasts of 1-hr peak O_3 in the Mid-Atlantic region. Others like Bell et al., (2004) [15] studied the sensitivity of tropospheric O₃ on changing biogenic emissions and Kim et al., (2005) [23] studied particulate matter (PM) sources in the mid-Atlantic region. Bell et al., (2004) [15] by performing CMAQ simulations found that a 100% increase of the biogenic VOC emissions had a greater increase in the ozone levels than a 100% increase of mobile NO_x and VOCs. They also found that increase in the temperatures due to climate change also increase the biogenic VOCs and thereby raise ozone levels.

The following paragraphs give more insight into the methods used for analyzing various pollutants from the past studies. Castellanos et al., (2011) [17] using the Community Multiscale Air Quality (CMAQ) modeling with version 4.5.1 have estimated the O_3 , NO_x and CO emissions in the Eastern United States during the pollution episodes and calculated the vertical mixing that are represented by K-Theory and calculated the eddy diffusion coefficient using the planetary boundary layer theory. The results showed CO was underestimated by 20-50% when the model captured correct boundary layer depth and no evidence was found that CO was overestimated by SMOKE/MOBILE6. They also suggested that NO_x was overestimated at urban monitoring sites and MOBILE6 NO_x emissions were also overestimated from cars.

Parrish et al., (2011) [29] discuss how there has been change in the air quality of North American mega-cities over the past several years. With the increasing smog, due to the photochemical production of O_3 in Los Angeles Basin, California became the first state in 1966 in the US to set standards from the motor vehicles by requiring automobiles to use catalytic converters and promoting zero emission vehicle fleets. This lead to significant decrease in the ambient concentrations of CO, SO₂, O₃, PM_{2.5}, lead and NO_x, though O₃ has been regularly above the NAAQS limitations during the summer.

There have been a lot of observational studies through field campaigns which helped to estimate the boundary layer depth, and sources of emissions and precursors. The satellite observations for the decade (2000-2010) have led to a more rigorous study of the ground based observations. In the northeast corridor of the US which extends from DC to Boston and includes big cities with large populations, emissions of O₃, aerosol precursors and greenhouse gases particularly in the New York City were lower when compared to that of LA megacity which were compared here based on the similar size of population. This is because of the transportation of emissions generated in the cities by prevailing winds from the southwest, and presence of a daytime deep convective boundary layer, emissions vertical mixing is allowed. Houston on the other hand, being an industrial city, had a huge concentration of O₃ during the summers and in the late 90s and early 00s had recorded the highest 1-hr average for O₃ concentrations which was recorded to be greater than 200ppbv and Houston put efforts to not record a maximum of 170ppbv after 2004. steps taken in Mexico City for reduction in emissions were similar to that of LA, such as installation of catalytic converters in automobiles, decrease in sulfur content in diesel, instrumentation and maintenance (I&M) programs strengthening and lead removal from gasoline. The field studies conducted in Mexico City showed that the production of O_3 may have shifted from NO_x sensitive emissions to a VOC limited emissions. The intercontinental transport of O_3 and precursors is another major issue as O_3 precursors from East Asian countries travel from across the Pacific ocean resulting in an increase of the background O_3 concentrations in California [29].

Anderson et al., (2014) [14] discussed the measured CO and NO_y emissions and the modeled emissions. They focused on comparing the modeled results from CMAQ using the NEI to observations such as satellite measurements and the data that was collected through the DISCOVER-AQ air campaign in the Baltimore-Washingtion Region (BWR). Parrish et al., (2014) have compared the O₃ data sets obtained from 7 sites in Europe, 3 sites in North America and 2 sites in Asia that lie in the mid-latitudes. The three models used in this study for calculating the long-term O₃ concentrations were Community Atmosphere Model with Chemistry (CAM-chem), Geophysical Fluid Dynamics Laboratory CoupleModel (GFDL-CM3) and Goddard Institute for Space Studies Model (GISS-E2-R). Each of these models differ in the resolution they run, the vertical layers they choose and the atmospheric chemistry involved with different chemical reactions. The results showed there was an overestimation of CO emissions in the NEI by 15 +/- 11% and mobile NO_x emissions were overestimated in the NEI by 51-70%.

He et al., (2011) [22] studied an air quality episode in the Baltimore region during an heat wave that recorded high temperatures and poor air quality. An air quality episode is an unexpected combination of emissions and meteorology which leads to increase in emission levels. The results of this research showed there was an elevated reservoir of pollutants that contain emissions such as O_3 , CO and NO_x from motor vehicles exhaust and aerosols and SO_2 from powerplants. They used aircraft observations and ground observations and compared them with the modeled output of O_3 from CMAQ, in which the modeled O_3 was overestimated for the in-situ ground observations and the model predicted very high ozone near the surface in an elevated reservoir.

He at al., (2013) [21] studied air quality and emission trends in the Baltimore/Washington region from 1997 to 2011 using various sources of data such as ground-based observations, satellite measurements, air-craft measurements and clustering analysis. The results showed CO and O_3 emissions in the region showed a decreasing trends near to 35 ppbv/year and 1.3 ppbv/year respectively, in the lower troposphere. They also found that for Eastern Maryland, major sources for NO_x emissions are from the power plants of upwind states Ohio and Pennsylvania.

1.2 Emission control in automobiles

1.2.1 Catalytic converters:

Emissions of elemental and oxides of carbon and nitrogen oxides and hydrocarbons are released due to the incomplete burning of fuel in the internal combustion engines of cars and other automobiles. These gases, when emitted directly into the atmosphere play a key role in the formation of other harmful pollutants that act as precursors in the formation of O_3 . To minimize these emissions, devices called catalytic converters are used in the internal combustion engines of automobiles [5]. Catalytic converters are located between the engine and the vehicle exhaust system. They are in the form of honeycomb structured ceramic beads on which noble elements like platinum, rhodium, palladium are coated as catalysts. The amount of these catalysts present is around 4-9 grams. Catalytic converters oxidize carbon monoxide and hydrocarbons to CO_2 and H_2O (steam) and reduce nitrogen oxides into nitrogen and oxygen. All the reactions are spontaneous in nature and proceed in the forward direction [4]. But, they are quite slow without the presence of any catalyst. Thus, a reduction catalyst composed of platinum and rhodium is used for reducing nitrogen oxides into molecular nitrogen and oxides and an oxidative catalyst composed of platinum and palladium decreases emissions of carbon monoxide by converting it into CO_2 and unburned hydrocarbons to CO_2 and H_2O .

Catalytic converters work best at high temperatures which makes them ineffective during the first few minutes after the engine starts running (cold start). Catalytic converters are also less efficient in diesel engines as the engines run at lower temperatures compared to gasoline engines.

1.2.2 Air-fuel ratio:

The ideal air fuel mixture contains air to fuel ratio of 14.7:1. That is, 14.7 parts of air by weight required to completely burn 1 part of fuel by weight. If the ratio is less than the ideal conditions, then it is termed as a rich mixture and if it is greater than 14.7:1, then it is called a lean mixture. A rich mixture provides inadequate oxygen for the fuel to be burnt completely which results in emission of unburnt gases through the tail pipe exhaust, while a lean mixture provides more oxygen than required resulting in slow burning leading to the power loss. For achieving maximum power and speed, the air fuel ratio should be rich in the engine and also during the cold start conditions. A leaner mixture provides maximum fuel economy, but burns slowly resulting in power loss irregularity. A carburetor in an automobile engine is the place where fuel which is turned into vapor and air is mixed in proper proportion and is passed to the engine for the complete combustion of the fuel [1]. A major disadvantage of carburetors is that an engine with four cylinders and one carburetor has difficulty in receiving the same air fuel mixture ratios to each cylinder due to their distance from the carburetor. In modern day vehicles, different types of fuel injectors replaced carburetor. Fuel injection is a system where a pump supplies fuel under pressure to each cylinder separately. Fuel injectors are either direct or indirect based on the type of vehicles. In indirect fuel injection, the fuel is turned into mist and mixed with air through an inlet manifold and this fuel/air mixture enters into the combustion chamber and many diesel engines use indirect fuel injection. Direct injection is where fuel is directly injected into the cylinders. Gasoline engines commonly use direct fuel injection.

1.2.3 Oxygen-sensor:

To maintain ideal air-fuel ratio conditions, engines use a device called an oxygensensor that is located near the exhaust pipe. The primary function of the device is to check whether the air-fuel mixture is burning lean or rich and to adjust the amount of air entering into the internal combustion engine [10]. Oxygen sensors are needed because amount of oxygen entering into depends on various factors such as the altitude, engine temperature, coolant temperature, air flow and engine load, etc. Most sensors work on the mechanism where a chemical reaction occurs that generates a voltage. The oxygen sensor element is a zirconium ceramic bulb that is coated with platinum on the outside and has two strips of platinum inside which serve as electrodes. The inside of the bulb is vented internally to the outside temperature while outside of the bulb is exposed to the hot exhaust gases. The difference in the outside and inside oxygen levels generates a voltage that flows through the ceramic bulb. The high voltage detected by the computer is a measure of rich mixture and it leans the fuel-air mixture while the low voltage is an indication of lean mixture and the computer makes the air-fuel mixture rich [11]. The engines computer responds to the voltage and takes cues from the oxygen sensor to determine rich or lean mixture and adjusts the mixture accordingly.

1.3 Past research on measurements and modeling data of mobile emissions

The paragraphs below discuss CO and NO_x emissions measurements from vehicles and changes in concentrations of these pollutants from different model year vehicles. Parrish et al., (2002) [28] discuss the change in the CO over NO_x ratios for a period of over one decade (1987-99) from the vehicular emissions and they found a decrease of 7-9% for this time period. McDonald et al., (2012) [25] studied long-term trends in NO_x emissions from motor vehicles at national, state and air basin scales. Some of the research findings were 1) At national scale between 1990 and 2007, there was an increase of 20% and 90% for gasoline and diesel fuel consumption respectively. While, diesel sales largely declined between 2007 and 2009 in the US, gasoline fuel sales slightly decreased. 2) NO_x emissions factors for diesel to gasoline vehicles were 3 in 1990 and it was found to be 8 in 2009. This is mainly due to increase in the effectiveness of catalytic converters in gasoline engines and improvement of technology in such type of vehicles and due to the increase in the number of diesel vehicles which emit more amount of NO_x compared to gasoline engines. 3) In Los Angeles area, motor vehicles account for nearly 80% of NO_x emissions making them the dominant sources.

Zavala et al., (2009) [34] studied mobile emissions contributions to Mexico City's emis-

sions inventory using on-road and cross-road emission measurements and ambient data. The measurements were made by setting up an Aerodyne mobile laboratory during March 2006; a fast time response instrumentation was also used to measure the emissions during transiting from place to place apart from stationary on-road measurements. Instruments used in this research include Tunable Infrared Laser Differential Absorption Spectroscopy (TILDAS) to measure pollutants like CO, NO₂, H₂CO and C₂H₄, Aerosol Mass Spectrometer (AMS) to measure nitrate, sulfate, ammonium, organics and chlorides and Non-Dispersive Infrared instruments (NDIR) unit (LICOR) to measure CO₂. The key findings of the research were 1) when compared to emissions in Mexico City, U.S cities like Denver and Phoenix had fuel-based CO and VOC mobile emissions that were lower, and this was due to the fact that Mexico City had a fleet consisting of older vehicles with no emission control technology. 2) The CO/NO_x ratio was decreased by 1.9 ppm/ppm/year from 2004 during early morning which was due to reduction in CO emissions because of the introduction of cleaner vehicles around 2000 and also due to the decrease of older vehicles in the fleet. 3) Though the vehicle fleet increased from 2000 to 2006 in Mexico City, the ambient levels of NO_x and CO emissions during the early mornings did not increase remarkably. The research suggested this was due to increase gasoline vehicles with good emission technology and removal of older vehicles.

Parrish et al., (2006) [27] have investigated the mobile inventories for emissions of NO_x , VOCs and CO in the US. They found inconsistencies in MOBILE6 (prior version of MOVES) modeling software program which was developed by EPA to calculate the mobile or on-road anthropogenic vehicular emissions. They found that MOBILE6 overestimated CO emissions of on-road vehicles by nearly a factor of 2 by comparing emissions estimates to tunnel and remote sensing measurements.

Fujita et al., (2012) [19] compared mobile emissions models such as MOVES2010, MO-BILE6.2 and EMFAC2007 with on-road traffic tunnel and remote sensing measurements. The on-road measurements were made in a Van Nuys tunnel, CA for 8 days with two 3-hr sampling periods each day from 9am-12pm and 12:15-15:15. Some of the important findings of the research were 1) Non-methane hydrocarbons (NMHC) measured are 3.5 times higher during high temperatures (85 °F-105 °F) than at low temperatures (65 °F-75 °F). All the 3 models predicted lower factors of NMHC at higher temperatures than measured since all models have showed insensitivity in estimating running evaporative emissions at higher temperatures, especially MOVES. 2) Selecting appropriate operating modes for project scale analysis in MOVES proved to be important, since there were uncertainties of modeled NO_x emissions when compared with measurements. when compared with measurements. 3) There were also variations observations among the models in estimating the contributions of gasoline and diesel fuel vehicles and also in predicting the emission factors. MOVES predicted lower contribution of NO_x emissions by diesel trucks compared to EMFAC, while contribution of total carbon emissions by diesel trucks by MOVES was greater than twice that of EMFAC.

In earlier studies Mulawa et al., (1997) [26] reported on the effect of temperature and E-10 fuel on the primary exhaust particulate matter emissions from light-duty vehicles. E-10 fuel is mixture of 10% ethanol and 90% regular unleaded gasoline [6]. Ethanol in E-10 fuel partly absorbs CO_2 , off setting green house emissions. They also expanded their study to CO and NO_x emissions temperature dependence. The study was conducted in Fairbanks, Alaska during the winter of 1994-95. For this study, they used 9 vehicles of different ages and technologies and one vehicle which was in compliance with the EPA's standard limits for CO emissions in 1996. These tests were also carried out at Research Triangle Park, North Carolina under similar conditions. All the tests were carried at 75 °F,

20 °F, 0 °F and -20 °F temperatures according to federal test procedure with both regular gasoline and gasoline with 10% ethanol in it. The research concluded that PM emissions increased with the decrease in temperatures except for the standard vehicle where emission rate at 75 °F was same as that of 20 °F. This lead to the conclusion that vehicles which met CO emissions federal standards produce less PM. PM emissions for E-10 fuel were considerably lower compared to the regular gasoline fuel. CO and HC emissions increased with decrease in the temperature, so PM followed similar trends. NO_x emissions increased when the fuel is switched to E-10 and did not show any trend with the temperature changes.

Weilenmann et al. (2004) [33] investigated the temperature dependence of cold start emissions in both diesel and gasoline cars for different car age groups in Europe. They measured emissions at -23 °C, 7 °C and 23 °C for 3 categories of cars in the research. They were Euro-0, Euro-2 and Euro-3. Euro-0 and Euro-3 were gasoline cars that mostly belong to the years 1985 and 2000 respectively. Euro-2 cars were diesel and the model years were from 1997-2001. The results showed CO emissions decreased about 180 g/start at -20 °C from Euro-0 to Euro-3 car models while that only decreased 72 g/start at 23 °C. CO emissions largely decreased at room temperature while they only decreased by a factor of 3 at -20 °C from Euro-0 to Euro-3 cars which means even with the modern emission technology, emissions were not reduced at very low cold start temperatures. On the other hand, NOx emissions were relatively less in both generations of cars and did not show any relationship to the ambient temperatures. The research also showed that CO cold start emissions for Euro-2 diesel cars were about 10 times lower compared to gasoline cars and observed a factor of four reduction between -20 °C and 23 °C, while cold start NOx emissions in Euro-2 cars were lower and increased at low ambient temperatures.

Chapter 2: MOVES software

2.1 Description

MOVES is short form for MOtor Vehicle Emission Simulator and its latest version is MOVES 2014a. It is used to model and estimate the emissions from automobiles and other motor vehicles both on-road and off-network. It has a Java based graphical based interface (GUI) platform and runs on MySQL database scripts. It has two modes, inventory and emission rates mode. Inventory mode outputs the overall emissions in grams while emissions rates mode outputs the emission factors, which when multiplied by the activity give the total emissions. The maximum time period a single MOVES run can be made for is one year. MOVES has three scales for running a simulation, they are the national scale, the county scale and the project scale. National scale contains the default inputs prepared from the data collected by EPA and can be adjusted if there are any updated data available. County scale is used as a more accurate method for modeling since all the inputs are manually entered and is modeled for each individual county or multiple counties together which have similar conditions. Project scale is used for a combination of various roads or for an intersection of roads and it is used for modeling more accurately for a specific time at a particular point. There are 5 different categories of roads in MOVES and to model ramps separately it uses 4 more categories. The different road types in MOVES are off-network, rural restricted and rural unrestricted with and without ramps and urban restricted and urban unrestricted with and without ramps. Restricted roads can be defined as roads that have limited access to vehicles likes bicycles and other vehicles that are driven by animals, and that have separation dividing both sides of roads and there is no intersection of streets. MOVES can be used to modeled various vehicles like motorcycles, cars, buses and trucks along with their sub-categories that are based on the weight of the vehicle. These automobiles can be further divided based on the various types of fuels such as gasoline, diesel, electricity and compressed natural gas (CNG), since, based on the composition of fuel, emission quantities change due to factors like airfuel ratio, combustion temperature and presence of catalytic converters. While running MOVES various pollutants can be selected whose emissions are to be simulated, while some pollutants have some prerequisites to be selected for them to be modeled. Pollutants can be further classified in output based on the process by which they are emitted. The division is necessary because cold-start produces a large quantity of emissions and once the vehicle is started and running the emissions are reduced and vary according to their speed and other fuel and engine properties.

2.2 County data manager

In this research, I only ran on county scale mode, so I explain county data manager (CDM) here in detail. County data manger is a separate interface where inputs for a county are given. The inputs include meteorology data, fuel formulation, average speed distribution, age distribution of vehicles, road type distribution, population of various sources, number of starts for each source, vehicle miles traveled (VMT), inspection & maintenance programs (I/M) and hotelling hours. Each input should be provided in the form of an Excel formatted worksheet, which should contain the modeling time period such as year, month and the day. If there is incomplete information, the MOVES contains a feature to show errors. Since temperature and humidity dependence is what this research

mainly focuses on, the input table for meteorology is briefly described as it has the inputs for temperature and humidity. The meteorology table consists of temperature and relative humidity values averaged for each hour of each day over a month in the modeling year. Temperatures and relative humidity cannot be inputted separately for each hour of the day. Thus, for the modeling all the changes to obtain temperature ranges are made in the meteorology table.

2.3 MOVES technical reports

The EPA-MOVES website describes quantitatively how the temperature and humidity dependence is accounted for by default in the MOVES. Below is a brief description:

2.3.1 Temperature adjustments for gasoline start emissions:

- (a) Adjustments for CO emissions are made for temperatures only below 75° F
- (b) The additional emissions in grams/mile due to changes in the ambient temperature are added to the calculated base emissions. These additive grams/mile adjustment equations are given by

Additive grams =
$$A * (T - 75) + B * (T - 75)^2$$
 (2.1)

Additive grams =
$$B * e^{A*(T-75)} + C$$
 (2.2)

The first equation is applied to model years earlier than 2001, while the other equation is applied to more recent vehicle models.

(c) All these adjustments were developed by fitting vehicle emissions data obtained by using various test procedures such as Mobile Source Observation Database (MSOD), Office of Research and Development (ORD), Mobile Source Air Toxic Program (MSAT) and Office of Transportation and Air Quality (OTAQ) Cold Temperature Program. (d) NO_x temperature adjustments are made by below equation.

$$NO_{\rm x}$$
 temperature additive ad justment = $A * (T - 75)$ (2.3)

where: A = -0.009, the above equation is applied only for temperatures below $75^{\circ}F$ and no additive adjustment is made for temperatures greater than $75^{\circ}F$.

(e) This factor is added to the estimated base NO_x to get ambient temperature adjusted emissions.

2.3.2 Temperature adjustments for gasoline running emissions:

Both CO and NO_x for running emissions do not depend on temperature and this is reflected by the adjustment factors being equal to 1 in the code. The observations data used for this conclusion consisted of analysis of emissions on 496 vehicles which was performed in 2004 and 2005. No statistical significance (relationship) was found between emissions and temperature.

2.3.3 Temperature adjustments for diesel fueled automobile vehicles:

- (a) Very small dependencies were found for CO and NO_x start emissions on temperature, so the temperature adjustments for CO and NO_x are set to be zero for cold-starts.
- (b) Since there is no significant effect of ambient temperature on cold start emissions, no analysis was made for running emissions. So, the temperature additive adjustment for diesel running emissions is zero in MOVES.

2.3.4 Temperature effects in Compressed Natural Gas (CNG) emissions:

All the start emissions temperature adjustments for CO and NO_x were adjusted similarly to running emissions and cold start emissions of diesel engines.

2.3.5 Humidity adjustments in MOVES:

- (a) NO_x emissions are adjusted for all processes and all modes in MOVES.
- (b) The base emissions are multiplied by a factor that depends on specific humidity, which bounded in between 21 and 124 grains of water per pound of dry air. And the adjustment factor K, is given by

$$K = 1.0 - ((bounded specific humidity - 75.0) * Humidity correction coefficient)$$
(2.4)

where bounded specific humidity is given as (greatest(21.0, least(specific humidity, 124.0))) and humidity correction coefficients are 0.0038 and 0.0026 for gasoline and diesel respectively that were obtained from extrapolation of the measured data by EPA.

2.4 Methods used in MOVES

2.4.1 Temperature dependence:

To find out solely the default temperature dependence in MOVES, the base meteorology file that goes as one of the inputs in to the county data manager was changed. Meteorology input contains average temperature and relative humidity values for each hour of the month and for all the 12 months of 2014. In this research, the month of October, 2014 was chosen because the observations analyzed were also for the month of October which makes comparisons more appropriate.

To vary temperature and keep specific humidity constant, relative humidity was changed accordingly. To see the variation at different temperatures at different hours, input meteorology files for the MOVES were created where the default temperature was added up to 10° C at an interval of 2° C and also subtracted up to 10° C at an interval of 2° C, thus forming a total of 11 temperature scenarios. In each of these 11 MOVES runs, only the meteorology input file was changed while rest of the inputs remained unchanged. The output emissions of CO, NO, NO₂ and CO₂ were obtained in grams/day and were converted into moles/day. The number moles of NOx were calculated by adding up the number of moles of NO and NO₂.

2.4.2 Specific humidity dependence:

To determine the default specific humidity dependence, MOVES runs were made in a similar way how temperature dependence runs were performed. Specific humidity dependence runs were made by keeping the default temperature for each hour of the day constant and changing the relative humidity each hour to maintain a specific humidity for 16 different runs. The constant specific humidity values were 5, 15, 20, 25, 35, 40, 45, 50, 55, 60, 65, 75, 85, 95, 110 and 125 grains of vapor per pound of air (MOVES default units for specific humidity) for 16 different scenarios respectively. While plotting the default units were converted to g/kg to match with the units of observational data.

By inputting the meteorological variables in county manager as described above, I obtained MOVES output consisted the emissions in grams for different pollutants, fuel types, road types, processes and day types (weekday and weekend). Since, the observational study is based upon measurements from a roadside monitor next to a highway only running emissions for the weekday and since highways are restricted, only rural and urban restricted roads form the MOVES output were used. The segregated output data were summed up for each pollutant and for each hour of the day (ambient temperature or specific humidity is different at each hour) and for both the restricted road types and for all vehicle and fuel types. For temperature dependence, since there are 11 different runs, the output emissions file contained a total of 264 emission values of CO, NOx and CO2 at different ambient temperatures. These 264 points are sorted in ascending order and were divided 25 points each into 10 bins and the last bin getting the rest 14 points. For each bin, 25th percentile, median and 75th values were calculated and a linear least squares regression is applied to the median values. Output is analyzed in a similar way for specific humidity dependence. The results are explained in Chapter 3.

Chapter 3: MOVES output results and discussion

3.1 MOVES temperature dependence

Figures 3.1 and 3.2 below, show CO/NO_x, CO₂/NO_x and CO₂/CO emission mole ratios versus ambient temperature in degrees celsius. Figure 3.1 shows the default output of MOVES i.e., without any adjustments nor corrections made in the software codes. Heat index which is also called apparent temperature, is a measure of how it actually feels when relative humidity is factored with temperature. Figure 3.2 shows the plots where the heat index value was changed to 1.0. Both the figures show emission ratios with four lines vs temperature in each plot, the top line in blue represents 75 percentile, the center line in red represents median of the data, the bottom line in blue show 25 percentile data and the black dotted line is the least square linear regression line for the median data. The emission ratio of CO₂/CO in Figure 3.1 starts decreasing at nearly 20 °C (68 °F) which means CO and CO₂ increase with increase in the temperature above 20 °C (68 °F) but CO emissions increase much faster than CO₂ emissions increase and in Figure 3.2 the slope is nearly zero i.e., CO is constant and independent of temperature, only heat index through AC affects CO. CO_2/NO_x nearly remain constant in both the figures, so I concluded change in the heat index has minimal impact on the NO_x emissions in MOVES. Heat index effects in MOVES are adjusted to air conditioner (AC) on/off in vehicles by a multiplicative adjustment, given by the Equation 3.1 and heat index is calculated by the Equation 3.2. Switching on AC in vehicles causes increase in the amount of fuel consumption which increases the emissions

of vehicles. MOVES default heat index value is equal to temperature if the temperature is below 78 $^{\circ}$ F and Equation 3.1 is applied only to temperatures above 78 $^{\circ}$ F.

$$\begin{aligned} \textbf{ACFactor} &= min(max(ACActivityTermA + heatIndex*(ACActivityTermB + ACActivityTermC*heatIndex), 0), 1.0)*ACPenetrationFraction \\ &* functioningACFraction \end{aligned} \tag{3.1}$$

 $\begin{aligned} \mathbf{heatIndex}[\mathbf{7}] &= least(-42.379 + 2.04901523 * temperature + 10.14333127 \\ &* relHumidity + -0.22475541 * temperature * relHumidity \\ &+ -0.00683783 * temperature * temperature \\ &+ -0.05481717 * relHumidity * relHumidity \\ &+ 0.00122874 * temperature * temperature * relHumidity \\ &+ 0.00085282 * temperature * relHumidity * relHumidity \\ &+ -0.00000199 * temperature * temperature * relHumidity * relHumidity, 120) \end{aligned}$

where *temperature* and *relHumidity* are the ambient temperature and relative humidity of the default inputs in the county data manager.

In Equation 3.1 the term heatIndex was changed to 1.0 in the MOVES runs to see only the effect of heat index on emissions, and the results are shown in Figures 3.2 and 3.4. By changing heat index value to 1.0, the AC multiplicative adjustment factor was made constant in the MOVES runs to see the effects of temperature or specific humidity exclusively.



Figure 3.1: MOVES output - emission ratios vs ambient temperature profile (°C), Oct 2014. (a) $\Delta CO/\Delta NO_x$, (b) $\Delta CO_2/\Delta NO_x$, (c) $\Delta CO_2/\Delta CO$

Figure 3.2: MOVES output - emission ratios vs ambient temperature profile (°C), Oct 2014. (a) $\Delta CO/\Delta NO_x$, (b) $\Delta CO_2/\Delta NO_x$, (c) $\Delta CO_2/\Delta CO$

3.2 MOVES specific humidity dependence

Figures 3.3 and 3.4 show plots of MOVES output emission ratios against specific humidity. Both figures are similarly plotted as the figures plotted for temperature dependence i.e., the former figure was plotted with MOVES default while the later figure was plotted by making heat index value 1.0 in MOVES. Both the figures have similar plots for CO/NO_x, CO₂/NO_x and CO₂/CO against ambient temperature. Therefore, I conclude that emission ratio estimates are unaffected by changes in specific humidity which has an effect on heat index. For the data we considered the highest temperature was 65.35 °F so heat index does not have any effect on output. And the plot of CO₂/NO_x ratio clearly shows that the ratio is increasing with increasing specific humidity values which means NO_x decreases with increase in the specific humidity since CO₂ is unaffected by specific humidity. The CO₂/CO ratio remains constant over specific humidity changes, so it can be concluded that CO emission estimates are constant and are unaffected by specific humidity changes.

Figure 3.3: MOVES output (default)- emission ratios vs specific humidity (g/kg), Oct 2014. (a) $\Delta CO/\Delta NO_x$, (b) $\Delta CO_2/\Delta NO_x$, (c) $\Delta CO_2/\Delta CO$

Figure 3.4: MOVES output (heat index = 1.0) - emission ratios vs specific humidity (g/kg), Oct 2014. (a) $\Delta CO/\Delta NO_x$, (b) $\Delta CO_2/\Delta NO_x$, (c) $\Delta CO_2/\Delta CO$

Chapter 4: MOVES output comparison to observations and adjustments in MOVES

4.1 I-95 observations measuring site

In this chapter I discuss about methods used in analysis of road side observations and their comparison to the MOVES output results. Figure 4.1 shows the location of on-road site AQS monitor site on Interstate-95, in Howard County, Maryland. This site monitors NO_x , CO^2 , CO, black carbon, $PM_{2.5}$, VOCs, meteorology and wind speed and is maintained by the MDE. The measured data was analyzed by Dolly Hall. Figures 4.1, 4.2 and 4.3 were prepared by Dolly Hall.

Figure 4.1: Location of AQS site on I-95 in the Howard County.

4.2 Observational emissions vs ambient temperature

Figure 4.2 shows below the hourly emission ratios, as estimated from an orthogonal least square regression of every 60 normalized 1-minute observations of CO, NO_x, and CO₂. Normalization was done to each 1-minute observation by dividing the mean of 60 1-minute observations in that hour. For each plot, outliers were filtered out (outliers were identified as 1-minute observations farther than twice the standard deviation from the mean) and also regression lines that were not statistically significant (p<0.05 is statistically significant). Finally, only the hours where r^2 of the observations that went into each regression was greater than 0.50 were used. The number of points in the plots **a** and **c** are 70, whereas the number of points in the plot **b** are 130. The greater number of points in plot **b** shows that the measuring instruments were more accurately calibrated for collecting NO_x emissions.

In Figure 4.2 plot **a** represents CO over NO_x emission ratio, plot **b** represents CO₂ over NO_x emission ratio and plot **c** represents CO₂ over CO emission ratio. All the plots were plotted emission ratios in mol mol⁻¹ versus temperature in °C. The red line in these plots represents the ordinary least square regression line with temperature as the independent variable. We see here that the CO/NO_x and CO₂/NO_x emission ratios are temperature sensitive (NO_x is decreasing with increases in temperature) which represents the fuel rich conditions of the engines. CO₂/CO is not temperature sensitive, with a slope of near 0 mol/(mol °C).

Figure 4.2: Observational data - Emission ratios (mol mol⁻¹) vs Ambient Temperature °C, Oct-Nov 2016. (a). $\Delta CO/\Delta NO_x$, (b). $\Delta CO_2/\Delta NO_x$, (c). $\Delta CO_2/\Delta CO_2$

4.3 Observational emissions vs specific humidity

The hourly emission ratios were calculated exactly the same as in the temperature dependence. The plots below in Figure 4.3 show the emission ratios as a function of specific humidity in g/kg.

The red line in these plots represents the ordinary least squares regression line with temperature as the independent variable. We see here that the CO/NO_x and CO_2/NO_x emission ratios are temperature sensitive (NO_x is decreasing with increases in specific humidity). CO_2/CO is not humidity sensitive, with a slope of only -1 mol/(mol g/kg).

All of this tells us that the NO_x is very temperature and humidity sensitive, as it is in MOVES. However, in MOVES the CO is also temperature sensitive above $18^{\circ}C$ (64.4 °F), which is not what we observe at the I-95 site.

Figure 4.3: Observational data - Emission ratios (mol mol⁻¹) vs specific humidity (g/kg), Oct-Nov 2016. (a). $\Delta CO/\Delta NO_x$, (b). $\Delta CO_2/\Delta NO_x$, (c). $\Delta CO_2/\Delta CO_2$

4.4 Comparisons of measured and modeled data

Although the near road measurements are for 2016, we are comparing the measurements to the modeled MOVES output of 2014 since the MOVES inputs are available only for 2014 because the input inventory is prepared every 3 years and no measurements are available for 2014, as the site started measuring air quality during summer 2016. I think though the years are different, comparing the same month (October in both cases) would be a good approach with all the resources that are available as of now. In this work, the main focus is to compare the observations and emissions estimates based on temperature and humidity variation. It is important to note that the meteorology is different in 2014 and 2016 for the compared estimates and observations respectively. However, by keeping specific humidity constant in MOVES while comparing effect of temperature dependence and by keeping the temperatures constant while comparing effect of specific humidity, a reasonable study can be performed because I am looking at individual factors of meteorology separately. Comparative analysis is not done for specific days of a month nor I am looking at diurnal profile variations.

4.4.1 Temperature dependence

On comparing the observations in Figure 4.2 and the MOVES base run output in Figure 3.1, it is clear that emission ratios do not match quantitatively. The emission ratio of CO_2/NO_x measured on-road is more than twice quantitatively for the same range of temperature change and the measurements slope is nearly 13 times greater than MOVES output.

The CO_2/CO measured emission ratio quantitatively is twice greater than MOVES output ratio. It is observed that CO is nearly constant with any change in temperature while MOVES output ratio starts decreasing around 20°C since CO starts increasing with the temperature. So, the MOVES defaults should be changed to correctly capture the CO emissions and should be kept constant for all the changes in temperature.

4.4.2 Specific humidity

Figures 4.3 and 3.3 show emission ratios vs specific humidity for the observations and MOVES output respectively. Specific humidity dependence matches to the observations more than temperature dependence in MOVES does. For CO_2/NO_x emission ratio of the observations slope is nearly 3.5 times greater than the MOVES output ratio for the same range of specific humidity change. Quantitatively, this emission ratio is twice as large that observed in measurements.

The CO_2/CO emission ratio is nearly constant in both measured and modeled results, but the quantitatively measured ratio is twice larger than MOVES output. Thus, by correcting and changing quantitatively CO_2 , NO_x and CO emissions dependencies on temperature and specific humidity in MOVES, more accurate mobile inventory can be prepared.

4.5 Plotting observations and MOVES output

Below Figures 4.4 and 4.5 show the comparisons of emissions for observational data on I-95 and MOVES output vs temperature and specific humidity respectively.

Figure 4.4: Observational data (Oct-Nov 2016) and MOVES output (Oct-2014) comparison - Emission ratios (mol mol⁻¹) vs ambient temperature °C. (a) $\Delta CO/\Delta NO_x$, (b) $\Delta CO_2/\Delta NO_x$, (c) $\Delta CO_2/\Delta CO_2/\Delta$

Figure 4.5: Observational data (Oct-Nov 2016) and MOVES output (Oct-2014) comparison - Emission ratios (mol mol⁻¹) vs specific humidity (g/kg). (a) $\Delta CO/\Delta NO_x$, (b) $\Delta CO_2/\Delta NO_x$, (c) $\Delta CO_2/\Delta CO_2/\Delta CO_2/\Delta CO_2/\Delta NO_x$, (c) $\Delta CO_2/\Delta CO_2$

4.6 Disagreement between MOVES and observations

The reason why MOVES does not account for the temperature dependence as seen in observations analysis by Dolly Hall might be because ambient temperature dependence on running emissions is not included in MOVES. The observations data MOVES used for estimating running emissions consisted only a sample of 496 vehicles and this study was conducted between 2004 and 2005. Since the sample size is very low, they found no statistical significance between ambient temperature and emissions. Another hypothesis for quantitative differences in the emission ratios maybe because of the different fleet size distributions (the number of vehicles on-road) in 2014 and 2016 and not accounting for temperature dependence at the same time. The results clearly show that MOVES overestimates both NO_x and CO emissions. There might be other reasons for these over estimations of emissions by MOVES such as catalytic converters working better than expected to reduce emissions or an offset because more vehicles are equipped with an advanced control systems at present compared to the time when observations were taken (2004-05) to develop the software. It is beyond the scope of this thesis to investigate the real reason behind the offset between MOVES and observations.

4.7 MOVES adjustments and comparisons to observations

By comparing observations and modeled MOVES output, it is evident that MOVES is not representing the ambient temperature dependence on emissions estimates well. In the default (without any changes in the software) MOVES code which calculates the base output modeled emissions of CO and NO_x, I improved these shortcomings by multiplying a linear temperature dependence adjustment factor which was found for both CO and NO_x emissions estimates. Since, CO and NO_x emissions estimates are in the denominators of the emission ratios, these linear temperature factors are divided in the MOVES calculator to get correct estimates of emissions ratios. MOVES calculators are files which contain code written in MySQL programming language, in which based on various input databases, outputs such as emissions estimates are calculated. For CO emissions calculator, a multiplicative factor of $1/(1.01^*10^{-3}$ * temperature + 1.727) and for NO_x emissions calculator, a multiplicative factor of $1/(2.54*10^{-2} * \text{temperature} + 0.132)$ [Appendix A] was multiplied to base emissions in the code and the results are shown in Figure 4.6, where temperature is in Fahrenheit. The base emissions were shown in the previous chapter and are obtained without making any temperature adjustments in the MOVES. CO2 emissions were unchanged and were estimated by the MOVES default code. The adjusted MOVES

is run for October, 2014 and were matched to observations of Oct-mid Nov, 2016 and the results are shown in Figure 4.6, the slopes of all 3 MOVES model ratios are nearly equal to those of observations. Thus, emissions are adjusted based on temperature dependence.

The factors were obtained using trial and error method. First, a linear factor in the form of '(m*temperature+c)' was assumed to be multiplied to MOVES output for CO and NO_x to match the modeled emission ratios with observations. Then two temperatures within the range of the plot were chosen such that they are nearest integers to the minimum and maximum values of temperature range; here I used temperatures 5 °C (41 °F) and 25 °C (77 °F). Then emission modeled emission ratio was multiplied by the assumed linear temperature dependence factor at both temperatures and set equal to observed emission ratios. Then the both equations were solved to get the values of **m** and **c**. The temperature linear factor was divided in the emissions calculator to see if the emissions estimates were near exact to observations. If the obtained values of **m** and **c** do not give the ratios of emissions estimates that exactly match observations, a trial and error method was used by changing these values until both estimates and observations were nearly matched. The values were chosen such that the deviation started to increase further on decreasing the values. A trial and error method was used because emissions estimates do not vary linearly.

Figure 4.6: MOVES output for Oct, 2014 adjusted to observational data (Oct-Nov 2016) - Emission ratios (mol mol⁻¹) vs Ambient temperature °C. (a) $\Delta CO/\Delta NO_x$, (b) $\Delta CO_2/\Delta NO_x$, (c) $\Delta CO_2/\Delta CO_2$

4.8 Adjusted MOVES model applied to November, 2014

The adjustments made to MOVES in the previous section are applied to November, 2014 to find out how the model would work for other months. Since there were no observational analysis for some other month, and as observation analysis performed by Dolly Hall consists of a half month of November I thought it is reasonable to compare adjusted MOVES output to the same observations. The results for November, 2014 MOVES output vs observations emissions ratios against temperature are shown in Figure 4.7. From the Figure 4.7, it is clear that slopes of emissions ratios for are nearly equal and the factor by which emission ratios differ for CO_2/NO_x is less than 0.2 and for CO_2/CO is less than 0.05 which is reasonably a good fit for the amount of observations data available. The offset in the CO_2/CO estimated emissions ratios from the observed emission ratios might be due to insufficient observations for November, 2014 and another hypothesis for this effect might be because since CO emissions are higher at low temperatures [26] the estimated emissions ratios (CO_2/CO) decreased and are lower than observations.

Figure 4.7: Observational data (Oct-Nov 2016) and MOVES adjusted output (Nov-2014) comparison - Emission ratios (mol mol⁻¹) vs Ambient temperature °C. (a) $\Delta CO/\Delta NO_x$, (b) $\Delta CO_2/\Delta NO_x$, (c) $\Delta CO_2/\Delta CO$

4.9 Observed vs MOVES vehicle distribution

4 miles from the AQS monitoring site, there is a traffic counter located on I-95. Figure 4.8 shows the fraction of gasoline and diesel vehicles observed and a median number of both types of vehicles at each hour of the day for the month of October 2016. MOVES does not produce vehicle counts as output, instead, it outputs the distance of the vehicle traveled for each hour. Figure 4.9 shows the MOVES vehicle miles traveled both for gasoline and diesel vehicles at each hour of the day for the month of October 2014. Both Figures show similar trends in variations of gasoline to diesel. From midnight to early mornings, the fraction of diesel to gasoline vehicle miles in MOVES is greater when compared to the number of diesel to gasoline vehicles, so more NO_x emissions estimates from MOVES can be higher than actual emissions observed on-road during this time period.

The reason why vehicle miles from MOVES are being compared to actual vehicle traffic count is because MOVES calculates emissions estimates using the vehicle miles traveled and not by using the number of on-road vehicles. Although MOVES has vehicle population, it is used to calculate only idle exhaust emissions such as start and evaporative. This approximation does not produce the same emissions result, because the number of trips using vehicle miles travelled does not exactly match the number of vehicles. In the current available data, though MOVES has vehicle population as one of the inputs, it is only used to calculate off-network emissions and no on-road emissions estimates are calculated using vehicle population.

Figure 4.8: Observational traffic data (Oct 2016). **(a)** fraction of gasoline vehicles, **(b)** fraction of diesel vehicles, **(c)** Bar graph for gasoline and diesel vehicles

Figure 4.9: MOVES vehicle miles estimations (Oct 2014). (a) fraction of gasoline miles, (b) fraction of diesel miles, (c) Bar graph for gasoline and diesel miles

Chapter 5: Conclusions and future work

5.1 Conclusions

From MOVES output and observations comparisons it is clearly evident that MOVES does not account of the ambient temperature and humidity dependence as is in the actual world. Thus, MOVES is adjusted based on observations and adjustment factors were multiplied to the MOVES default emission calculators in the code accordingly. To check the credibility of adjustment factors, another month was modeled and compared to the observations, in this study, for November, 2014. Though only half month observations are not available for this month, the MOVES output nearly matched to the observations. MOVES estimations of CO emissions are nearly twice that of the observed CO which can be observed in 4.4. Also, the hourly fraction of gasoline to diesel for the month of October, 2014 in MOVES input (vehicle miles fraction) and for October, 2016 from on-road traffic (vehicle count) counter seems to be similar except for the early mornings.

5.2 Future work

MOVES is adjusted only for temperature dependence in this work, adjusting the emissions based on specific humidity also would produce more realistic mobile emissions estimates. For more rigorous approach, future work should include comparing the MOVES model output and observations for the same month of the same year to produce a more useful modeling output that could be used for predicting future case studies. Another approach for this kind of research is by using project scale in MOVES to model the emissions estimates of near road measurements with proper MOVES inputs since the project scale approach is used for a smaller region like I-95 monitoring site. Future work should also include MOVES modeling comparisons with observations collected at various near road monitoring sites to include different fleet compositions and to include wide range of meteorology.

Appendix A: Appendix

A.1 Adjustments in the MOVES default code

Below Figures A.1 and A.2 show where in the MOVES code the adjustment factors were multiplied for CO and NO_x emissions estimates respectively. In the below snippets of the codes A.1, it is written that when the pollutant ID is 2 (pollutantID for CO in MOVES is 2), the base emissions should be multiplied by the factor [1/(1.01*10-3* temperature + 1.727)] and similarly in A.2, whenever the pollutant IDs are 3,32 and 33 (pollutantID in MOVES for NO_x is 2, NO is 32 and NO₂ is 33) the base emissions should be multiplied by the factor [1/(2.54*10-2* temperature + 0.132)].

Figure A.1: Adjustments made to calculate CO emissions estimates in MOVES

Figure A.2: Adjustments made to calculate NO_x emissions estimates in MOVES

Bibliography

- [1] The basics: Air fuel ratios and their importance! The basics: Air fuel ratios and their importance! *http://www.treadstoneperformance.com/blog/the-basics-air-fuel-ratios-and-their-its-importance/*. Accessed on 2017-03-12.
- [2] Overview of the Clean Air Act and air pollution. *https://www.epa.gov/clean-air-act-overview*. Accessed on 2017-03-16.
- [3] U.S. car sales from 1951 to 2016 (in units). U.S. car sales from 1951 to 2016 (in units) https://www.statista.com/statistics/199974/us-car-sales-since-1951/. Accessed on 2017-03-12.
- [4] Catalytic converters. *http://www.explainthatstuff.com/catalyticconverters.html*. Accessed on 2017-03-12, .
- [5] How catalytic converters work. How catalytic converters work*http://auto.howstuffworks.com/catalytic-converter.htm*. Accessed on 2017-03-12,
- [6] What is E10 fuel and how could it affect you? What is E10 fuel and how could it affect you?*https://www.rac.co.uk/drive/advice/driving-advice/what-is-e10-fuel-and-how-could-it-affect-you/*. Accessed on 2017-03-12.
- [7] The heat index equation. *http://www.wpc.ncep.noaa.gov/html/heatindex'equation.shtml/*. Accessed on 2017-02-12.
- [8] Epa takes final step in phaseout of leaded gasoline. EPA takes final step in phaseout of leaded gasoline*https://archive.epa.gov/epa/aboutepa/epa-takes-final-step-phaseout-leaded-gasoline.html*. Accessed on 2017-03-12.
- [9] MOVES2014a: Latest version of MOtor Vehicle Emission Simulator (MOVES). https://www.epa.gov/moves/moves2014a-latest-version-motor-vehicle-emissionsimulator-moves/. Accessed on 2017-03-12.

- [10] How does the oxygen sensor in a car work? How does the oxygen sensor in a car work?http://auto.howstuffworks.com/question257.htm. Accessed on 2017-03-12, .
- [11] What does an oxygen sensor do? https://www.meineke.com/blog/oxygen-sensor. Accessed on 2017-03-12, .
- [12] 2015 National Ambient Air Quality Standards (NAAQS) for ozone. https://www.epa.gov/moves/moves2014a-latest-version-motor-vehicle-emissionsimulator-moves/. Accessed on 2017-03-12.
- [13] Air Quality National Summary. *https://www.epa.gov/air-trends/air-quality-national-summary*. Accessed on 2017-03-12.
- [14] DC Anderson, CP Loughner, G Diskin, A Weinheimer, TP Canty, RJ Salawitch, HM Worden, A Fried, T Mikoviny, A Wisthaler, et al. Measured and modeled co and no_y in discover-aq: An evaluation of emissions and chemistry over the eastern us. *Atmospheric Environment*, 96:78–87, 2014.
- [15] M Bell and H Ellis. Sensitivity analysis of tropospheric ozone to modified biogenic emissions for the mid-atlantic region. *Atmospheric Environment*, 38(13):1879–1889, 2004.
- [16] SM Bernard, JM Samet, A Grambsch, KL Ebi, and I Romieu. The potential impacts of climate variability and change on air pollution-related health effects in the united states. *Environmental Health Perspectives*, 109(Suppl 2):199, 2001.
- [17] P Castellanos, LT Marufu, BG Doddridge, BF Taubman, JJ Schwab, JC Hains, SH Ehrman, and RR Dickerson. Ozone, oxides of nitrogen, and carbon monoxide during pollution events over the eastern united states: An evaluation of emissions and vertical mixing. *Journal of Geophysical Research: Atmospheres*, 116(D16), 2011.
- [18] CI Davidson. Air pollution in pittsburgh: A historical perspective. *Journal of the Air Pollution Control Association*, 29(10):1035–1041, 1979.
- [19] EM Fujita, DE Campbell, B Zielinska, JC Chow, CE Lindhjem, A DenBleyker, GA Bishop, BG Schuchmann, DH Stedman, and DR Lawson. Comparison of the moves2010a, mobile6. 2, and emfac2007 mobile source emission models with onroad traffic tunnel and remote sensing measurements. *Journal of the Air & Waste Management Association*, 62(10):1134–1149, 2012.
- [20] JC Hains, BF Taubman, AM Thompson, JW Stehr, LT Marufu, BG Doddridge, and RR Dickerson. Origins of chemical pollution derived from mid-atlantic aircraft profiles using a clustering technique. *Atmospheric Environment*, 42(8):1727–1741, 2008.

- [21] H He, JW Stehr, JC Hains, DJ Krask, BG Doddridge, KY Vinnikov, TP Canty, KM Hosley, RJ Salawitch, HM Worden, et al. Trends in emissions and concentrations of air pollutants in the lower troposphere in the baltimore/washington airshed from 1997 to 2011. Atmospheric Chemistry and Physics, 13(15):7859–7874, 2013.
- [22] H He, CP Loughner, JW Stehr, HL Arkinson, LC Brent, MB Follette-Cook, MA Tzortziou, KE Pickering, AM Thompson, DK Martins, et al. An elevated reservoir of air pollutants over the mid-atlantic states during the 2011 discover-aq campaign: Airborne measurements and numerical simulations. *Atmospheric Environment*, 85: 18–30, 2014.
- [23] Eugene Kim and PK Hopke. Identification of fine particle sources in mid-atlantic us area. *Water, Air, and Soil Pollution*, 168(1-4):391–421, 2005.
- [24] AC Lewis, MJ Evans, J Methven, N Watson, JD Lee, JR Hopkins, RM Purvis, SR Arnold, JB McQuaid, LK Whalley, et al. Chemical composition observed over the mid-Atlantic and the detection of pollution signatures far from source regions. *Journal of Geophysical Research: Atmospheres*, 112(D10), 2007.
- [25] BC McDonald, TR Dallmann, EW Martin, and RA Harley. Long-term trends in nitrogen oxide emissions from motor vehicles at national, state, and air basin scales. *Journal of Geophysical Research: Atmospheres*, 117(D21), 2012.
- [26] PA Mulawa, SH Cadle, K Knapp, R Zweidinger, R Snow, R Lucas, and J Goldbach. Effect of ambient temperature and e-10 fuel on primary exhaust particulate matter emissions from light-duty vehicles. *Environmental Science & Technology*, 31(5):1302– 1307, 1997.
- [27] DD Parrish. Critical evaluation of us on-road vehicle emission inventories. *Atmospheric Environment*, 40(13):2288–2300, 2006.
- [28] DD Parrish, M Trainer, D Hereid, EJ Williams, KJ Olszyna, RA Harley, JF Meagher, and FC Fehsenfeld. Decadal change in carbon monoxide to nitrogen oxide ratio in us vehicular emissions. *Journal of Geophysical Research: Atmospheres*, 107(D12), 2002.
- [29] DD Parrish, HB Singh, L Molina, and S Madronich. Air quality progress in north american megacities: A review. *Atmospheric Environment*, 45(39):7015–7025, 2011.
- [30] JA Patz, M Susan MA McGeehinand Bernard, LK Ebi, PR Epstein, A Grambsch, DJ Gubler, P Reither, I Romieu, BJ Rose, et al. The potential health impacts of climate variability and change for the united states: executive summary of the report of the health sector of the us national assessment. *Environmental health perspectives*, 108 (4):367, 2000.
- [31] CE Rogers and JP McCarty. Climate change and ecosystems of the mid-atlantic region. *Climate Research*, 14(3):235–244, 2000.

- [32] WF Ryan, CA Piety, and ED Luebehusen. Air quality forecasts in the mid-atlantic region: Current practice and benchmark skill. *Weather and Forecasting*, 15(1):46–60, 2000.
- [33] M Weilenmann, P Soltic, C Saxer, A Forss, and N Heeb. Regulated and nonregulated diesel and gasoline cold start emissions at different temperatures. *Atmospheric Environment*, 39(13):2433–2441, 2005.
- [34] M Zavala, SC Herndon, EC Wood, TB Onasch, WB Knighton, Linsey C Marr, CE Kolb, and LT Molina. Evaluation of mobile emissions contributions to mexico city's emissions inventory using on-road and cross-road emission measurements and ambient data. Atmospheric Chemistry and Physics, 9(17):6305–6317, 2009.