OZONE FORMATION ATTRIBUTABLE TO EMISSIONS FROM RURAL INTERSTATE TRAFFIC

Final Report

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Report No. UVA/29472/CE01/103

Center for Transportation Studies
University of Virginia
Charlottesville, VA 22904

Prepared for
Mid-Atlantic Universities Transportation Center

May 2001

Technical Report Documentation Page

1. Report No. UVA/29472/CE01/103	2. Government Accession No.	3. Recipient's Catalog No.

4. Title and Subtitle Ozone Formation Attributable to Emissions from Rural Interstate Traffic	5. Report Date May 2001 6 Performing Organization Code III-0103
7. Author(s) Steven L. Jones, Michael J. Demetsky, Jose D. Fuentes	8. Performing Organization Report No. UVA/29472/CE01/103
9. Performing Organization Name and Address Center for Transportation Studies University of Virginia PO Box 400742 Charlottesville, Virginia 22904-4742	10. Work Unit No. (TRAIS) 11.Contract or Grant No. CE-PSU-0703-01
12. Sponsoring Agency Name and Address Office of University Programs, Research and Special Programs Administration US Department of Transportation 400 Seventh Street, SW Washington DC 20590-0001	13. Report Type and Period Covered Final 14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

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17. Key Words air quality, ozone, mobile source emissions, photochemical modeling, heavy-duty vehicle emissions	18. Distribution Statement

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 143	22. Price

Form DOT F 1700.7 (8-72) Reproduction of completed page authorized

ABSTRACT

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ACKNOWLEDGEMENTS

I would very much like to thank Professor Michael J. Demetsky of the Department of Civil Engineering. His support, encouragement, and friendship were absolutely essential to my completing this degree. I would also like to thank Professor Jose D. Fuentes from the Department of Environmental Sciences who was willing to mentor me in my study of atmospheric sciences. I am grateful that he had the vision to see the potential for collaboration between our two departments. I am also grateful to Professor Nicholas J. Garber, Professor Brian L. Smith, and Professor Lester A. Hoel for their input and support throughout my doctoral education.

I must express my gratitude to the Mid-Atlantic University Transportation Center without whose financial support none of this would have been possible. To that end, I must also thank Mike Perfater and the Virginia Transportation Research Council (VTRC). My time a the VTRC also provided financial support for my education. Most importantly, however, it acquainted me with some of the finest people I have ever worked with and taught me the value of great work environment.

I want to thank my wife, Franny, for whom I do all that I do. No amount of financial assistance or mentoring can match the support she provided and sacrifices she made over the past seven years to make this possible. Finally, I want to thank Abby, Emma Claire, and Lucy who, without knowing, made every step of the way richer and more worthwhile.

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Chapter 1. INTRODUCTION

1.1. Background

Although there has been considerable study of the interaction between transportation and air quality, with the exception of several large-scale regional studies, it has been largely confined to the urban environment (Russell & Dennis, 2000). Efforts have ranged from the first scientific paper published on automobile-related air pollution in 1919 to analysis of the Los Angeles ozone episodes in the 1950's and 1960's which provided the impetus for the automobile emissions regulation promulgated in the 1965 Motor Vehicle Air Pollution Control Act (Perkins, 1974). Substantial work on rural, ground level ozone formation was conducted during the 1970's and has been well documented (Martinez & Singh, 1979; Isaksen et al., 1978; NRC, 1991). Several of the early works on rural ozone addressed the role of local emissions, but few were explicitly concerned with mobile sources. Two recent studies in Europe have addressed non-urban and regional ozone formation attributable to traffic emissions but neither isolated the effects of a single roadway facility (Brücher et al., 2000; Toll et al., 2000).

Complex photochemical processes involving meteorological factors and chemical precursors dictate the formation of tropospheric, or ground level, ozone (O_3). The primary chemical precursors to O_3 are oxides of nitrogen (NO_x), organic hydrocarbons (HC), and carbon monoxide (CO). In studies of photochemical processes, nitric oxide (NO) and nitrogen dioxide (NO_2) are identified as the two NO_x species of primary importance. HC are chemical compounds comprised of some combination of carbon and hydrogen such as methane (CH_4).

NO_x and HC react in the presence of sunlight to form ozone. Ozone precursors are emitted directly into the atmosphere anthropogenic sources such as power plants, industrial facilities, and motor vehicles. Emissions from biogenic sources (e.g., trees) can contribute ozone precursors to the atmosphere as well (Lopez et al., 1989; NRC, 1991; Chameides et al., 1992; Fehsenfeld et al., 1992; Finlayson-Pitts & Pitts, 1993; Guenther et al., 1995). Figure 1 is a schematic representation of the ozone formation process in a rural environment. In addition to well-documented deleterious effects on human health, tropospheric ozone has been shown to significantly damage agricultural crops and reduce forest vitality (NRC, 1991).

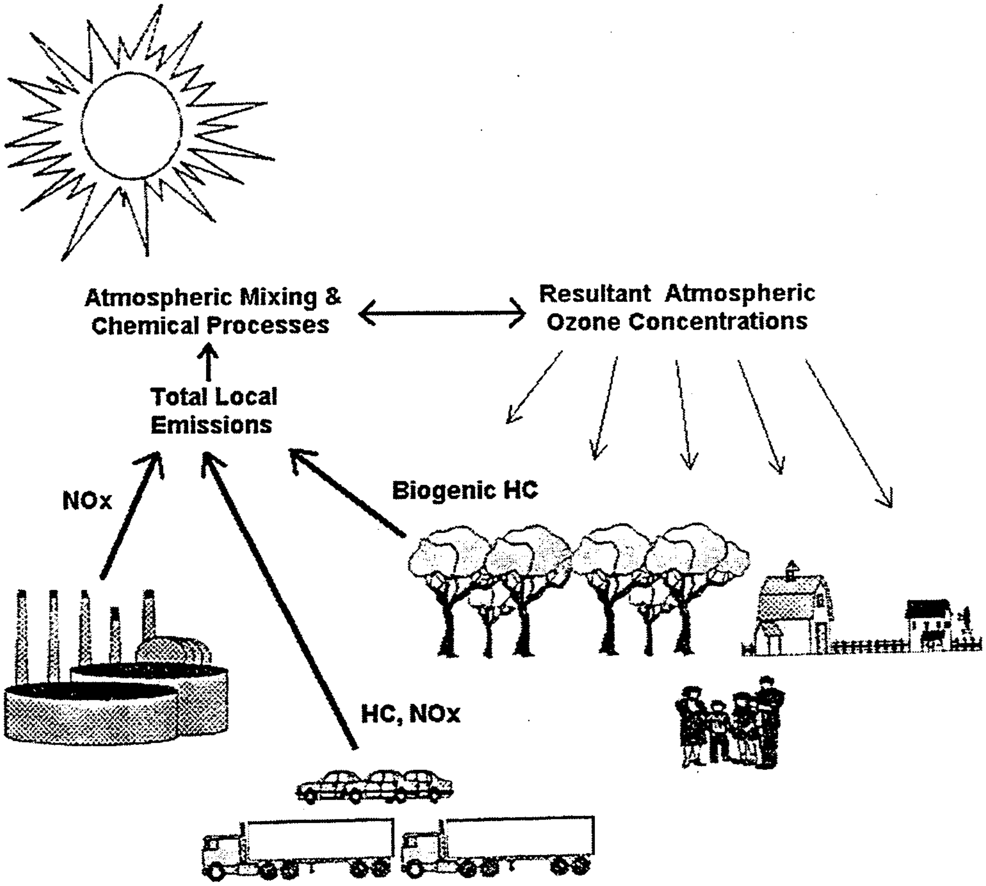

Figure 1. Ozone formation process in rural environments.
Source: NRC, 1991.

Ozone is the primary photochemical oxidant in the atmosphere and has been regulated by the Environmental Protection Agency (EPA) since 1971 (Baumgardner, 1998). Currently, the EPA promulgates standards to maintain tropospheric ozone levels acceptable to state environmental authorities. The standards are described in the *National Ambient Air Quality Standards* (NAAQS). The current standards are categorized into primary and secondary standards. The primary standards are intended to limit tropospheric ozone levels and minimize exposure to protect human health. The secondary standards are aimed at the protection of the public welfare by limiting the exposure of vegetation and personal property to tropospheric ozone. Generally, the secondary standards are applied to rural areas where lower population densities reduce the overall risks of human exposure and concerns for vegetation damage are more germane.

The EPA has recently conducted a comprehensive review of the NAAQS and has established several new and revised standards. The new standards for tropospheric ozone require that the 4th highest daily eight-hour mixing ratio averaged over a three-year period not exceed 0.08 parts per million (ppm). The previous standard was set at a one-hour level of 0.12 ppm not to be exceeded more than once per year averaged over a three-year period. The new criteria apply to both the primary and secondary standards for ozone. In the case of the secondary standard, the objective is to mitigate the effects of tropospheric ozone on vegetation (agricultural and forest) in rural and remote areas (EPA, 1997). As traffic continues to increase and environmental policies necessarily evolve, there is an increasing need to account for the impact of motor vehicles on air quality in the rural environment.

The 1997 revisions to the NAAQS have provided the impetus for aggressive research in the area of transportation and air quality. Most prominent is the research project entitled "Transportation Effects of the 1997 Changes to the National Ambient Air Quality Standards" initiated by the National Cooperative Highway Research Program (NCHRP) as NCHRP 25-17. Other recent NCHRP efforts relevant to transportation and air quality are presented in Table 1.

Table 1. Active and Potential NCHRP Research in Transportation and Air Quality.

Project	Status
NCHRP 8-33: Quantifying Air-Quality and Other Benefits and Costs of Transportation Control Measures	Active
NCHRP 25-21: Assessment of Short-Term Versus Long-Term Air Quality Effects	Active
Ambient Microscale Monitoring for Project Compliance with the National Ambient Air Quality Standards	Suggested
Subfleet Technology and High Emitter Characterization	Suggested
Pollution Emissions from Specialty Vehicle Fleets	Suggested
Modification of HPMS for Air Quality Analysis	Suggested
Seasonal and Episodic Transportation Measures to Avoid Exceedances	Suggested

1.2. Problem Statement

The combination of emissions from a rural interstate and biogenic emissions inherent to rural areas provides for the potential of substantial ozone formation. The current state-of-the-practice in vehicle-emissions modeling for air quality analyses does not provide adequate detail for estimating emissions from rural interstate traffic.

Similarly, models used to describe ozone formation are inappropriate for modeling the ozone formation attributable to a rural interstate. Current models either insufficiently account for biogenic emissions or are intended to model areas too large to adequately describe the photochemical processes relevant to a rural interstate.

1.3. Purpose and Scope

The purpose of the research was to develop a modeling procedure to assess the contribution of rural interstate traffic to local ozone formation. The scope of the research includes:

- The development of a methodology to post-process FRESIM emissions estimates into atmospheric concentrations of specific chemical species.
- Modifications to an existing rural photochemical model to accommodate:
    - the emissions of pollutants from the interstate traffic
    - the effects of the traffic-related emissions in chemical processes.
- The application of the modeling procedure to test scenarios.
- The interpretation and presentation of results.

The modeling procedure developed herein is intended to serve as a potential research tool for traffic engineers and transportation planners to ascertain the air quality impacts of rural interstates. Potential applications include:

- Environmental impact assessment of major transportation investments (e.g., new facility location and design, roadway widening, lane addition),

- Environmental impact assessment of changes in traffic operations (e.g., speed limit changes, separation of passenger cars and trucks, ITS/COV applications),
- Analysis of transportation-related environmental policies (e.g., vehicle emissions regulation, vehicle inspection/maintenance programs, alternative fuels), and
- Analysis of the effects of microscale air quality impacts in regional scale modeling.

The modeling procedure builds on the capabilities of the FRESIM traffic operations simulation software to produce environmental performance measures from interstate facilities (FHWA, 1994). The procedure also employs a detailed photochemical model to calculate resultant ozone concentrations from biogenic and traffic-related emissions in the rural interstate environment (Makar et al., 1999).

Chapter 2. LITERATURE REVIEW

2.1. Policy Issues

2.1.1. Vehicle Emissions

The principal pollutant types emitted from mobile sources are NO_x, HC, and CO. NO_x and HC are direct chemical precursors to ozone formation (Sawyer et al., 2000). CO also plays an important role in photochemical processes (Jenkin et al., 2000). The emission of pollutants from motor vehicles has been regulated by the federal government since 1966 (Papacostas and Prevedouros, 1993). Over the past thirty years, the emphasis of these regulations has shifted from one pollutant to another (e.g., CO to HC), but the overall trend has been towards stricter emissions control on all types of motor vehicles (White, 1982). In particular, NO_x emissions from heavy-duty vehicles (e.g., gasoline- and diesel-powered intercity freight trucks) have been the target of aggressive regulation during the last decade (Schimek, 1998). Table 2 summarizes the evolution of heavy-duty vehicle emissions standards over the past ten years. Emission rates in Table 2 are given in grams of pollutant per brake-horsepower per hour of vehicle operation. In 1995, the EPA announced an agreement with heavy-duty diesel manufacturers setting a new heavy duty vehicle NO_x emission standard at approximately half of its 1998 value. The new standard is planned to go into effect for heavy vehicles manufactured after the year 2004 and is intended to reduce the role trucks play in ozone formation (TRB, 1995; EPA, 1997).

Table 2. Heavy-Duty Vehicle Emissions Standards.

Model Year	NO_x (g/bhp-hr)	HC (g/bhp-hr)	CO (g/bhp-hr)
1988	10.7	1.3	15.5
1990	6.0	1.3	15.5
1991	5.0	1.3	15.5
1993	5.0	1.3	15.5
1994	5.0	1.3	15.5
1996	5.0	1.3	15.5
1998	4.0	1.3	15.5

Source: TRB, 1995.

2.1.2. Ozone

The 1990 Clean Air Act Amendments (CAAA) explicitly provided for air quality modeling intended to predict the effects of emissions on critical pollutant levels identified in the NAAQS. With specific attention directed toward transportation, Section 108 of the 1990 CAAA requires that maintenance of a continuous transportation-air quality planning process with specific attention to "methods of reviewing plans on a regular basis as conditions change or new information is presented." In addition, Section 108 provides for the explicit assessment of risks to individual ecosystems posed by criteria air pollutants such as ozone (CAAA 108, 1990). Section 107 describes the official designations given to areas with respect to their ambient pollutant levels. An area is designated as a "non-attainment" area if the ambient levels of specific pollutants exceed the limits promulgated in the NAAQS. In addition, Section 107 states that an area currently exhibiting air pollution levels within the acceptable limits of the NAAQS that contributes background air pollution to a nearby non-attainment area can itself be classified as a non-attainment area (CAAA 107, 1990). In other words, a rural area that can be shown to be a significant source of ozone or ozone precursors transported to an urban non-attainment area can technically be classified as a non-attainment area. In July 1998, the EPA proposed a policy to provide flexibility in setting a target date for an area to achieve ozone attainment if it is known that ozone or precursor sources upwind contribute to ground-level ozone formation in that non-attainment area (EPA, 1998).

As promulgated in the 1990 CAAA, states containing geographical areas in violation of the NAAQS must submit a Statewide Implementation Plan (SIP) to the EPA for review. Once approved by the EPA, the SIP functions as a contract between federal and state environmental authorities detailing the means by which the state intends to bring non-attainment area(s) into attainment. Transportation investments included in an area's long-range transportation plan or transportation improvement program (TIP) must be shown to be in conformance with the SIP of the state. In other words, it must be shown that construction of new transportation facilities, modifications to existing facilities, or changes in traffic operations will not exacerbate vehicle-related air pollution or impair a state's ability to obtain the goals outlined in its SIP (TRB, 1995). A 1992 USDOT Policy Discussion Series publication illuminates the effects of the 1990 CAAA on transportation, stating that, "these provisions seem likely to necessitate much more detailed examination of transportation-air quality relationships, and methodologies that adequately address key issues will be needed (Harvey and Deakin, 1992)."

In concert with the 1990 CAAA, the 1991 Intermodal Surface Transportation Efficiency Act (ISTEA) emphasized the requirements that TIPs be consistent with long-range transportation plans as well as the SIPs (FHWA, 1994). Although the provisions in the ISTEA were primarily aimed at urban non-attainment areas, it clearly indicated the commitment of the federal government to address the air quality impacts of transportation. The relationship between transportation and air quality was again addressed by the federal government in the Transportation Equity Act for the 21st Century (TEA-21) through specific provisions to ensure that states have adequate guidance from the EPA to satisfy the requirements of the newly revised NAAQS (USDOT, 1998).

2.2. Mobile Source Emissions

Motor vehicles are a major source of atmospheric pollutants. NO_x emissions from mobile sources, however, generally play a more significant role than HCs in ozone formation in rural environments. Mobile source emissions of CO also contribute to ozone formation by aiding in the production of important ozone precursors. High ozone concentrations, in rural as well as urban locations, generally occur during the summer months. During this time of the year, radiation levels received from the sun are higher than other times of the year (NRC, 1991). This radiation plays a direct role in the chemical reactions that form ozone as well as contribute to the biological processes that cause certain vegetation to release important ozone-forming HC (Chameides and Cowling, 1995). Figure 2 is a graph of the monthly distribution of rural traffic from data published in the 1996 FHWA report, *Highway Statistics* (Teets, 1996). As rural traffic is greater during the late spring and summer months (May, June, July, and August), it is reasonable to assume that mobile source emissions in rural areas are greater as well.

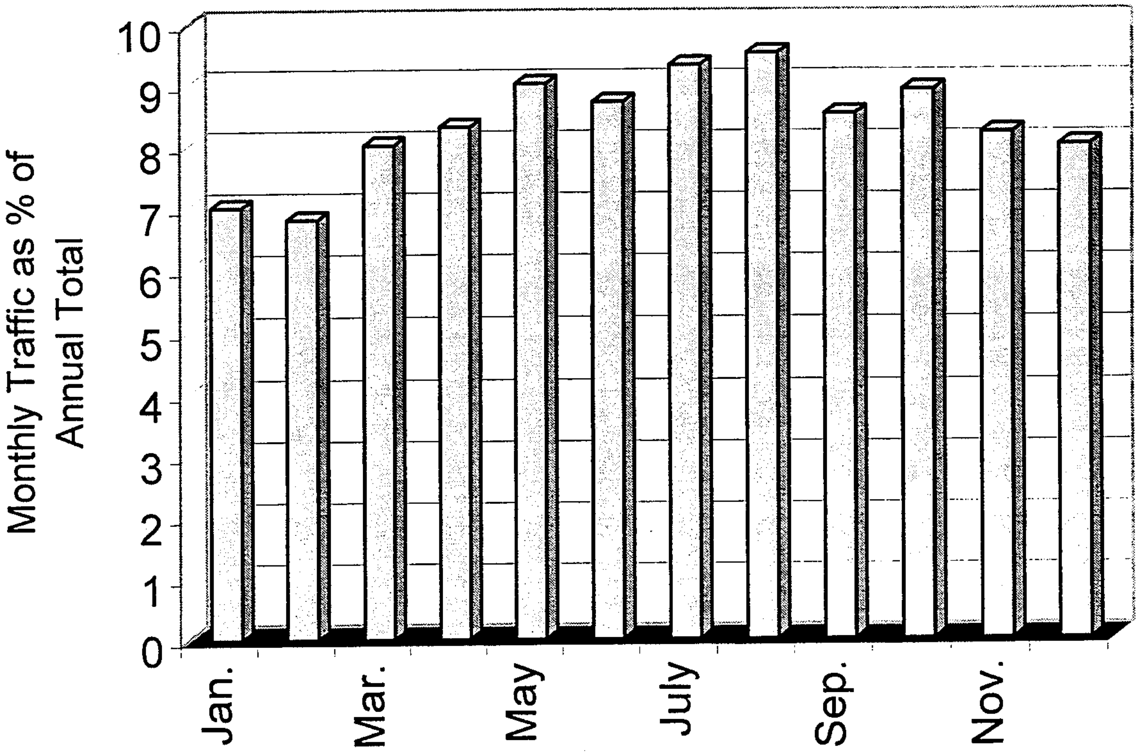

Figure 2. Monthly distribution of rural traffic in U.S.
Source: Teets, 1996.

The amount and rate of emissions from motor vehicles is dependent on the characteristics of how a particular vehicle is driven. Figure 3 is schematic representation illustrating the variation with vehicle speed of NO_x, HC, and CO emissions as described using the EPA's MOBILE model (FHWA, 1994). Figure 3 indicates that all emissions increase with speeds above 50 mph. Vehicles on rural interstates generally exhibit speeds in excess of 50 mph. Thus, large traffic volumes traveling at relatively high speeds on rural interstates can contribute significant emissions to the local atmosphere.

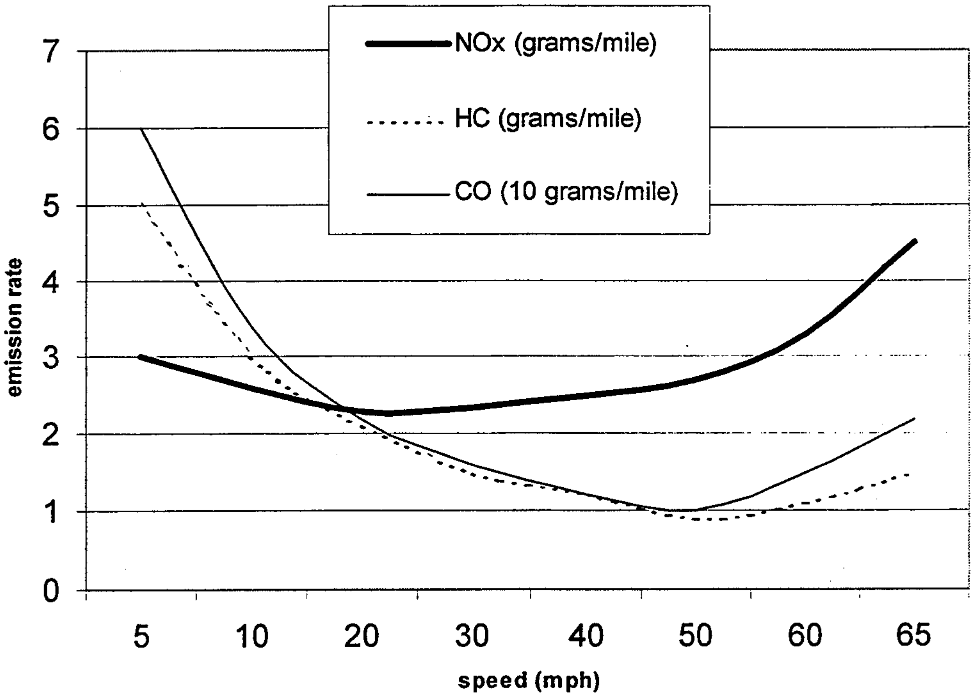

Figure 3. Variation of NO_x, HC, and CO emissions with speed. Source: FHWA, 1994.

The rate at which vehicles emit ozone precursors is dependent on vehicle speed as well as the individual components of the driving cycle. The Federal Test Procedure (FTP), developed by the EPA, is the standard method of measuring vehicle emissions (Federal Test Procedure, 1989). The FTP measures emissions over a driving cycle containing three vehicle operating states: *cold start*, *hot stabilized*, and *hot start*. These operating states characterize the various parameters involved in a vehicle engine's combustion processes relevant to operating condition. For instance, the *cold start* state is tested to gather information on the amount of vehicle emissions emitted during initial operation. The *hot stabilized* state refers to emission conditions for vehicles that have been in operation long enough to allow the engine and exhaust components to achieve normal operating temperatures. Emissions under *hot stabilized* conditions are of particular interest to the application of a rural interstate, where much of the travel consists of long distance travel and is, therefore, less influenced by vehicle start-up conditions. Within each operating state, a vehicle can be classified as participating in one of four driving modes: acceleration, deceleration, cruising, or idling. Table 3 shows the percentages of total NO_x, HC, and CO emissions emitted during the FTP test cycle for each of the four modes (Barkawi, 1997). Clearly, the majority of pollutants are emitted while vehicles are accelerating. This fact is particularly pronounced in the case of NO_x emissions. The second largest proportion of emissions for all three pollutants is contributed during the cruising mode. Traffic on rural interstates generally operates in the cruising mode with varying amounts of acceleration and deceleration governed by traffic and roadway conditions as well as individual driver characteristics. As vehicles change their speeds with roadway conditions (e.g., horizontal or vertical curvature) or change lanes and/or pass slower moving vehicles, the degree of acceleration/deceleration increases. Thus emissions of all three ozone precursors increase.

Table 3. Percentage of Emissions by Driving Mode Measured in the FTP.

Driving Mode	NO_x (%)	CO (%)	HC (%)
Acceleration	83.5	64.9	56.1
Deceleration	1.7	6.3	9.2
Cruising	12.0	24.1	26.2
Idling	2.8	5.7	8.5

Source: Barkawi, 1997.

2.2.1. Oxides of Nitrogen (NO_x)

Mobile sources emit between 31% and 48% of the total nationwide NO_x emissions (Bellomo and Liff, 1984; Nizich et al., 1994; EPA, 1996; BTS, 1998; Sawyer et al., 2000). NO_x emissions from mobile sources occur as a result of physical conditions present in an internal combustion engine that enable the chemical processes that form nitric oxide (NO) to take place. For this reason, NO_x are not particularly sensitive to changes in fuel types or chemical compositions (Schäfer and van Basshuyen, 1995). The majority of NO_x emissions from mobile sources is associated with vehicles accelerating or cruising at high speeds (Perkins, 1974; Barkawi, 1997). Such driving performance is characteristic of interstate traffic in non-congested, non-urban areas.

Generally, ambient air consists of 3.76 moles of nitrogen (N_2) for every mole of oxygen (O_2) present. The combustion process results in sufficient temperatures and pressures to allow the N_2 and O_2 in the air drawn into a vehicle's engine cylinder to combine to form two moles of NO. This phenomenon is represented by what is called the Zeldovich mechanism and is shown below as reactions *NO1* and *NO2* (Schäfer and van Basshuyen, 1995).

(*NO1*)[1] $N_2 + O \rightarrow NO + N$

(*NO2*) $O_2 + N \rightarrow NO + O$

---

[1] N_2 = nitrogen molecule, O = oxygen atom, NO = nitric oxide, O_2 = oxygen molecule, N = nitrogen atom

After the NO is emitted into the atmosphere from the vehicle's exhaust system it reacts with O_3 in the ambient air to form NO_2 which plays an important role in ozone formation (Perkins, 1974; Jenkin et al., 2000).

2.2.2. Hydrocarbons (HC)

Emissions of HC from transportation sources have been reported as accounting for as much as 40% of the total nationwide HC emissions (EPA, 1996). Numerous species of HC are emitted from motor vehicles. Motor vehicle fuels, both gasoline and diesel, are composed of a complex mixture of hydrocarbons. These hydrocarbon-based fuels are then burned to produce energy in a vehicle's engine. Fuel combustion is a chemical process that can be represented as a reaction involving reactants and products, primarily the reaction of fuel and air. The combustion of fuel can be generally represented by the following chemical reaction[2]:

$$C_nH_m + (n + {}^{n}\!/_{4})O_2 + 2(3.76\ N_2) \rightarrow (n)CO_2 + ({}^{m}\!/_{2})H_2O + 2(3.76\ N_2)$$

There are many different intermediate reactions implied in the chemical reaction above. Also, the reaction shown above implies *stoichiometric* conditions. In other words, all of the hydrocarbon-based fuel and all of the oxygen (O_2) introduced into the combustion chamber are completely expended in combustion and the reaction achieves equilibrium between reactants and products.

---

[2] C_nH_m represents a HC constituent of fuel (Schäfer and van Basshuyen, 1995)

In actuality, the progress of the combustion process is limited by chemical kinetics within the combustion chamber and does not reach equilibrium. As a result, the combustion process is incomplete. Incomplete combustion prevents some of the complex intermediate reactions from occurring or reaching equilibrium resulting in some HC species being "left over" (Schäfer and van Basshuyen, 1995). Studies have suggested that unburned fuel constitutes 50% or more of total HC exhaust emissions (Leppard et al., 1992; McLaren et al., 1996). These leftover HC species are then emitted into the atmosphere to participate in photochemical processes.

2.2.3. Carbon Monoxide (CO)

Incomplete combustion also results in vehicles emitting CO (Schäfer and van Basshuyen, 1995). The emission of CO from motor vehicles accounts for approximately 62% of the total nationwide CO emissions (Nizich et al., 1994). Gasoline-powered passenger vehicles account for the majority of CO emissions from mobile sources. Heavy-duty trucks also contribute CO. Diesel-powered heavy-duty trucks emit slightly less CO than passenger cars, whereas gasoline-powered heavy-duty trucks emit between 3 to 5 times as much CO as passenger cars (NRC, 1981).

2.2.4. Heavy-Duty Vehicle Emissions

Studies have shown that heavy-duty trucks contribute a significant portion of the overall mobile source emissions of NO_X (Nelson et al., 1991; TRB, 1995; Sawyer et al., 2000). In many cases, diesel-powered heavy trucks constitute a small percentage of total traffic volumes. On some rural interstates, however, trucks may account for as much as

20% of the total daily traffic volumes (BTS, 1998). Traffic volumes along heavily traveled rural corridors are often in excess of 80,000 vehicles per day (HPMS, 1997). Table 4 presents average daily traffic (ADT) ranges for several rural interstates in southeastern states where ozone formation is often governed by the amount of NO_x emitted locally (HPMS, 1997). Ozone levels in these rural environments, although not as high as in urban areas, may become critical in the light of the 1997 revisions to the NAAQS. In addition, truck traffic continues to increase in total vehicle-miles traveled, implying that heavy-duty vehicles have an increasingly important role in the emission of ozone precursors. Table 5 presents some nationwide interstate statistics compiled by the USDOT's Bureau of Transportation Statistics (BTS, 1998).

Table 4. ADT Ranges for Rural Interstate Sections in Southeastern States.

Interstate	States with Rural Sections	ADT Range (vpd)
I-16	Georgia	9,900 – 28,100
I-24	Kentucky, Tennessee	9,000 – 58,300
I-30	Arkansas, Texas	17,300 – 71,000
I-40	North Carolina	14,100 – 81,000
I-49	Louisiana	8,400 – 25,800
I-55	Mississippi, Tennessee, Missouri	9,500 – 58,000
I-59	Alabama, Mississippi	9,100 – 41,000
I-64	Kentucky, West Virginia	9,500 – 48,000
I-65	Alabama, Tennessee, Kentucky	16,200 – 74,000
I-75	Georgia, Kentucky, Tennessee	2,100 – 102,900
I-77	South Carolina	24,200 – 82,100
I-81	Tennessee, Virginia	25,000 –90,000
I-85	Alabama, Georgia, South Carolina	21,000 – 116,000

Source: HPMS, 1997.

Table 5. Nationwide Interstate Truck Statistics.

	1960	1970	1980	1990	1994	1995	1996
Rural interstate VMT (millions)	10,514	79,516	135,084	200,173	215,568	223,382	232,447
Rural interstate truck VMT (millions)	No data	10,069	25,111	35,789	40,034	43,351	45,697
Rural % trucks	-	12.6	18.6	17.9	18.6	19.4	20.1
Rural % annual growth in truck VMT	-	-	14.9	4.2	3.0	8.3	5.4

Source: BTS, 1998.

Studies have shown that diesel-powered heavy-duty vehicles account for greater NO_x emissions per vehicle than gasoline-powered passenger cars due to the relatively high combustion temperatures and pressures associated with diesel engines (Guensler et al., 1991; TRB, 1995; Sawyer et al., 2000). The mobile source emissions model developed by the EPA, *MOBILE5*, reports NO_x emission rates for trucks seven times greater than those of passenger cars (Schimek, 1998). Figure 4 depicts the variation of NO_x and HC emission rates with the percentage of heavy-duty vehicles in a traffic stream. These data were part of a 1988 study that demonstrated the usage of microscopic traffic simulation model to describe emissions. The emission rates shown in Figure 4 were generated for a range of traffic volumes from 1560 to 1940 vehicles per hour traveling at roughly 50 mph (Al-Omisdhy and Al-Samarrai, 1988). Figure 4 supports the evidence that heavy-duty vehicles indeed represent a significant portion of NO_x emission from mobile sources. It also reveals the increase in overall HC emissions attributable to heavy-duty vehicles.

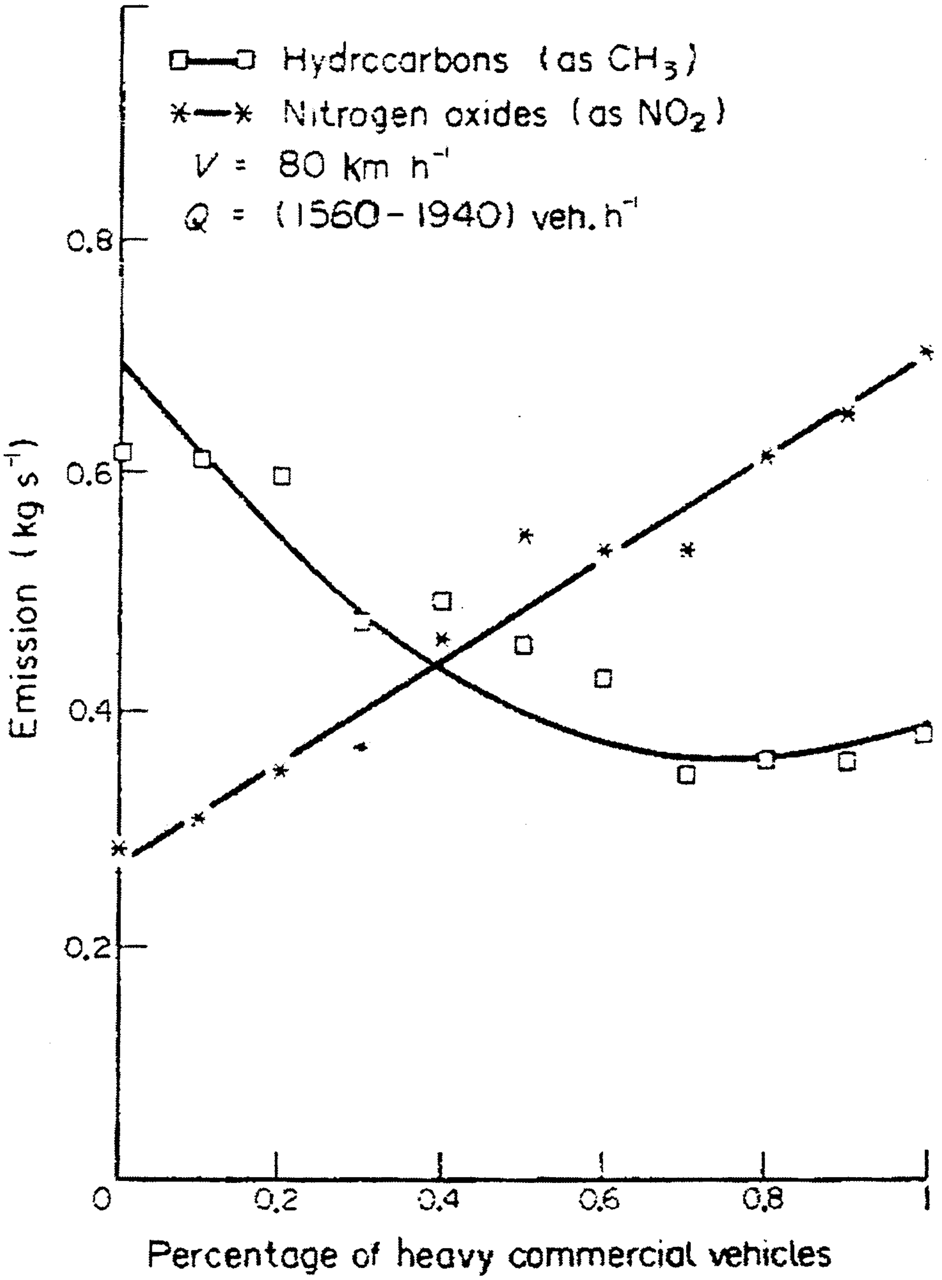

Figure 4. Relationship between HC & NO_x emissions and % heavy-duty vehicles. Source: Al-Omisdhy and Al-Samarrai, 1998.

2.3. Biogenic Emissions

Biogenic HC play a significant role in the chemistry of the troposphere and have been shown to exhibit overall regional-scale emission rates as large as those HC emitted from anthropogenic sources (Lopez et al., 1989; NRC, 1991; Chameides et al., 1992; Fehsenfeld et al., 1992; Finlayson-Pitts and Pitts, 1993; Guenther et al., 1995). Biogenic HC are highly reactive, relatively short-lived species. The most reactive biogenic HC, with respect to ozone formation, is isoprene (C_5H_8). It is a major constituent in many rural atmospheres as it is emitted directly from certain types of vegetation (NRC, 1991). Isoprene emissions are generally attributed to deciduous trees (Guenther et al., 1994). Recent research, however, has revealed other significant sources such as kudzu (Sharkey and Loreto, 1993). Kudzu is a rapidly-growing vine that is abundant in locations throughout the southeast U.S. where native vegetation has been disturbed (e.g., near roadways and interstates) (Chameides and Cowling., 1995).

Isoprene is especially common in the mid-Atlantic and southeastern United States and has been shown to be a significant precursor to ozone formation in these areas (Guenther et al., 1994; Trainer et al., 1987). Isoprene exhibits the largest global flux of any non-methane based HC (Pierotti et al., 1990). Concentrations of isoprene and its oxidation products were shown to be greatest during the summer when photochemical activity (i.e., ozone formation) is also generally at its highest levels due to the availability of solar radiation (Lamb et al., 1987). Isoprene emissions at a rural site in Alabama were shown to peak between the hours of 10:00 to 18:00 (Montzka et al., 1993). Studies at other rural locations indicate similar diurnal patterns of isoprene emissions corresponding to the hours of maximum photochemical activity (Trainer et al., 1987).

2.4. Rural Ozone Formation

Information derived from both field measurements and simulation models has revealed that ozone formation over much of the mid-Atlantic and southeastern U.S. is limited primarily by the availability of NO_x (Trainer et al. 1993; Chameides et al., 1992; Sillman et al, 1990; Jacob et al., 1995; Sillman, 1999). The limiting capacity of NO_x in ozone formation is particularly important in the rural environment where the ratio of HCs to NO_x concentrations is typically larger than those found in urban areas. The local atmosphere is referred to as "NO_x-limited" when emissions of relatively small amounts of NO_x in the presence of large HC concentrations result in increases in ozone formation (Finlayson-Pitts and Pitts, 1993; Sillman, 1999).

The rural environment is typically characterized by a NO_x-limited regime as a result of large emissions of biogenic hydrocarbons from vegetation and relatively small sources of NO_x emissions (Chameides et al., 1995). Anthropogenic sources constitute 90% of total NO_x emissions in the U.S. with the rest being attributable to natural sources such as: lightning, microbial activity within soils, and direct injection from the stratosphere into the troposphere (NRC, 1991). The primary anthropogenic sources of NO_x are the combustion processes involved in industrial and power-generation facilities as well as in transportation vehicles (Nizich et al., 1994). In many rural areas, motor vehicle traffic is concentrated along rural interstate corridors. In this case, traffic volumes may be large enough to generate NO_x emissions sufficient to form ozone in a NO_x-limited regime.

2.4.1. Ozone Chemistry

Ozone formation is an extremely complicated atmospheric process that is still not completely understood by the scientific community. The basic chemical reactions of ozone formation are shown below.

(*O1*)[3] $HO_2 + NO \rightarrow NO_2 + OH$

(*O2*) $NO_2 + h\nu \rightarrow NO + O$

(*O3*) $O + O_2 + M \rightarrow O_3 + M$

In order to examine rural ozone formation, a general understanding of the myriad chemical reactions preceding reactions *O1*, *O2* and *O3* must be developed. Of particular interest are the reactions leading up to reaction *O1* in which the hydroperoxyl radical (HO_2) is formed and made available for its reaction with NO to form nitrogen dioxide (NO_2). The NO_2 is then photolyzed in reaction *O2* to provide the oxygen atom necessary to produce ozone as shown in reaction *O3*.

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[3] HO_2 = hydroperoxyl radical, NO_2 = nitrogen dioxide, $h\nu$ = sunlight $\lambda < 420nm$, O = oxygen, M = air molecule (provides reaction energy) (NRC, 1991).

2.4.2. Role of NO_x

It has been shown that ozone in the rural southeastern U.S. is generally formed rapidly and fairly close to the source of NO_x precursors (Trainer et al., 1993). A 1993 study of the relationship between ozone production and NO_x levels in NO_x-limited rural atmospheres yielded results suggesting the potential to form 8.5 molecules of ozone for every molecule of NO_x consumed (Trainer et al., 1993). Another study used observational methods to explore the ozone-NO_x relationship in a rural atmosphere in Tennessee. The results of the regression analysis used to examine the correlation between ozone-NO_x suggested that every molecule of NO_x consumed could yield as much as 10 molecules of ozone (Olszyna et al., 1993). The significance of NO_x in ozone formation is illustrated in reaction *O1* presented in previous sections. The products of this reaction are fundamental ozone precursors, OH and NO_2 (see reactions *O1* through *O3*).

2.4.3. Role of Hydrocarbons

The primary role HC, whether anthropogenic or biogenic, play in ozone formation is the generation of important precursors, primarily HO_2. These compounds are products of the oxidation reaction of a HC with an OH-radical. In general, the oxidation mechanism for HCs can be represented by the following formulation (reactions *R1* through *R4*), where R is used to represent a generalized hydrocarbon (NRC, 1991). In actuality, HC oxidation reactions are much more complicated, vary among different HC species, and include many intermediate reactions. Nonetheless, reactions *R1* through *R4* illustrate how the HO_2 and NO_2 are formed by the reaction between a hydrocarbon and an

OH-radical. These compounds are then available to participate in the *O1* through *O3* reactions to produce ozone.

(*R1*)[4] $RH + OH \rightarrow R + H_2O$

(*R2*) $R + O_2 + M \rightarrow RO_2 + M$

(*R3*) $RO_2 + NO \rightarrow RO + NO_2$

(*R4*) $RO + O_2 + M \rightarrow HCHO + HO_2 + M$

Early work in the area of rural ozone formation indicated the possibility of ozone concentrations of 100-180 ppb in the presence of anthropogenic sources of NO_x. These early efforts indicated that the oxidation of methane, the most abundant HC in the rural atmosphere, could only account for ozone formation up to 60 ppb (Hov et al., 1978, Isaksen et al. 1978). It was later shown that introduction of anthropogenic NO_x into an atmosphere laden with non-methane based biogenic HCs could lead to ozone concentrations upwards of 100 ppb (Trainer et al., 1987).

2.4.4. Role of CO

An estimate of the atmospheric CO budget for the eastern U.S. indicated that the oxidation of isoprene is an important source of CO. It is also injected directly into the atmosphere from the exhaust systems of motor vehicles. The significance of CO in ozone formation is shown in reactions *CO1* through *CO3* [5].

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[4] RH = a general HC; R = alkyl radical formed during HC oxidation; RO_2 = alkyl peroxy radical; RO = alkoxy radical; HCHO = formaldehyde (NRC, 1991).

[5] (NRC, 1991).

$$(CO1)\ \mathrm{CO} + \mathrm{OH} \rightarrow \mathrm{CO_2} + \mathrm{H}$$

$$(CO2)\ \mathrm{H} + \mathrm{O_2} + \mathrm{M} \rightarrow \mathrm{HO_2} + \mathrm{M}$$

$$(CO3)\ \mathrm{HO_2} + \mathrm{NO} \rightarrow \mathrm{NO_2} + \mathrm{OH}$$

The relationship between CO and ozone is sufficient enough to encourage several authors to use the O_3-CO correlation as a proxy for quantifying the relative importance of anthropogenic sources in ozone formation (Fishman et al., 1987; Chameides et al., 1987, 1989). A recent study of the O_3-CO relationship at several rural sites indicated a strong correlation. Results from this study indicated O_3-CO correlations of 0.78, 0.84, and 0.57 from rural sites in Massachusetts, Pennsylvania, and Alabama, respectively (Chin et al., 1994). As mentioned previously, CO is a major constituent in mobile source emissions. Therefore, the presence of CO may be used as an indicator of vehicle emissions.

2.5. Mobile Sources and Ozone Formation

Several studies of urban ozone formation have indicated that mobile source emissions are capable of contributing to ozone levels around 120 ppbv (Winner et al., 2000; Proyou et al., 1998; Harley et al., 1997; Dunker et al., 1996). The studies cited above represent work done in urban environments and, in several cases, urban street canyons. A regional study in Barcelona presented results that indicate roadway emissions contribute to ozone formation on the order of 120 ppbv in areas well outside the city (Toll and Baldasano, 2000). Another study of ozone formation in North Rhine-Westphalian region of Germany indicated ozone levels up to 100 ppbv attributable to NO_x emissions from roadway traffic (Brücher et al., 2000).

2.6. Existing Models

2.6.1. Emission Models

2.6.1.1. Current Practice

Presently, there exists no appropriate means of modeling the potential ozone formation associated with a rural interstate. The first shortcoming lies in the state-of-the-practice for modeling vehicle emissions. In most cases, vehicle emissions are currently tabulated for area-wide or regional mobile source emission inventories. These inventories are generally conducted through the use of the MOBILE model developed by the EPA of the California Air Resources Board EMFAC model (FHWA, 1994; TRB, 1995). Estimating vehicle emissions using MOBILE involves developing a set of emission factors for each model application and applying these factors to a specific level of vehicular activity measured in vehicle-miles traveled (VMT). The emissions factors used in MOBILE are developed for each application by accounting for the ambient temperature, fuel type distributions, vehicle type distributions, and the average speed exhibited throughout the study area. These emission factors are then multiplied by the total VMT for the study area to produce emissions estimates in grams of pollutant emitted per mile of vehicle travel (FHWA, 1994).

By using average speed, the MOBILE model does not explicitly account for the differences in pollutant emissions across different driving modes (acceleration, cruising, etc.). Such an approach seems inappropriate for microscale analyses. For example, a vehicle that travels 10 miles at a steady average speed of 50 mph will emit less overall pollutants than a vehicle constantly accelerating and decelerating but maintaining a 50 mph average over the 10 mile distance. This point is particularly relevant to large trucks traveling on rural interstates through hilly areas where their speed and acceleration are affected by roadway grade.

Use of microscopic traffic simulation models allows for a detailed description of the driving cycle through resolution of speeds and acceleration rates for individual vehicles for each time step specified in the model run. These models produce what is referred to as *modal* emission rates that reflect the different emissions associated with different vehicle operating *modes* (e.g., acceleration/deceleration, cruising). CORSIM is a software package developed by the Federal Highway Administration (FHWA) to simulate traffic operations. CORSIM is based on the Traf-NETSIM model and also includes the FRESIM model. Traf-NETSIM is used for simulating traffic operations on surface streets (e.g., arterials) and FRESIM is a freeway simulation model. FRESIM is used specifically for freeway simulations in which the performance of individual vehicles is modeled to provide a detailed description of the overall traffic operations along the freeway. In addition to operational measures of performance such as speed, delay, and lane changes, FRESIM provides estimates of fuel consumption and emissions of three pollutants, NO_x, HC, and CO. FRESIM is a generalized model allowing users to specify traffic and roadway-related parameters for a particular facility to be analyzed (FHWA, 1994). There are other modal emission models currently available. Among them are the VEMISS developed by the EPA, a model developed at the University of California, Riverside, the GIS-based Mobile Emissions Assessment System for Urban and Regional Evaluation (MEASURE) developed at Georgia Tech, and the INTEGRATION model developed at Virginia Polytechnic Institute and State University (Van Aerde, 1998; Ahn, 1998). None of the above models are designed to explicitly address interstate traffic operations and emissions. INTEGRATION, like CORSIM, is capable of simulating transportation network containing both surface streets and freeways (Van Aerde, 1998). It is worth noting that the University of California at Berkeley developed the FREQ model for simulating freeway operations. FREQ estimates total vehicle emissions based on VMT and average speeds (Ahn, 1998). FRESIM is a widely accepted tool that allows for the simulation of a single freeway facility and is considered more appropriate for application to the current research than other available microscopic traffic simulation package.

FRESIM estimates emissions based on the speed and acceleration/deceleration trajectories of a vehicle at each time step during the simulation. For illustrative purposes, the assignment of emission rates for NO_x, HC, and CO to speed and acceleration from the Traf-NETSIM model are shown graphically in Figures 5, 6, and 7, respectively[6].

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[6] Traf-NETSIM is a sister software package to the FRESIM model used to analyze arterial street networks (Lieberman and Rosenfield, 1977).

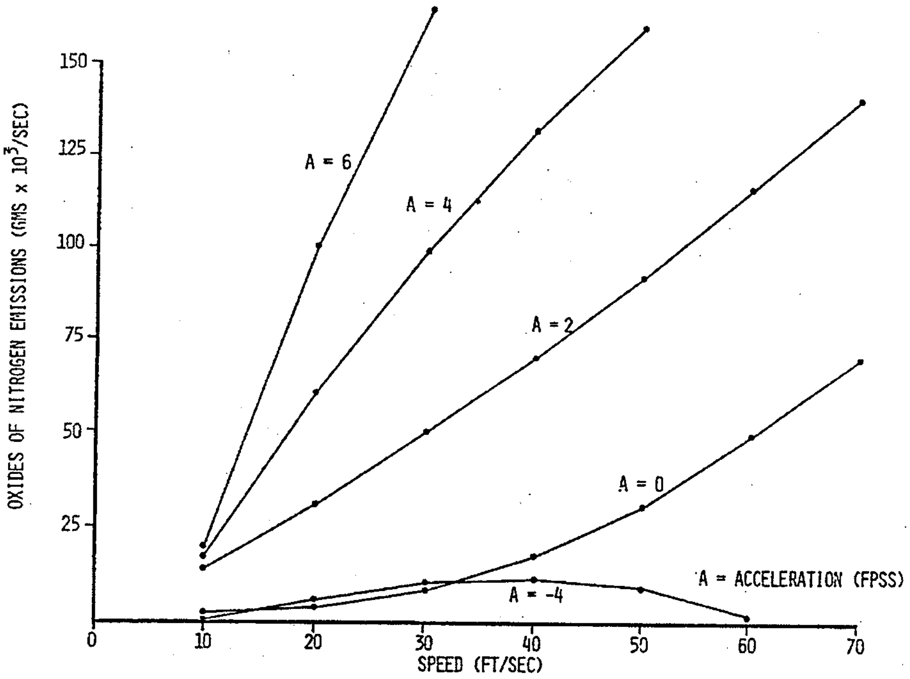

Figure 5. NO_x emission rate vs. speed for several acceleration rates.
Source: Lieberman and Rosenfield, 1977.

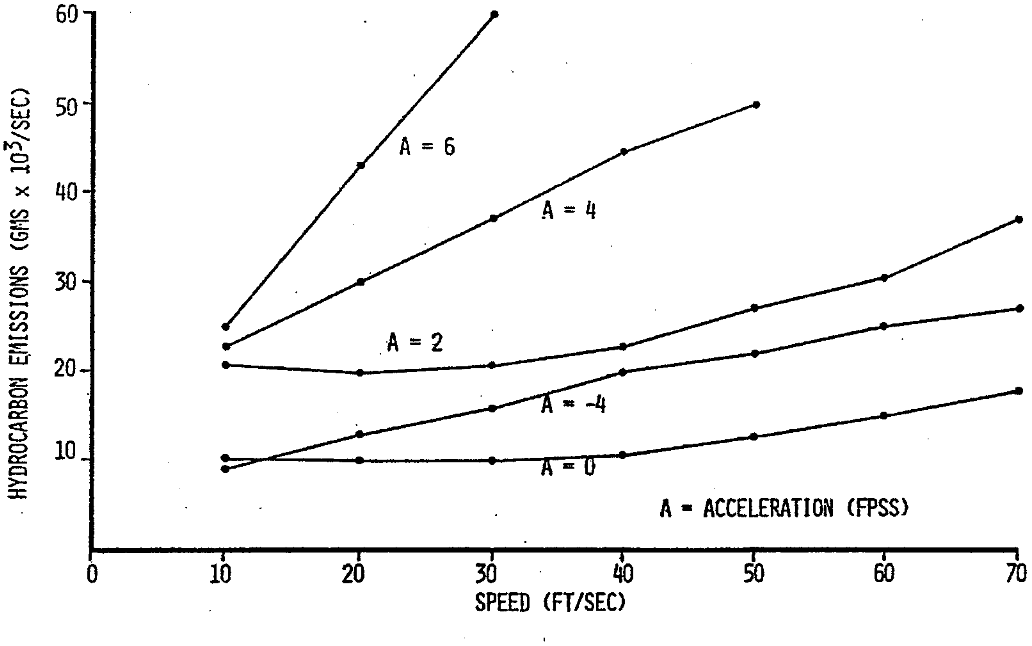

Figure 6. HC emission rate vs. speed for several acceleration rates.
Source: Lieberman and Rosenfield, 1977.

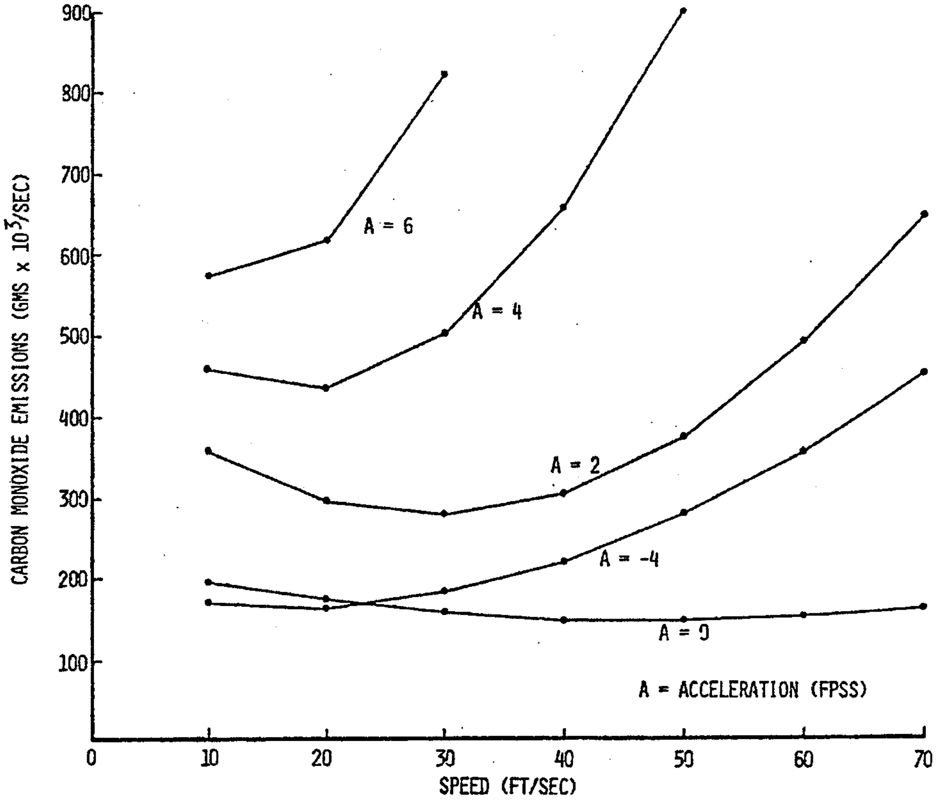

Figure 7. CO emission rate vs. speed for several acceleration rates.
Source: Lieberman and Rosenfield, 1977.

The information in Figure 5 is concurrent with other evidence that NO_x emissions increase with speed. The interesting point revealed by Figure 5 is the increase in emissions rate at increasing acceleration rates. Figures 6 and 7 support the relationship between HC and CO emissions and speeds reported previously. They also suggest a relationship between emission rates and acceleration rates. The range of speed shown in these figures is less than that generally encountered on rural interstates. Also, the emission rates reported in these curves are somewhat dated as they were derived in some of the seminal efforts at quantifying modal emission rates (Automotive Environmental Systems, 1973; Kunselman, 1974). Nonetheless, the curves reemphasize the importance of vehicle operations on the emission of pollutants.

2.6.1.2. Future Modeling Developments

In recognition of the need to more clearly define the relationship between transportation and air quality, there has been considerable effort and progress towards integration of transportation and air quality models. Recently, a team of air pollution and traffic engineering consultants was awarded a NCHRP contract to develop an integrated intersection air quality model. The proposed model will utilize the Traf-NETSIM micro-simulation model to produce emission estimates. The developers cite its ability to provide modal emissions estimates as the basis for its selection in the proposed integrated model (Smith, 1998).

The engineering and scientific communities have recently expressed concern over what was interpreted to be a gap in the body of knowledge regarding vehicle emissions, particularly those associated with heavy-duty vehicles. The U.S. Department of Energy, the Department of Aerospace and Mechanical Engineering at West Virginia University, and the Colorado Institute for Fuels and High Altitude Engine Research conduct emissions tests on heavy-duty vehicles. These program uses a mobile testing apparatus to monitor NO_x, HC, CO, as well as particulate matter and other important pollutants and has been in use across the country since 1992 (DOE, 1998). In addition, the College of Engineering Center for Environmental Research and Technology (CE-CERT) at the University of California, Riverside is active in vehicle emissions research. The results of these research efforts are intended to directly enhance the accuracy of existing emissions models such as MOBILE and FRESIM and improve the overall ability to model transportation impacts on air quality.

2.6.2. Pollutant Dispersion Models

Another limitation of existing vehicle emission models is the fact that the emissions they report are only a description of the pollutants directly emitted from vehicles (i.e., leaving the exhaust system). Pollutant emissions are given as rates (grams per unit time or distance) and are insufficient for photochemical modeling. The pollutants emitted from vehicles must be expressed in atmospheric concentrations (e.g., grams/m^3) or in mixing ratios (e.g., parts per million) in order to ascertain their relative roles in atmospheric chemistry processes. The relative concentration of each pollutant emitted from mobile sources depends on how that chemical is dispersed into the atmosphere after leaving the vehicle's exhaust system. The dispersion of each pollutant is dependent on a complex set of physical and, in some cases, chemical parameters.

The scientific principles of pollutant dispersion are well-understood and there are several types of dispersion modeling techniques currently available (FHWA, 1976; Bellomo and Liff, 1984). The current models range from detailed techniques (including limited chemistry) to describe pollutants emitted from stationary sources to rudimentary methods of describing the dispersion of relatively inert chemical species from roadway line sources. There has been considerable work in the area of line source dispersion models. Among these models are the HIWAY model developed by the EPA and the AIRPOL-4A model developed by the Virginia Transportation Research Council (Petersen, 1980; Carpenter et al., 1976). The CALINE family of models, developed by the California Department of Transportation (CALTRANS) are generally considered to be the industry standard for highway line source dispersion modeling (Bellomo and Liff, 1984; Wayson, 1999).

2.6.3. Photochemical Models

Currently there are no models used to explicitly study the relationship between transportation and ozone formation, and certainly none intended for specific application to the rural interstate environment. The majority of photochemical studies involving mobile source emissions are conducted using complex, large-scale models such as the Urban Airshed Model (UAM) (Russell and Dennis, 2000). The current state-of-the-practice for modeling ozone formation in non-attainment areas entails the use of the UAM. The UAM is a three-dimensional photochemical grid model designed to calculate the concentrations of both inert and chemically reactive pollutants. For regulatory purposes, the UAM is generally applied to simulate a past high ozone episode resulting from adverse meteorological conditions (Morris and Myers, 1990; Wu et al., 1996). As the name implies, it is generally used to analyze ozone-related phenomena in an urban environment. The UAM has been shown to exhibit deficiencies in its ability to simulate photochemical processes involving biogenic chemical species. An application of the UAM to the Atlanta non-attainment area revealed that the model substantially under predicted isoprene concentrations when compared to actual field measurements. The use of "corrected" isoprene concentrations resulted in significant increases in the model-simulated ozone concentrations in the presence of anthropogenic NO_x (Chang et al., 1996).

The EPA currently operates two atmospheric models for application to large regions. These models, the ROM and the RADM, require the use of "supercomputers" (Whitten et al., 1985; EPA, 1986). The ROM is a grid-based photochemical model designed to simulate chemical and physical processes responsible for the formation of ozone. The model is appropriate for application on scales of 1000 km, or several days of pollutant transport time. Within the ROM, photochemical processes are mathematically simulated in a 3-D grid model with horizontal resolution of approximately 18.5 km. The exact grid cell size varies as the coordinate system used is based on latitude-longitude (Lamb, 1983). The RADM, also a grid-based regional scale model, is designed to describe the atmospheric physical and chemical processes related to transport, photochemistry, aqueous chemistry and acidic deposition due to major changes in precursor emissions. RADM was developed to simulate atmospheric conditions over several days for grid-sizes ranging from 18 to 80 km. It was developed for specific application to eastern North America, from the Rocky Mountains eastward to the Atlantic Coast, including southeastern Canada (EPA, 1986; Carter and Lurmann, 1990). All of the regional photochemical models rely on VMT-based mobile source emission inventories (Russell and Dennis, 2000). Thus, detailed modal vehicle emissions are not accounted for in these models. Also, the regional models are inappropriate for specific applications, such as the current research, due to the very fact that they are such large-scale models.

There has been considerable research effort in the last ten years devoted to the study of "sub-grid" processes underlying the regional-scale activity simulated by large-scale models. These studies have focused on resolving the local effects of ozone formation within power plant emission plumes. The premise being that chemical processes at the local scale are important to overall regional pollution but are not adequately addressed at the grid scales required by the regional models (Sillman et al., 1990; Gillani and Pleim, 1996; Russell and Dennis, 2000; Liang and Jacobson, 2000; Blanchard and Stoeckenius, 2001).

2.6.4. Future Directions

In recognition of the complex nature of photochemical modeling studies, the EPA has recently released a new air quality modeling system called Models-3. Models-3 represents a comprehensive approach to photochemical modeling. The Models-3 system consists of several different modules including pollutant emissions, pollutant dispersion, and photochemical models. It is intended for regional-scale studies with a particular emphasis on urban areas. The main modeling component of Models-3 is called the Community Multiscale Air Quality (CMAQ) model. Like previous regional air quality models, mobile source emissions processing is performed using the VMT-based format embedded in EPA's MOBILE program (EPA, 1998).

2.7. Summary

The previous sections have provided a detailed description of engineering, scientific, and policy-related issues relevant to the problem of rural ozone formation. The following is a concise summary of the points revealed in the literature review.

1. The Federal government aggressively monitors and regulates the emission of pollutants from motor vehicles.

2. The EPA has recently lowered the levels of ozone pollution acceptable to State environmental authorities.

3. The new regulations apply to rural air quality to protect vegetation (natural and agricultural).

4. Motor vehicles emit three chemical precursors to ozone, NO_x, HC, and CO.

5. Motor vehicles emissions tend to increase at speeds typical of rural interstates (> 60 mph) and are at their greatest during periods of acceleration or cruising.

6. Diesel-powered heavy-duty vehicles constitute a significant portion of rural interstate traffic.

7. Diesel-powered heavy-duty vehicle are a significant source of NO_x emissions.

8. Highly photochemically reactive biogenic HC such as isoprene are common in rural areas.

9. Methane is generally the most abundant HC in the rural environment. Although not as reactive as isoprene, it may be an important ozone precursor due simply to its abundance.

10. Biogenic HC in rural areas may potentially react with pollutants emitted from motor vehicles, particularly NO, to form ozone.

11. Vehicle emissions have been shown to contribute to ozone levels around 120 ppbv.

12. Modal emission models more closely reflect actual driving conditions and therefore provide more realistic emissions estimates for microscale analyses.

13. Large-scale regional photochemical models exist. They have an inherent inability to adequately describe and account for smaller-scale phenomena.

14. Rural interstates may generate sufficient emissions, especially NO_x, to be important sources of rural ozone. There are currently no photochemical models appropriate for application to a rural interstate environment.

Chapter 3. PROBLEM APPROACH

3.1. Estimating Emissions Using FRESIM

The microscopic traffic simulation model, FRESIM, was chosen to develop emission rates from a rural interstate in the present research. FRESIM uses car-following, queue-discharge, and lane-changing algorithms to "track" the operations of individual vehicles as they travel along the freeway. During a simulation, FRESIM calculates each individual vehicle's speed and acceleration/deceleration at user-specified time intervals (e.g., once every second of simulated freeway operations) and records them as a speed/acceleration trajectory. These speed/acceleration trajectories are then used to calculate emission rates for NO_x, HC, and CO at each time-step using "look-up tables" embedded in the model (FHWA, 1994).

The look-up tables provide emission rates in grams/second over vehicle operating ranges of 10 to –10 fps^2 for acceleration and 0 to 110 fps for speed. The cells of the look-up table contain pollutant-specific emission rates corresponding to the acceleration/speed pair defining the cell's location. After FRESIM has determined a vehicle's speed and acceleration for a given time-step, it "looks-up" the appropriate emission rate (based on the vehicle's speed/acceleration trajectory) and records that value for later tabulation (McGill, 1985; FHWA, 1994; Barkawi, 1997).

In determining modal emissions, FRESIM allows the user to specify up to sixteen different vehicle types. The sixteen vehicle types are described using some combination of the seven vehicle performance indices shown in Table 6 where indices 1 and 2 refer to light-duty (LD) vehicles and 3 though 7 refer to heavy-duty (HD) vehicles (FHWA, 1994; Barkawi, 1997). LD vehicles refer to passenger cars and trucks and typically implies gasoline-powered vehicles. This capability allows for explicit investigation into the effects of trucks, which are an important component of rural interstate traffic. FRESIM allows the user to apportion the overall percentage of trucks among the four truck-related vehicle performance indices. FRESIM also specify these proportions (FHWA, 1994). For illustrative purposes, Figure 8 presents example configurations of the four truck performance indices (3 through 6) used in FRESIM.

Table 6. Vehicle Performance Indices used in FRESIM.

Vehicle Performance Index	Vehicle Performance Description
1	Low-performance passenger car (LD)
2	High-performance passenger car (LD)
3	Single-unit truck (HD)
4	Semi-trailer truck with medium load (HD)
5	Semi-trailer truck with full load (HD)
6	Double-bottom trailer truck (HD)
7	Intercity bus (HD)

Source: FHWA, 1994.

3.1.1. Current Limitations of FRESIM

FRESIM emission rates are presently based on vehicle tests performed at the Oak Ridge National Laboratory in the mid-1980s (McGill, 1985; Barkawi, 1997). The emission factors used in these models were originally compiled from a small sample of the vehicle fleet. Unfortunately, HD vehicles were not represented in the original sample. The emission factors used for HD vehicles were empirically derived from LD vehicle emission factors (Barkawi, 1998).

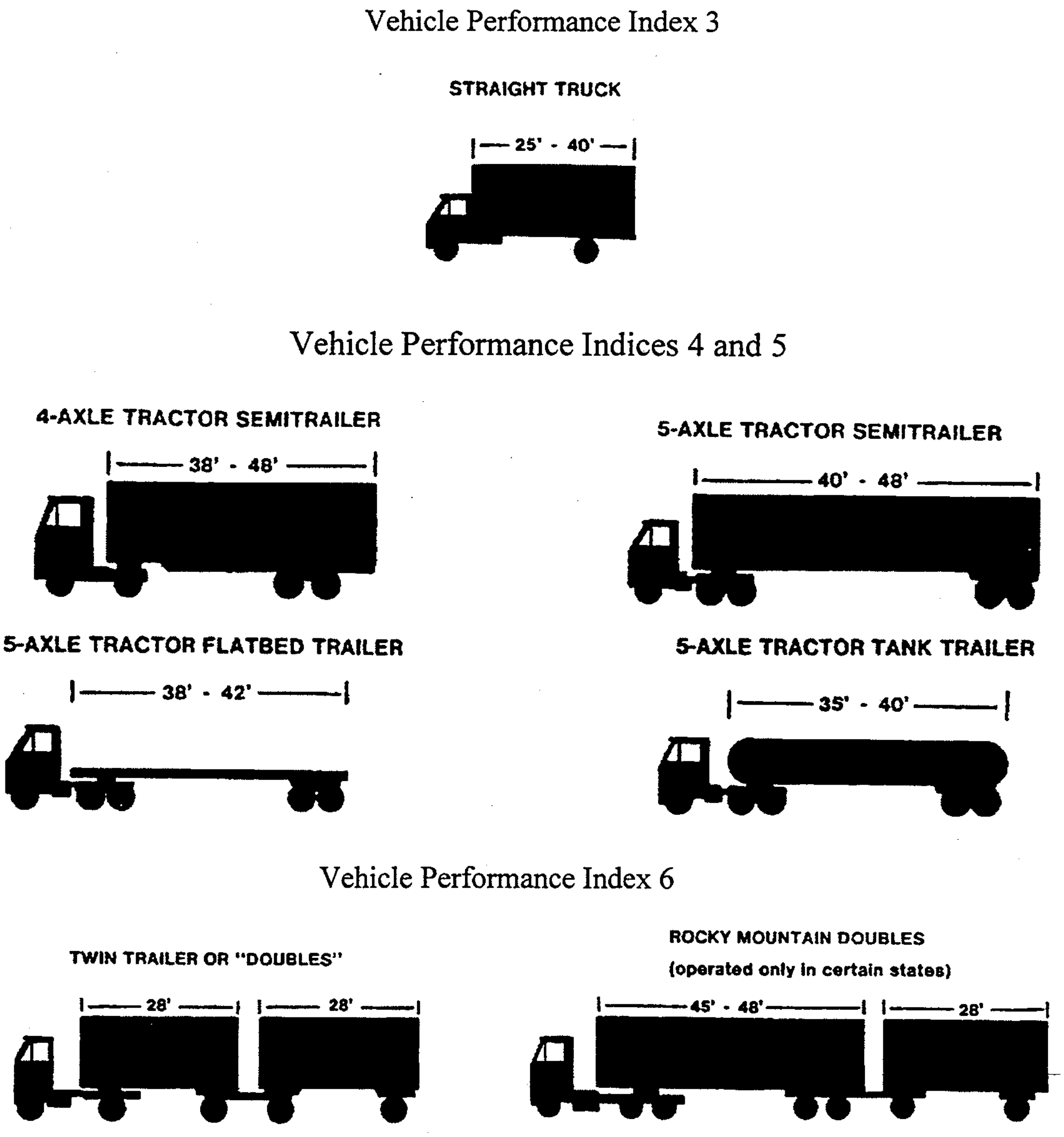

Figure 8. Example configurations of FRESIM truck performance indices. Source: Ostria, 1996.

Since the original efforts to gather vehicle emissions data for use in emissions modeling (e.g., FRESIM), there have been several studies conducted on a more recent sample of the vehicle fleet, including HD vehicles. Some of these studies have been conducted in the laboratory to test emissions under controlled conditions. Other studies have been conducted in the field to measure actual emissions from vehicles traveling along a roadway. Both the lab and field studies monitored emissions from vehicles over a broad range of speeds and operating conditions (acceleration/deceleration, grade, load, etc.). Such studies are essential to the advancement of emissions and air pollution modeling. Figures 9 through 14 summarize the emission rates published in grams of pollutant emitted per unit distance from some of the previous studies. The lower and upper bound for the emission rates are given for both LD and HD vehicles where available. Sample FRESIM results for operating conditions similar to those presented in the previous studies are shown in the figures for comparison.

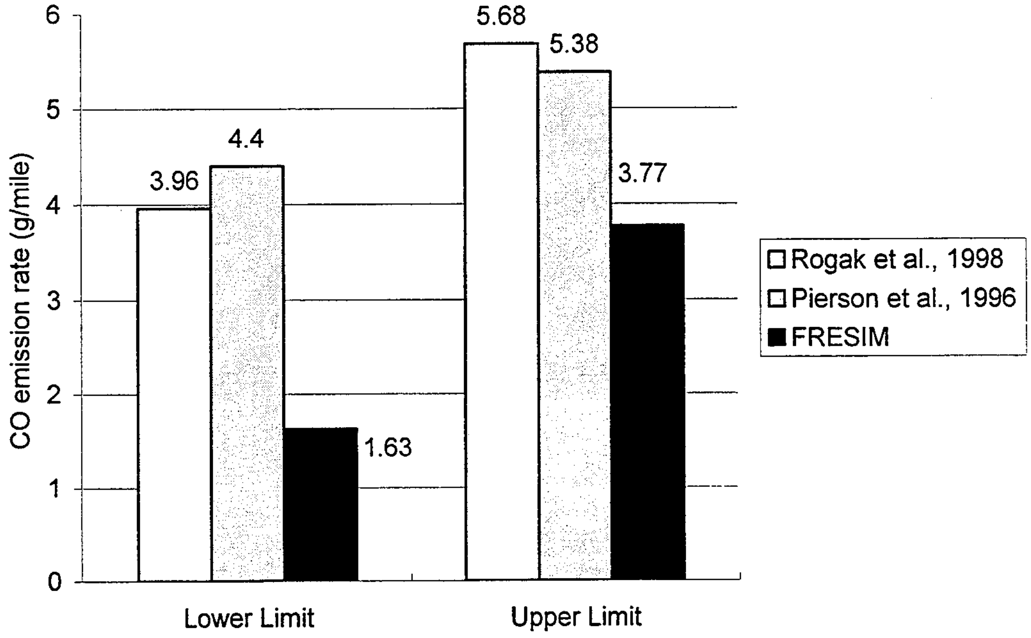

Figure 9. Measured and modeled CO emission rates from light-duty vehicles.

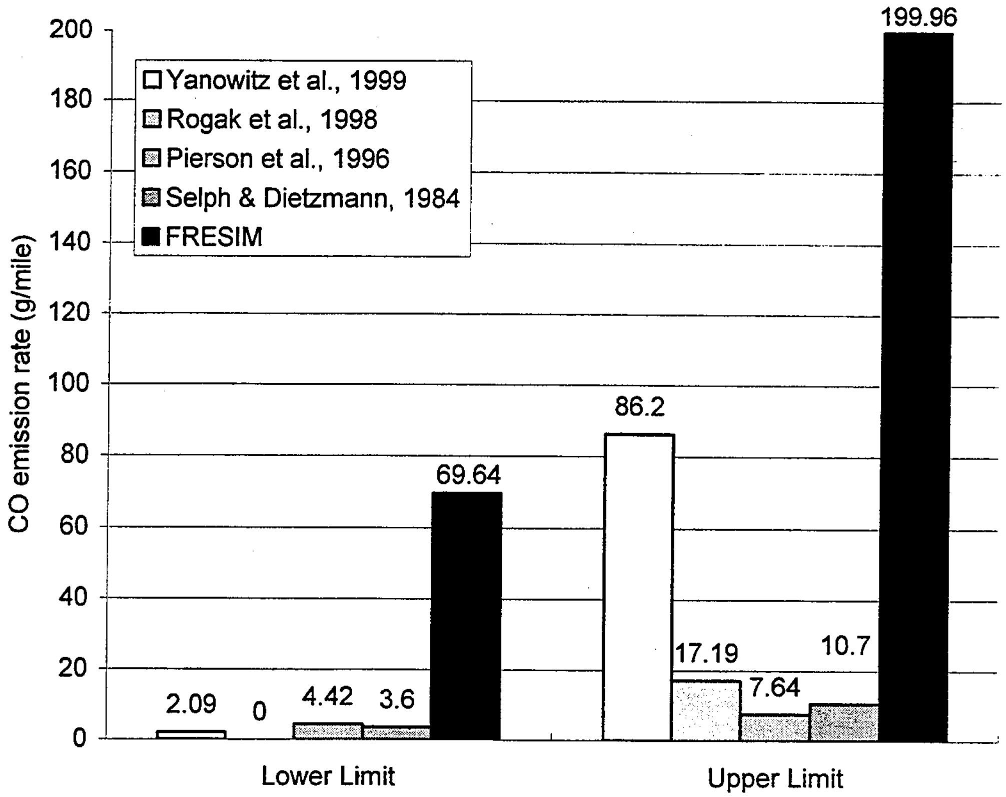

Figure 10. Measured and modeled CO emission rates from heavy-duty vehicles.

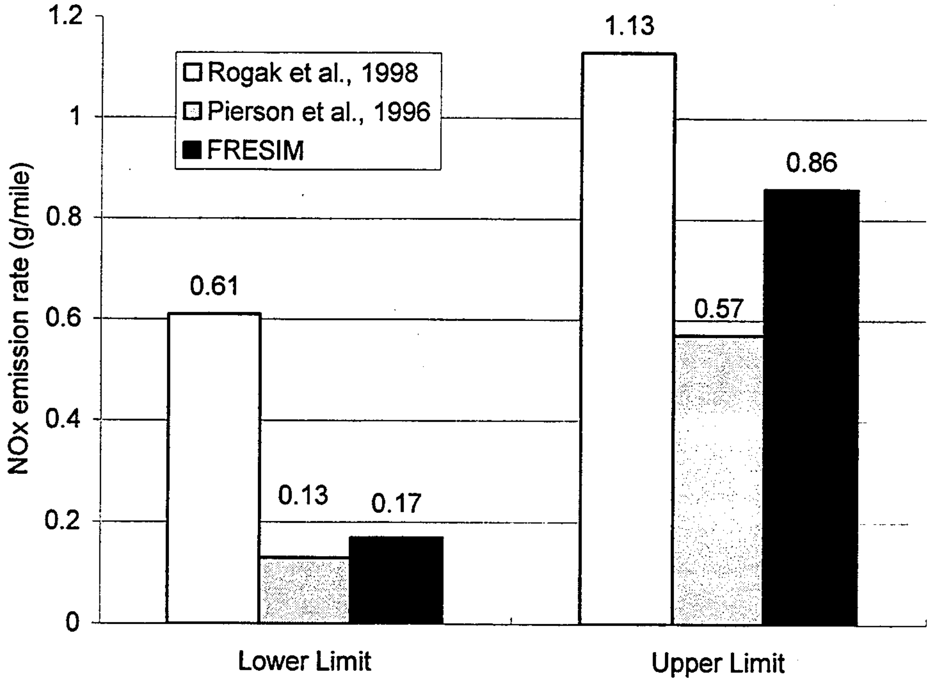

Figure 11. Measured and modeled NO_x emission rates from light-duty vehicles.

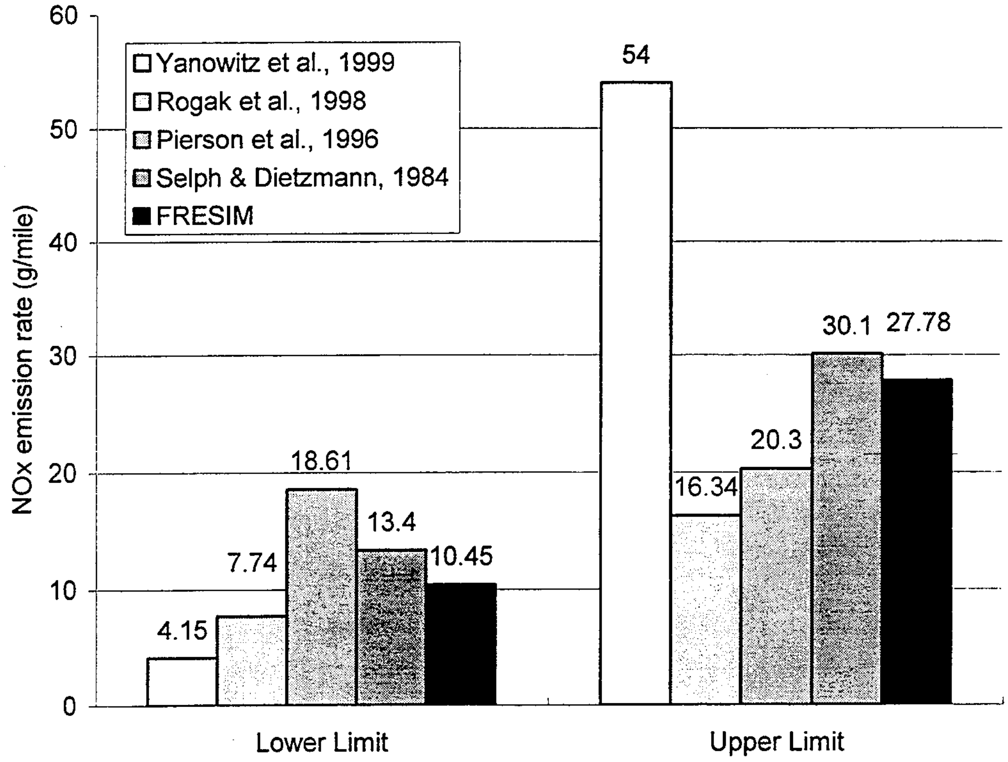

Figure 12. Measured and modeled NO_x emission rates from heavy-duty vehicles.

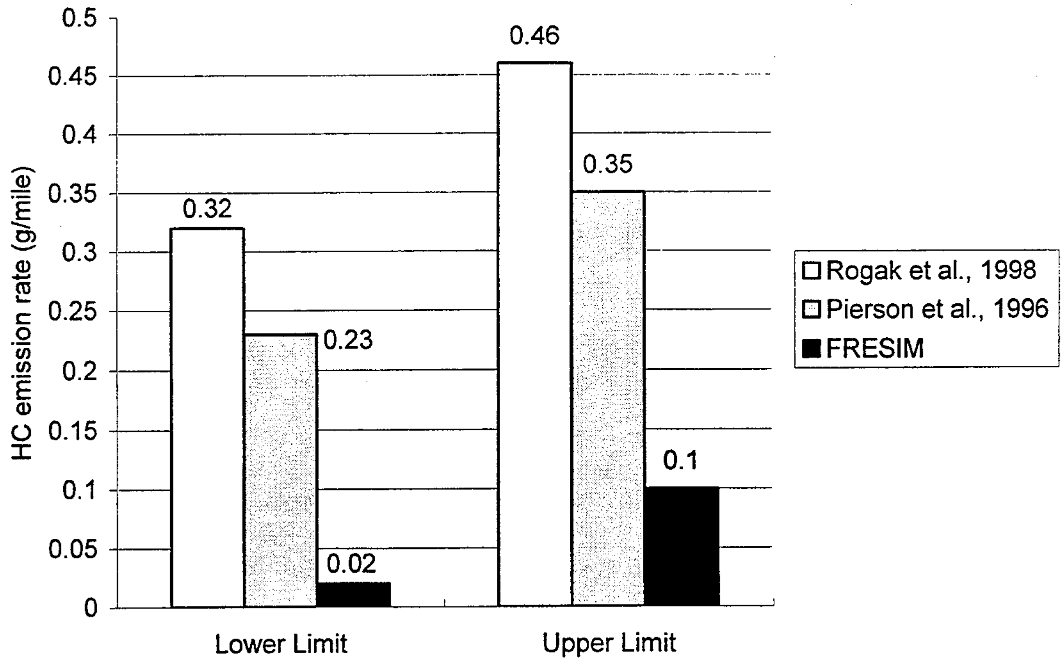

Figure 13. Measured and modeled HC emission rates from light-duty vehicles.

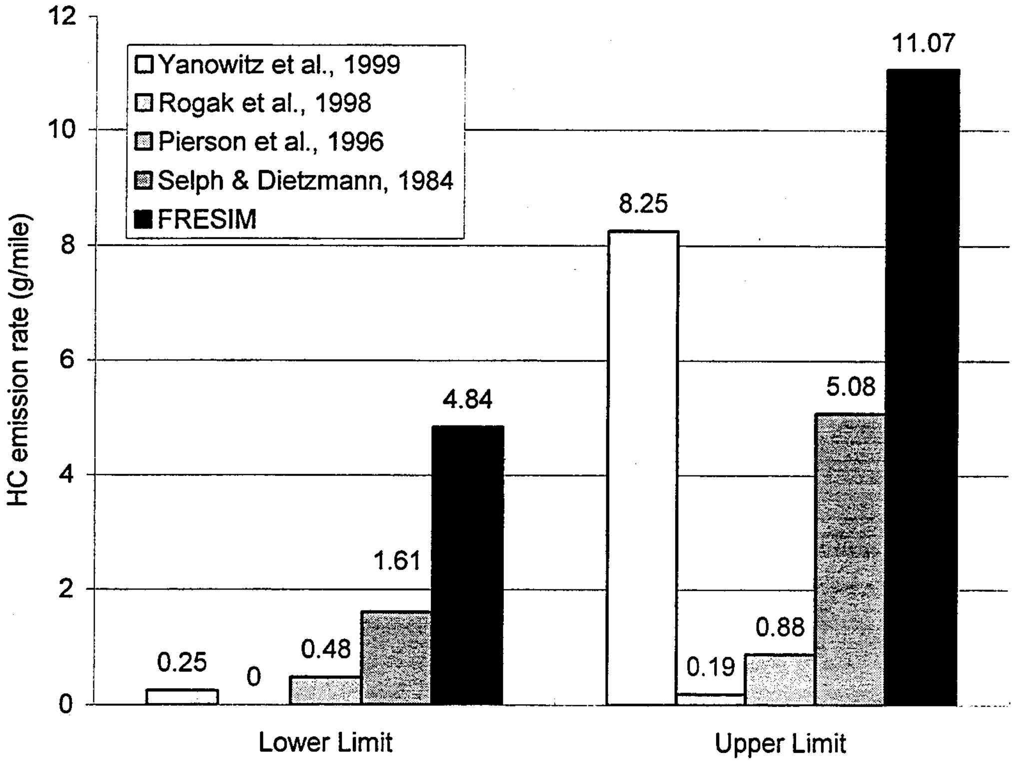

Figure 14. Measured and modeled HC emission rates from heavy-duty vehicles.

It is observed from Figures 9 through 14 that the FRESIM outputs for LD vehicle emission rates are in reasonable agreement with recent studies. The HD vehicle NO_x emission rates produced by FRESIM agree well with the published data. The HD vehicle emission rates for HC and CO, however, are much greater than those measured in the field and laboratory experiments. As previously explained, the values embedded in the FRESIM environmental look-up tables were derived from data obtained from emissions testing of six LD vehicles operating under steady-state conditions. No HD vehicles were used in the development of the original look-up tables in the FRESIM model (McGill, 1985; Barkawi, 1998). In addition, differences among the rates result from factors such as: variations in actual driving conditions, vehicle maintenance (or lack thereof), distribution of vehicle age, etc. Also, there has been progress in vehicle emission controls since the time of the original tests performed to develop the FRESIM look-up tables.

Corroboration between the FRESIM estimates and actual emission rates is needed to provide the most realistic description possible of rural interstate emissions. This is particularly important for the HD vehicle CO emissions. The FRESIM estimates for CO are generally an order of magnitude larger than the measured values. The HC emission rate estimates for HD vehicles from FRESIM are also greater than the measured values. Unrealistic estimates of HC and CO emissions may overestimate ozone production.

3.1.2. Modifications to Improve FRESIM Emissions Estimates

In an attempt to improve the accuracy of the emissions estimates produced by FRESIM, the current study examined data from HD vehicle tests performed at the Colorado Institute for Fuels and High Altitude Engine Research (Yanowitz et al., 1999) using multiple linear regression analyses. Regression analyses are often used by several researchers to correlate vehicle emissions with speed and acceleration/deceleration trajectories (Childress and Wilson, 1994; Pierson et al., 1996, Cicero-Fernandez et al., 1997; Ahn, 1998 Ho and Winer, 1998; Yanowitz et al., 1999). The majority of the research cited in the previous statement was concerned with LD vehicle emissions. Yanowitz et al focused on HD vehicle but most of the vehicles tested were not intercity freight trucks and these vehicles were tested for urban driving conditions.

For use in the current study, the emission rate of each pollutant (grams/second) was calculated from the Colorado data. The calculated emission rates were then recorded with the vehicle speed and acceleration/deceleration measured every second during testing. Emission rates, speed, and acceleration/deceleration data were complied from test runs representing two HD vehicles. This resulted in a total of 390 observations. Multiple-linear regression analysis was then used to develop equations describing the relationship between emission rate, vehicle speed, and acceleration/deceleration for each pollutant. In these analyses, vehicle speed and acceleration/deceleration were treated as independent variables determining the dependent variable, emission rate. The results of the regression analyses are summarized in Table 7. The regression coefficients of all three equations are positive. These results agree with the relationship between emission rates and speed and acceleration shown in Figure 3, 5, 6, and 7. The large coefficients for the acceleration term reflect the importance of acceleration on emissions as reported in Table 3 and shown in Figures 5, 6, and 7.

Table 7. Summary of Regression Analysis of Heavy-Duty Vehicle Emissions Data.

Chemical	Equation	R^2	F-value	Significant
HC	0.04755 SPEED + 0.3348 ACC/DEC + 5.6778	50%	197.38	Yes
NO_x	1.0382 SPEED + 12.8446 ACC/DEC + 1.9576	65%	364.07	Yes
CO	0.3661 SPEED + 30.6268 ACC/DEC + 64.5427	14%	31.21	Yes

As evidenced by their relative R^2-values shown in Table 7, the regression equation developed for CO emissions did not describe the variation in emission rates among the speed and acceleration/deceleration parameters as well as the equations developed for NO_x and HC. According to the F-statistic computed for each equation, however, the equations developed can be concluded to be “useful” but fall short of fully describing the relationship between emission rate and speed and acceleration/deceleration (Devore, 2000). The regression equations were then used to develop new FRESIM look-up tables. Speed values from 0 to 100 fps and acceleration/deceleration values from –10 to 10 fps^2 were input into the equations to calculate new emission rates (grams/second) for the FRESIM look-up tables. Additional FRESIM runs were simulated using the HD look-up tables developed in this research from the regression analysis of the Colorado data. The new emission rates are compared to the published studies as well as the original FRESIM estimates in Figures 15 through 17.

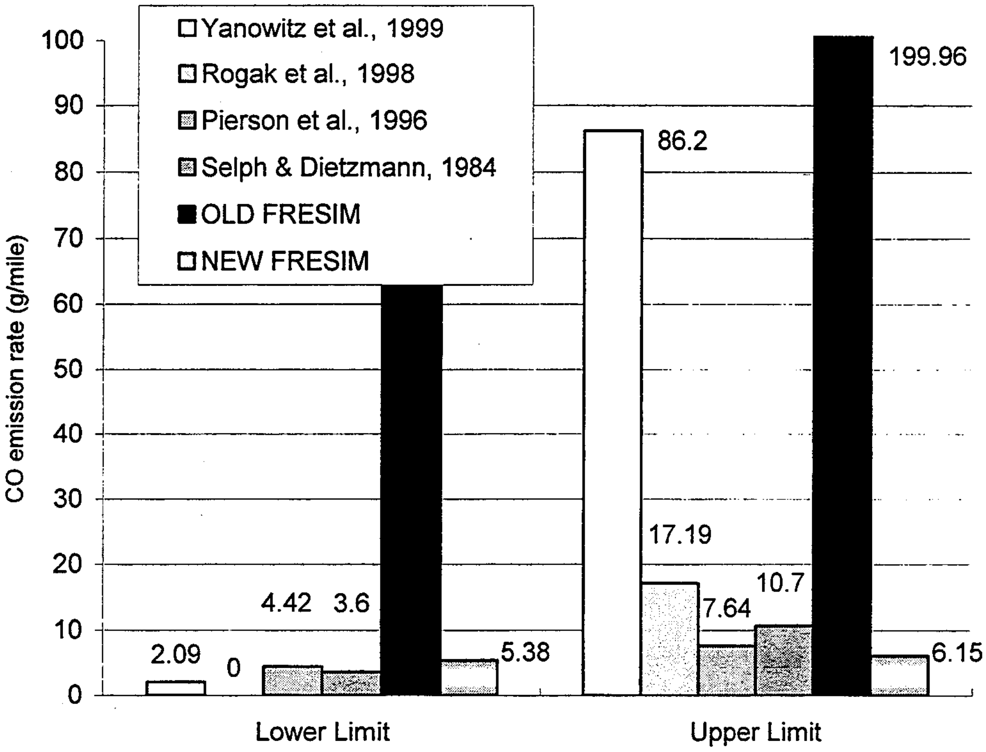

Figure 15. Comparison of modified CO emission rates from heavy-duty vehicles.

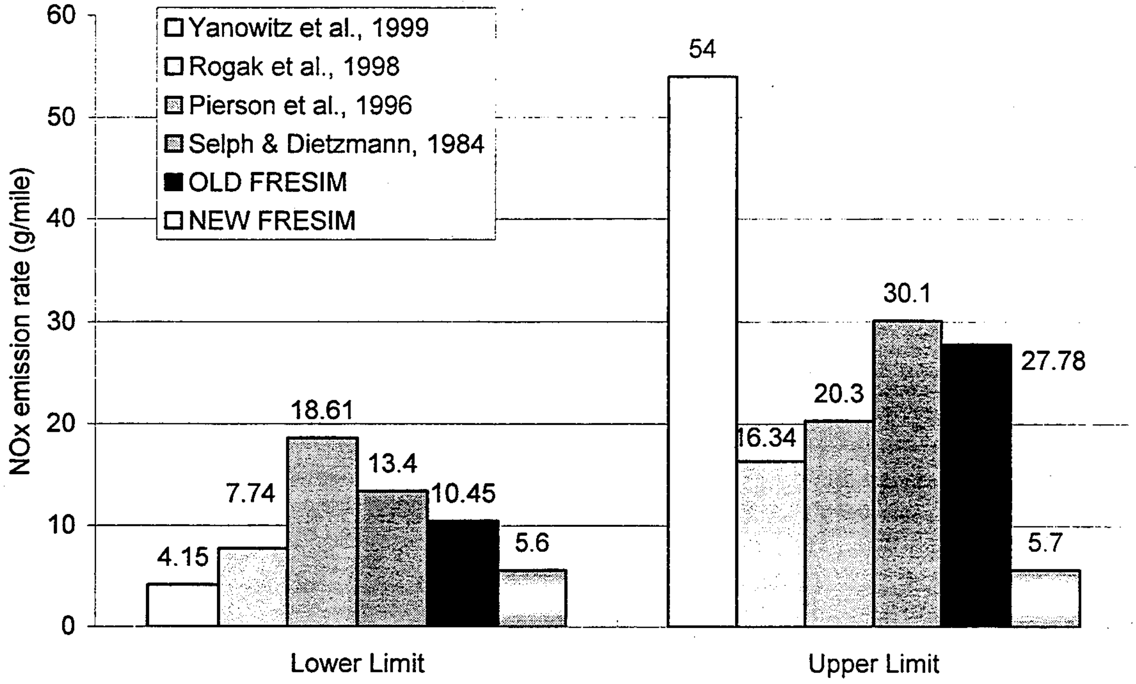

Figure 16. Comparison of modified NO_x emission rates from heavy-duty vehicles.

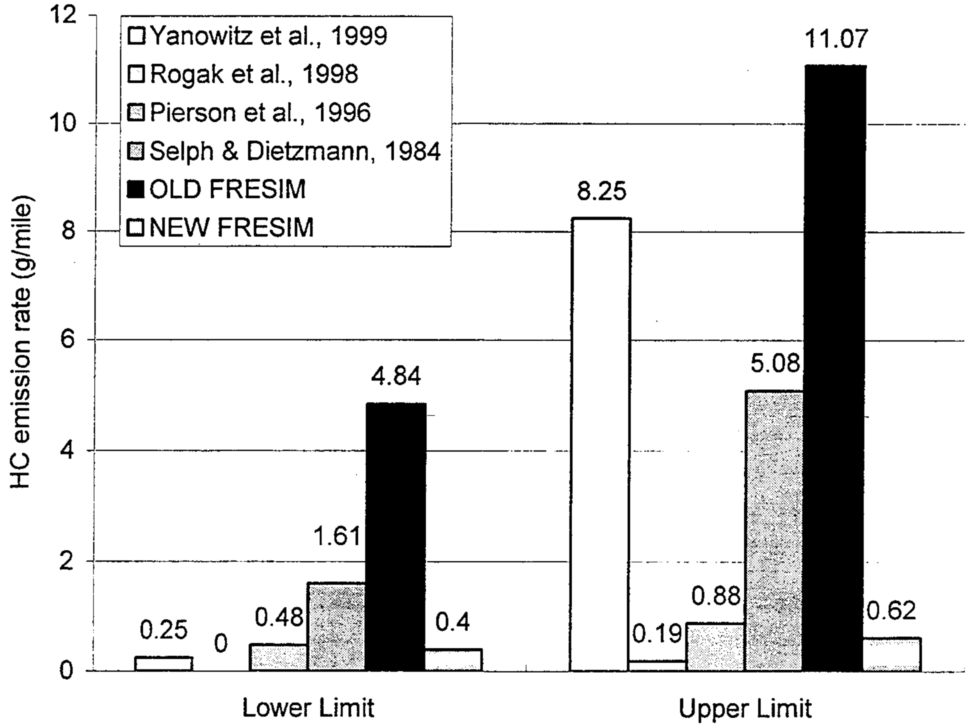

Figure 17. Comparison of modified HC emission rates from heavy-duty vehicles.

Although the regression equations did not describe the relationship between emissions and the speed and acceleration/deceleration trajectories well (i.e., low R^2), particularly for CO, some improvement in FRESIM's ability to produce representative HD emission estimates was realized. As seen from Figures 15 through 17, the look-up tables developed in this study provide emission rate estimates that resemble the results from recently published studies more closely than the original FRESIM data. It is of particular interest that the new emission rate estimates were most similar to those measured in the Tuscarora Mountain Tunnel Study since data from this study is used in another part of this research as described in the following section (Pierson et al., 1996).

The primary reason for the lack of statistical correlation shown for the regression results is the limited sample size. Although 390 observations were used, these observations were recorded for only two individual vehicles. The observations used represent the variability of emissions among speed and acceleration trajectories at each second for the two HD vehicles as tested over a specified driving cycle. Thus, there may have only been a few measurements for any given speed/acceleration trajectory. A larger sample size of vehicles and longer driving cycles would have provided more emission rate data points for each speed/acceleration trajectory and would likely have resulted in better R^2-values. The fact that data from only two HD vehicles were used also limited the robustness of the relationships developed in the regression analyses. As developed, the relationships do not account for any variability among different vehicle characteristics (age, mileage, control technologies, fuel type, etc.) reflected in the numerous vehicle represented in the tunnel studies such as those conducted by Pierson et al.

Regardless of the statistical significance (or lack thereof) of the relationships, Figures 15 and 17 clearly indicated that the updated FRESIM emission estimates are an improvement over the original estimates. The NO_x emissions rates developed herein appear to be low (Figure 17). The driving cycles used in all the tests reported in the Figure 15 through 17 reflect urban driving conditions where acceleration rates would be accepted to be higher and speeds lower. Studies have shown the dependence of NO_x emissions on acceleration rate and this fact is correctly reflected in by the regression coefficients as described above (Perkins, 1974; Lieberman and Rosenfield, 1977; Barkawi, 1997; Sturm et al., 1997). The acceleration rates associated with high speed operations on freeways are generally much lower than those associated with urban (stop-and-go) driving. The NO_x emission rates predicted herein, then, would be expected to lower than those measured and predicted for urban driving cycles. The NO_x regression equation exhibited the best R^2, 65%, of the three equations developed. The NO_x emission rates predicted by the regression equation were also lower than those measured by Pierson et al for the rural interstate through the Tuscarora Mountain Tunnel. Pierson et al measured emissions from a much larger sample size reflecting different vehicle characteristics. Again, a larger sample of data would have greatly improved the predictive capabilities of the emission equations developed herein. The overall modeling procedure used in the present research allows for the incorporation of larger sample sizes as they become available. Further efforts to update and refine the FRESIM look-up tables are suggested but were not the intended focus of this study.

Additional details from the FRESIM simulations are presented in Figure 18. Inspection of Figure 18 supports previous statements regarding the composition of emissions from LD and HD vehicles. Figure 18 indicates a strong correlation between the amount of NO_x emissions and HD vehicle traffic as evidenced by the fact the curves for these two values exhibit very similar shapes over the simulation period. Similarly, the CO emissions curve strongly resembles the LD vehicles curve indicating a correlation between the two. These results are expected since LD vehicles are typically gasoline-powered and emit more CO than do diesel-powered engines (generally associated with HD vehicles).

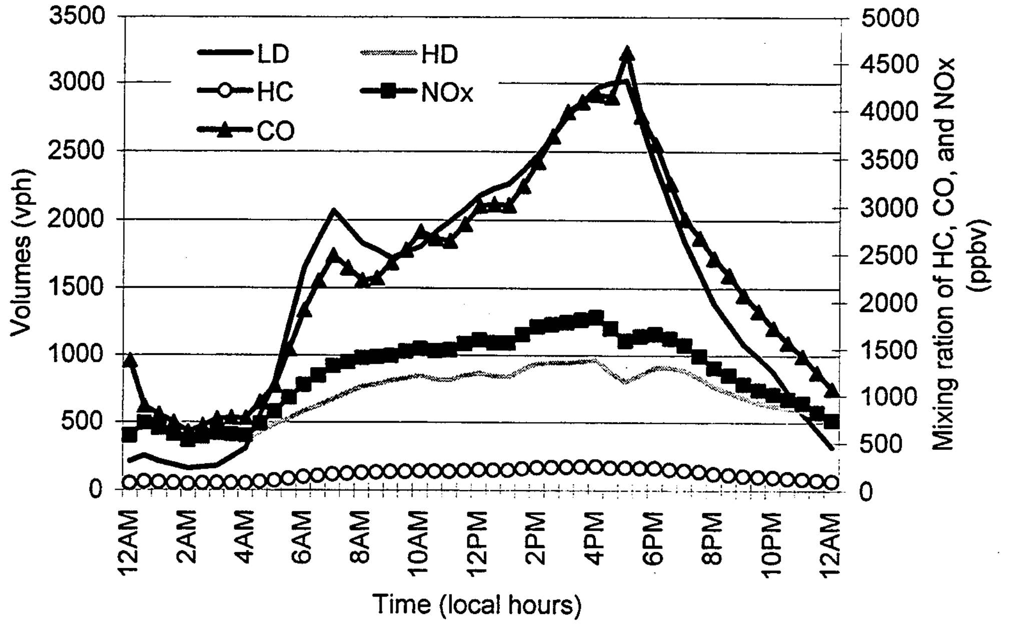

Figure 18. Volumes versus emitted CO, HC, and NO_X.

3.1.3. Accounting for the Stochastic Nature of FRESIM

FRESIM is a stochastic model in that the arrival distribution of vehicles, lane distribution of vehicles, and the distribution of different vehicle types within a simulation period is random. The value of a modal emissions model such as FRESIM is the fact that it accounts for the effect of driving mode, particularly acceleration, on emissions. This fact was evidenced in the results of the regressions analyses presented above and was shown for the Traf-NETSIM model in Figures 5 through 7. Since acceleration has such an effect on emissions, it is logical to conclude that factors affecting acceleration would affect emissions. One factor affecting vehicle acceleration along an interstate section is the interaction among vehicles traveling at different speeds, changing lanes, and passing slower moving vehicles. The random distribution of vehicle arrivals and vehicle types in the FRESIM model results in a stochastic effect on acceleration among vehicles during a simulation period. FRESIM allows the initial distribution of its stochastic variables to be controlled by the input of a “random seed.” FRESIM allows a default value for the random seed or allows the user to modify the random seed to change the initial distribution of stochastic variables (FHWA, 1994).

The default random seed was used in the FRESIM simulations conducted for the present research. In order to examine the effects of the stochastic nature of FRESIM, several test simulations were done using the same traffic input data while arbitrarily varying the random seed among runs. Some slight variation in the vehicle volumes and densities occurred as a result of varying the random seed. These variations, however, produced no discernible change in the resultant atmospheric mixing ratio of emitted pollutants.

The results indicated virtually no change in grams/mile emission rates estimated by FRESIM. FRESIM reports pollutant emission rates at the end of each simulation time step as a cumulative average grams/mile emitted per vehicle for each of the specified vehicle types. While varying the random seed would be expected to affect the distribution of vehicle arrivals and types, the fact that the emission rates are reported as cumulative averages masks any changes in speed and acceleration/deceleration distributions over the course of a simulation period. In other words, varying the random seed affects the distribution of the speed and acceleration/deceleration trajectories used to determine the emission rate at each time step during a simulation, but the cumulative average emission rate is then reported over all time steps during a simulation period.

Thus, the emissions estimates produced by FRESIM do not have sufficient resolution to be significantly affected by the stochastic variations used to describe traffic operations in FRESIM.

3.2. Chemical Speciation of HC Emissions

There has been considerable experimental and analytical effort expended to determine the specific chemical composition of vehicle emissions. In particular, a series of experimental tests to monitor actual vehicle emissions in roadway tunnels has provided a great deal of information on this subject. In these field tests, gas-sampling sites were set up inside the tunnels to collect samples of the exhaust gases emitted from passing vehicles. Chemical analysis techniques such as gas chromatography were then used to determine the specific chemical species present in the ambient exhaust gas (Pierson et al., 1996). These types of studies have resulted in the development of data sets that characterize the chemical speciation of HC emissions from vehicles in the immediate vicinity of a roadway.

Studies relevant to the present research, with respect to traffic and roadway conditions, were reviewed to determine which chemical speciation regimes was most appropriate for application to vehicle emissions from a rural interstate. The chemical speciation data from the Tuscarora Mountain Tunnel was chosen for application to the present research. The Tuscarora Mountain Tunnel was identified as being along a rural interstate in Pennsylvania. The tunnel exhibited grade of less than ± 0.30% through its eastbound and westbound legs. Each leg of the tunnel contains two lanes. The HC emissions data were collected over an 11-hour period over which 5,928 vehicles passed through the eastbound leg of the tunnel. The percentage of heavy-duty vehicles observed over the emissions sampling period varied between 6% and 80% with an overall average of 18%. Light-duty vehicles exhibited an average speed of 59.4 mph over the sampling period while heavy-duty vehicles exhibited an average speed of 54.0 mph (Pierson et al., 1996).

The Tuscarora study analyzed HC sampled from the tunnel to identify individual HC species. The present study derived emission rates (grams/mile) of individual HC species as a percentage of total HC emission rates and then grouped them into categories suitable for photochemical modeling. The HC speciation and percentage of emissions for light- and heavy-duty vehicles are presented in Figure 19. The calculated percentages were applied to the overall HC emission rates calculated by the FRESIM model to estimate the emission rate of individual HC species for use in the photochemical model.

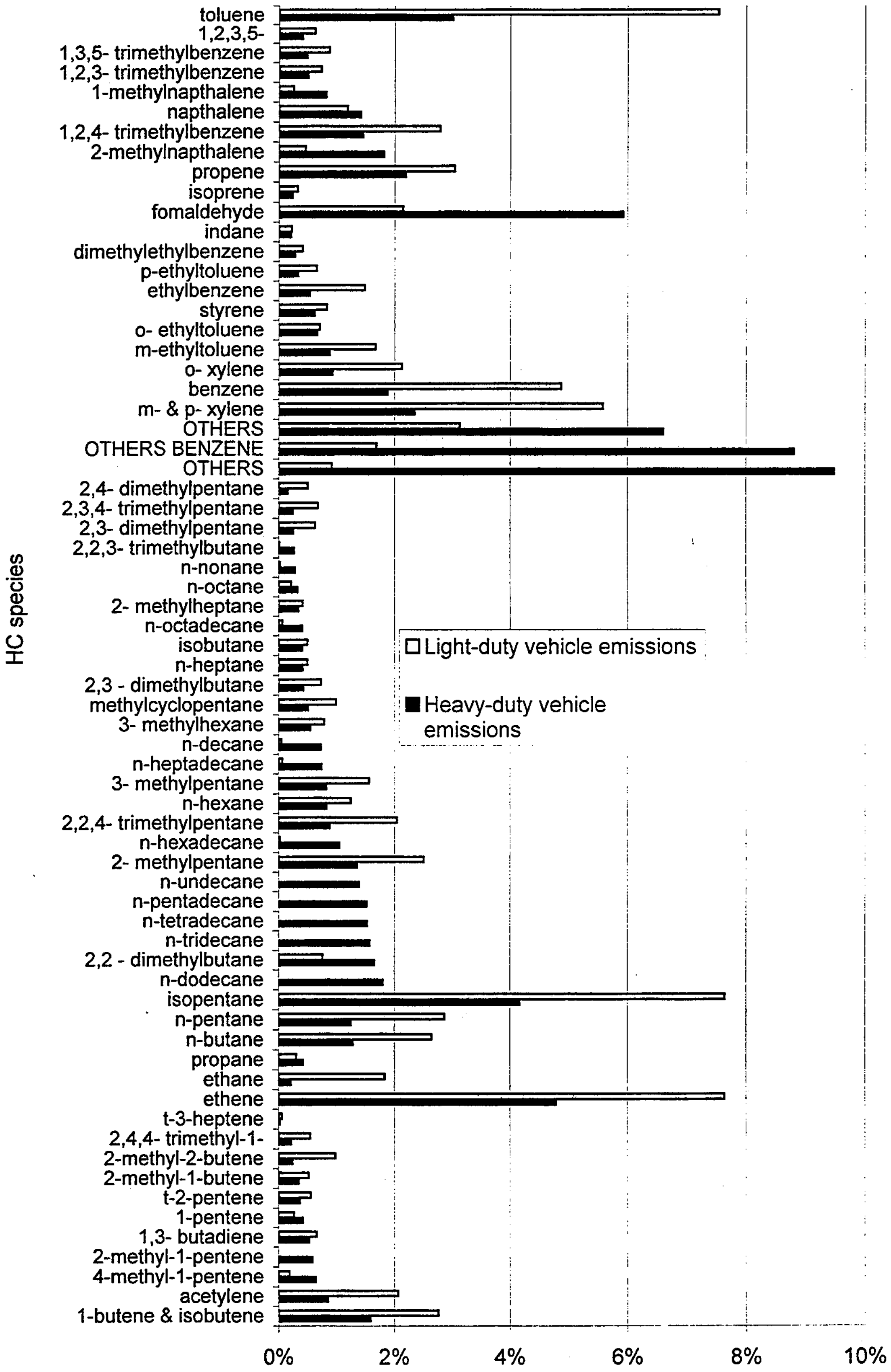

Figure 19. HC species percentages by vehicle type.

3.3. Emissions Dispersion

The emission estimates produced by FRESIM represent only the rate at which pollutants are directly emitted from vehicles. For use in the photochemical model, the vehicle emissions were required in atmospheric concentrations (mixing ratios). The literature review revealed several estimates and methodologies for determining pollutant dispersion from and within a traffic stream (FHWA, 1976; Bellomo and Liff, 1984; Papacostas and Prevedouros, 1993; Masters, 1998). A box model formulation was chosen to describe the dispersion of vehicle emissions after being emitted from the vehicle (Papacostas and Prevedouros, 1993; Masters, 1998). A schematic representation of the box model formulation is presented in Figure 20.

The rate of vehicle emission into the box model are converted to atmospheric concentrations (g/m^3). The concentrations were then converted to atmospheric mixing ratios. The units of atmospheric mixing ratios used throughout this research is parts per billion (ppbv) and refers to the number of volumes of an individual pollutant in 10^9 volumes of air (Masters, 1998). The mixing ratio was calculated using the molecular weights of each pollutant and the Ideal Gas Law[7].

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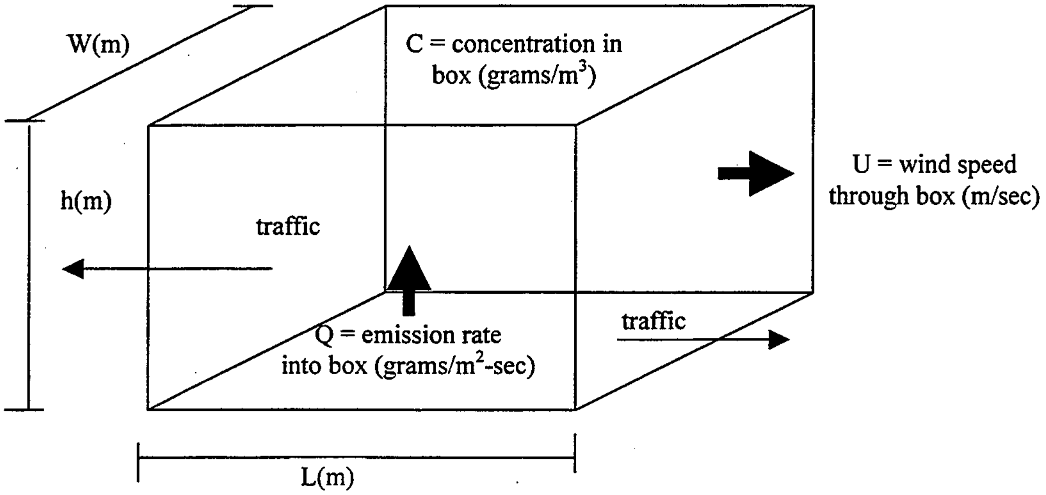
[7] For simplicity, standard conditions (298 K and 1 atm) were assumed in mixing ratio calculations.



$$C = \left(\frac{QL}{Uh}\right)\left[1 - e^{-\left(\frac{Ut}{L}\right)}\right]$$

Where;

W = width of box over roadway (m);

h = height of mixing cell (10 m);

L = length of box over roadway (m);

U = mean wind speed through box generated by turbulence from traffic (6 m/sec);

Q = emission rate per unit area (grams/m^2-sec); and

C = resultant concentration in box for each pollutant species (g/m^3).

Figure 20. Formulation of box model for dispersion of vehicle emissions.
Source: Papacostas and Prevedouros, 1993; Masters, 1998.

The height of the box was assumed to be 10 meters. The 10-meter height was chosen from data published in a recent study of the effects of vehicle-generated turbulence on exhaust gas dispersion and accounts for large trucks traveling at highway speeds (Karim and Hiroshi, 1998; Karim et al., 1998). The assumption of a uniform mixing within the box model is a common simplification referred to as a *Complete Mix Box Model* (Masters, 1998; Sportisse, 2001). The complete mix box model assumption is simply an idealization that the concentration of pollutants within the box is uniform. Assuming a complete mix box model within the effect of vehicle wakes is supported by published results from field tests conducted at the General Motors Milford Proving Ground (Sedifan et al., 1981). Dispersion of pollutants above the 10-meter mixing cell was then modeled according to the atmospheric parameters described in the photochemical model (Makar et al., 1999).

The mean wind speed used in the box model was assumed to be 6 m/sec. This value is intended to represent the total effects of the ambient wind and the turbulence generated by traffic passing through the box. It was considered to be a reasonable assumption for relatively fast-moving interstate traffic. Karim et al. showed resultant wind speeds in the microenvironment of the roadway to range from 1 m/sec to almost 20 m/sec depending on vehicle size distribution, traffic speed, and the angle (relative to the direction of traffic flow) at which the ambient wind crosses the roadway. In general, the wind speed in the roadway microenvironment increased with vehicle size and speed as well as wind angle to the roadway (Karim et al, 1998).

3.4. Evaluation of Emission Estimates

Prior to any photochemical modeling, it was necessary to evaluate whether or not the emissions estimates produced in this research were reasonable. The assumptions made during the development of the emissions estimates are summarized below.

- The original FRESIM look-up tables for passenger car emission rates were considered reasonable and maintained in this study.
- The heavy-duty vehicle look-up tables in FRESIM were modified using laboratory measurement data obtained from the Colorado Institute for Fuels and High Altitude Engine Research.
- The dispersion (atmospheric mixing) of vehicle-emitted pollutants was described using a box model formulation over the length and width of the simulated interstate section. It was assumed that atmospheric mixing inside the box was uniform due to vehicle-induced turbulence. The uniformly mixed cell was assumed to extend 10 m above the roadway.
- The resultant, traffic-induced wind speed inside the box was assumed to be 6 m/sec.

Review of the literature indicated that the results produced using the box model formulation presented herein appeared reasonable when compared with emissions estimates reported from other modeling studies and field measurements. The vehicle-emitted pollutant mixing ratios estimated in the current research and those reported in previous studies are summarized in Table 8. Proyou et al. measured and modeled CO emissions in a 15 meter tall by 25 meter mixing cell in an urban street canyon in Athens, Greece. The CO mixing ratios reported by Proyou et al. are higher due to relatively large traffic volumes (1,200 - 4,000 vph) of predominately LD vehicles. Pierson et al. measured as much as 6000 ppbv CO at a rural interstate location with less LD vehicle traffic (Pierson et al., 1996). The Pierson et al. CO results more closely reflect the CO estimates produced in the current research that reflect less LD vehicle traffic as well. The NO_x mixing ratios reported in Proyou et al. relate to the absence of large trucks in the urban setting (Proyou et al., 1998). Jimenez et al., however, explictly measured NO_x mixing ratios in the wake of large trucks by remote sensing (Jimenez et al., 2000). The results from Jimenez et al. supported the earlier assertion than the NO_x emission estimates produced in the current research are slight underestimated. It was concluded from the comparison with these studies and other evidence in the literature that the estimated mixing ratios of vehicle-emitted pollutants produced in this study were suitable for the purposes of the present research.

Table 8. Comparison of Emission Estimates with Results from Previous Studies.

	Pollutant mixing ratios					
	CO (ppbv)		HC (ppbv)		NO (ppbv)	
Study	Low	High	Low	High	Low	High
Current research	614	4,814	47	194	524	1,931
Proyou et al. (measured)	4,000	16,000	15	130	120	600
Proyou et al. (modeled)	4,000	15,000	10	95	90	500
Pierson et al.	N/A	6,000	N/A	N/A	N/A	N/A
Jimenez et al.	N/A	N/A	N/A	N/A	567	3,672

3.5. Photochemical Modeling

3.5.1. Description of Photochemical Model

An existing photochemical model was used to explore the relationship between emissions from rural interstate traffic and ground-level ozone formation. The existing model was originally developed to simulate ozone formation above and within a remote forest canopy away. The forest site, the measurement techniques, and the model are described in by Makar et al. (1999). The model simulates the emission, atmospheric dispersion, and photochemical processes of ozone precursors from natural sources. It is a one-dimensional model used to simulate ozone concentrations at every meter in an atmospheric column extending 1,001 meter from the ground. The model processes chemical and physical input parameters and reports ozone mixing ratios, among other hemicals, in half-hour intervals at each of the 1,001 model levels. Ozone concentrations are determined in the existing model through solution of the following equation:

$$\underset{\text{Concentration}}{\text{Resultant Ozone}} \longrightarrow \frac{\partial C_{i,j}}{\partial t} = \underset{\substack{\uparrow \\ \text{Emissions}}}{E_{i,j}} + \underset{\substack{\uparrow \\ \text{Chemical} \\ \text{Properties}}}{f_{i,j}} + \left[k(z_j) \underset{\substack{\uparrow \\ \text{Physical} \\ \text{Properties}}}{\times} \frac{\partial C_{i,j}}{\partial z} \right]$$

Where:

$C_{i,j}$ = concentration of *i*th chemical species in layer *j*;

$f_{i,j}$ = rate of change of *i*th chemical species due to chemical reactions in layer *j*;

$k(z_j)$ = coefficient of dispersion at height *z*; and

$E_{i,j}$ = emissions of *i*th chemical species in layer *j*.

Each of the three terms in the above equation is the "output" of a specific module in the model. These outputs are determined for a simulation time-step and the equation is solved iteratively to account for the interaction among the three components (emissions, chemical, and physical) (Makar et al., 1999).

The existing model utilizes 266 chemical reactions to describe photochemical processes involving 79 chemical species. For computational efficiency, many chemical species are grouped together according to chemical similarities. For example, all of the HC known as *terminal-bond alkenes* are represented in the chemical mechanism as *propene*. Categorizing species with similar properties into groups reduces the overall number of individual chemical species that must be accounted for in the chemical mechanism and therefore the complexity of the model. The model utilized a total of 12 HC categories (Makar et al., 1999). For the purposes of the present research, the 120 HC species obtained from the Tuscarora Mountain Tunnel Study were grouped into these 12 categories. The vehicle-emitted HC species were grouped into categories based on their relative OH-reactivity using the same methodology employed in the original development of the photochemical model (Middelton et al. 1990).

Figure 21 is a logarithmic plot of the traffic volumes and mixing ratios of the HC species-categories used in the photochemical model. The logarithmic format was chosen to accommodate the wide range of mixing ratios on a single plot for easy comparison of the mixing ratios of different HC species. The ethane (C2H6) curve shows a strong correlation with the passenger car curve since ethane emissions are associated with light duty vehicles (Gertler et al., 1996; Rogak et al., 1998). The formaldehyde (HCHO) and higher HC species (C4AK, C7AK) more closely follow the changes in truck volumes as expected (Sagebiel et al., 1996; Zelinska et al., 1996).

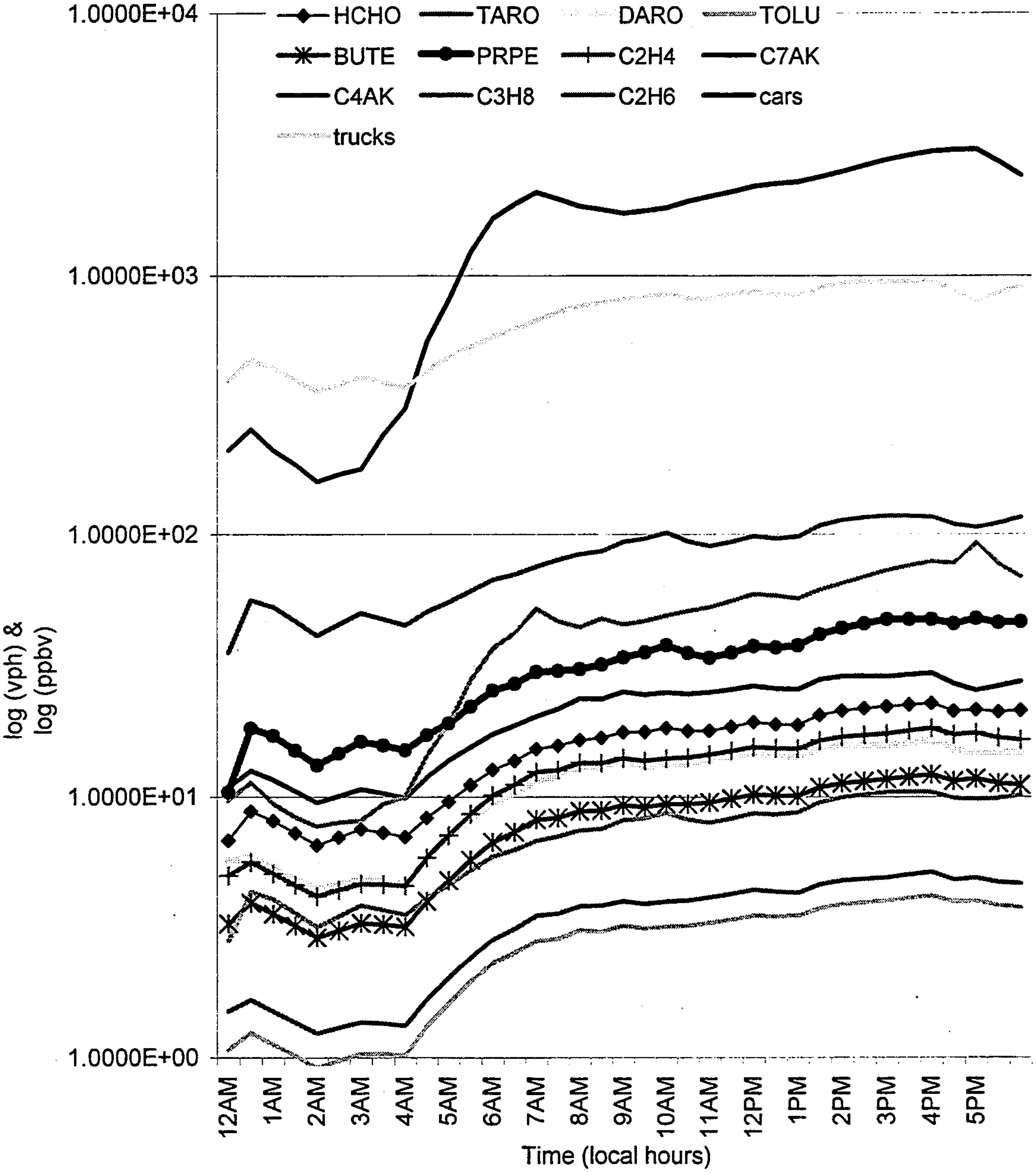


Figure 21. Log (volumes) versus Log (HC species).

3.5.2. Modifications to Photochemical Model

In order to incorporate the vehicle emissions into the simulation of ozone formation, the input file for the photochemical model was modified to include the vehicle emissions mixing ratios and the source code of the model was modified to read in the vehicle emissions data at the appropriate point in the simulation. In addition, code was added to introduce the various species of vehicle emissions into the model at the beginning of the chemical operator step.

3.6. Modeling Procedure

In order to study the effects of emissions from rural interstate traffic on ozone formation, a modeling procedure was developed that combined the various models and procedures described in the previous sections. A flowchart of the modeling procedure is presented in Figure 22.

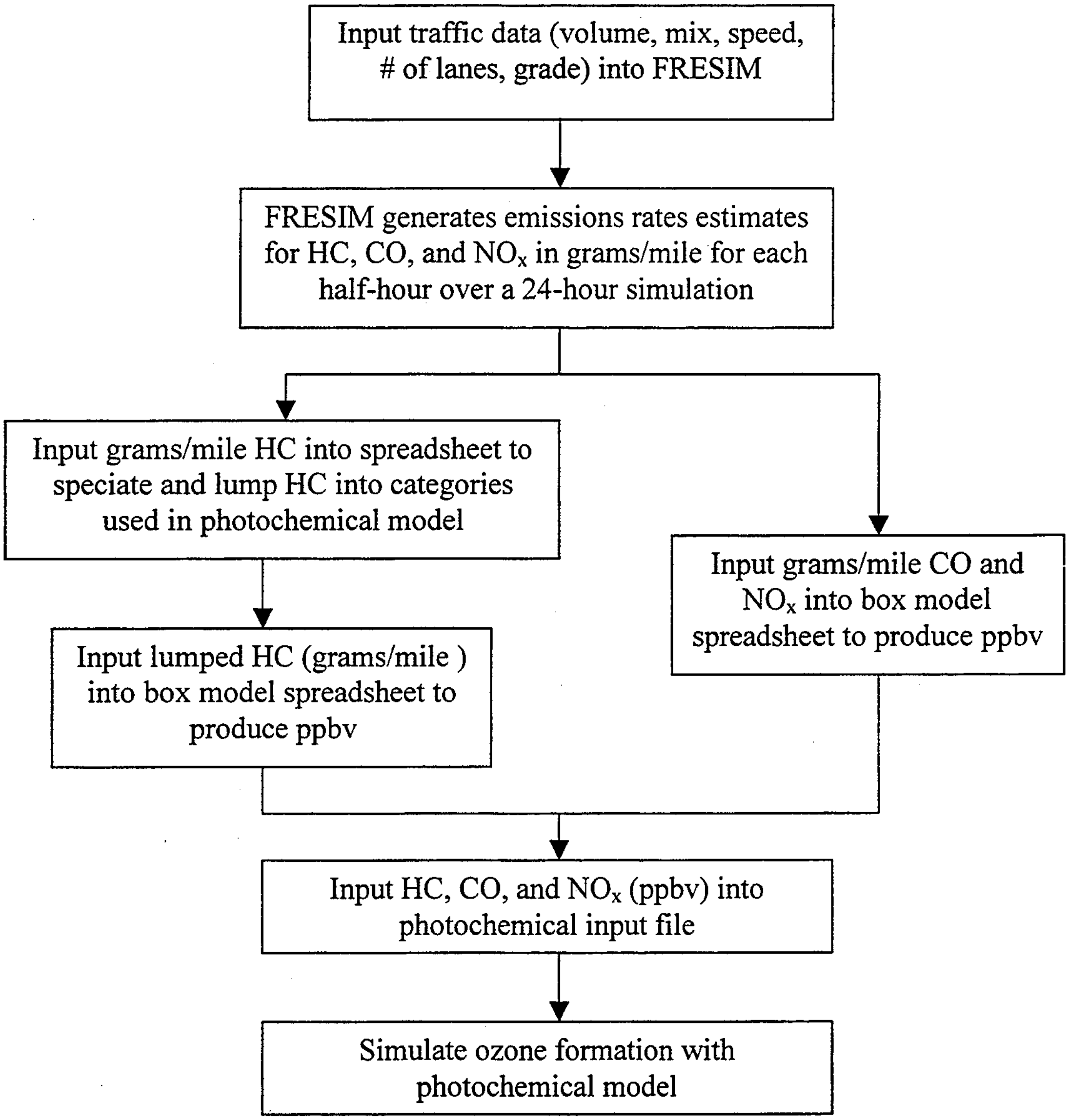


Figure 22. Flowchart of modeling procedure.

3.7. Simulation of Scenarios

Several scenarios were examined using the modeling procedure described above. Traffic data for a four-lane section of I-81 in rural Frederick County, Virginia was obtained from the Virginia Department of Transportation (VDOT). The data consisted of hourly volume and classification counts for a weekday in July 2000 from one of VDOT's permanent counting stations. The I-81 volume data was coded into FRESIM in half-hour intervals and the 12 vehicle and truck classifications provided by VDOT were lumped into the 6 vehicle classifications used in the FRESIM model. The I-81 traffic was simulated and the emission rate estimates (grams/mile NO, CO, and HC) were input into the spreadsheet for post-processing into atmospheric mixing ratios. The emission rates were converted into mixing ratios using the 10 meter tall box model.

The length of the box was set at 3,170 meters which is the length of the link on I-81 represented by the traffic volume data. The same link length was simulated using FRESIM for which the emission rate estimates were produced. It was assumed that the calculated emission rates were constant over the entire link length. The width of the box was arbitrarily set to 30 meters to represent a four-lane interstate (two in each direction) with a 3.2 meter median. The width also includes roughly 6 meters on the outside of each set of directional lanes where mixing occurs due to traffic-generated turbulence (Sedifan et al., 1981; Karim et al., 1998). By superimposing the interstate (box model) onto the forest environment, the emissions from the interstate traffic are mixed into the atmosphere and then participate in the photochemical processes simulated by the model. Superimposing the traffic emissions onto the forest was accomplished by placing the calculated mixing ratios of the vehicle-emitted pollutants into the input file for the photochemical model. Simulation of each scenario was then performed by varying the source code to include/exclude certain emissions depending on the objective of the particular run. After completion of each model run, the resultant ozone mixing ratios were graphed and inspected.

3.8. Description of Scenarios

Several scenarios were developed to illustrate certain aspects of the relationship between emissions from rural interstate traffic and ozone formation. Each of the scenarios involved the manipulation of the emission inputs to reflect various conditions intended to isolate the effects of the traffic emissions. A summary of the other scenarios is presented in Table 9. The various scenarios were run for two primary reasons:

- to evaluate the performance of the photochemical in handling the introduction of anthropogenic species; and
- to isolate various emissions to ascertain their relative roles in ozone formation.

Each of the scenarios was simulated using the modeling procedure described in the previous section. Comparisons among scenarios were performed to assess the relative contribution of the different emissions sources on ozone formation. The results of the comparisons are presented in the following sections.

Table 9. Summary of Scenarios[8].

Test scenarios	Biogenic Emissions		Anthropogenic Emissions		
	CH_4	NMHC	NO_x	CO	HC
Baseline	+	+	-	-	-
Baseline+Vehicles	+	+	+	+	+
Vehicles	+	-	+	+	+
Vehicles-NOx	+	-	-	+	+
Vehicles-CO	+	-	+	-	+
Vehicles-HC	+	-	+	+	-
Vehicles, 50% NOx	+	-	50%	+	+

All of the above scenarios were conducted using data from the remote Canadian forest (Borden, Ontario) used in the original application of the model (Makar et al., 1999). Figures 23 through 27 present relevant meteorological parameters from the Borden data [9].

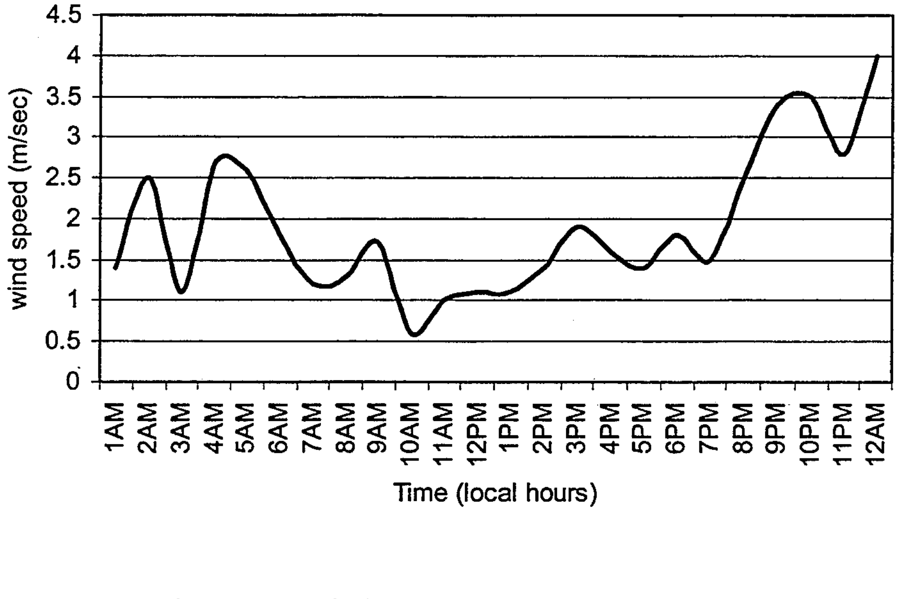


Figure 23. Wind speed measured at Borden.

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[8] + indicates the compound(s) (column) was used in that run (row). – indicates that the compound(s) was not used in the run identified by the row.

[9] Units provided in Figures 23 through 27 reflect those used in the photochemical model.

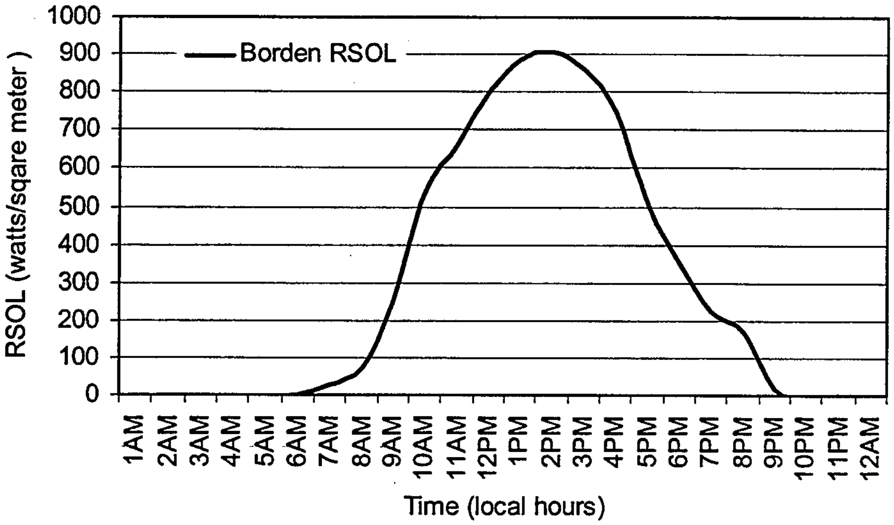

Figure 24. Solar radiation (RSOL) measured at Borden.

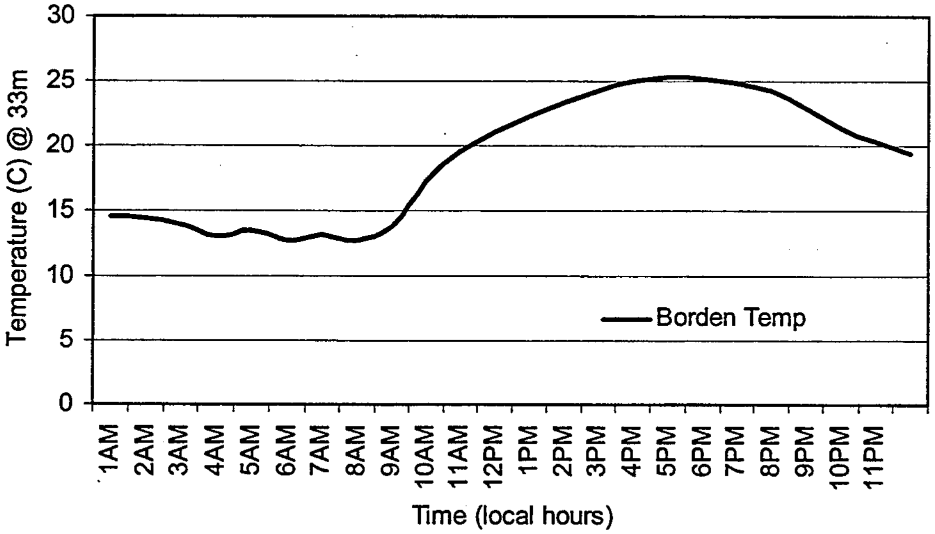

Figure 25. Temperature measured at Borden.

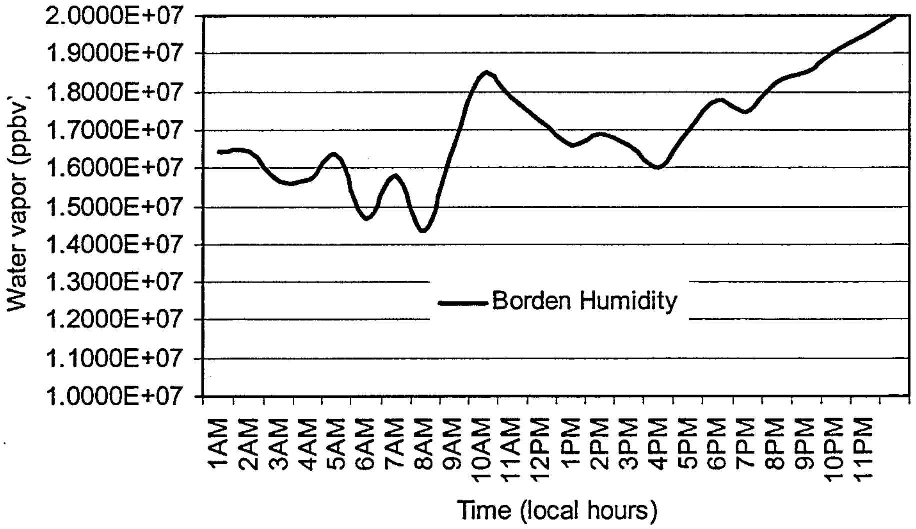

Figure 26. Humidity (water vapor) measured at Borden.

Chapter 4. RESULTS

4.1. Forest Versus Forest+Vehicles

The initial comparison was conducted to illustrate the overall effect of adding the vehicle emissions to the otherwise pristine rural environment. For this comparison, two scenarios were examined: one containing only the biogenic emissions and background chemicals specified in the original forest data and the other containing the vehicle emissions in addition to the biogenic emissions. The results of these scenarios are shown in Figures 27 through 30. The figures show the resultant ozone mixing ratios at different heights over the simulation period for both scenarios. The 10 meter, 22 meter, 30 meter, and 50 meter, heights were chosen to represent the atmospheric column above the roadway. The 10 meter height represents the height of the uniform mixing cell over the roadway where the vehicle emissions occur. The 22 meter height displays the resultant ozone at the top of the forest canopy. The 30 meter and 50 meter heights were chosen to display the effects of the roadway emission well above both the roadway and the forest canopy.

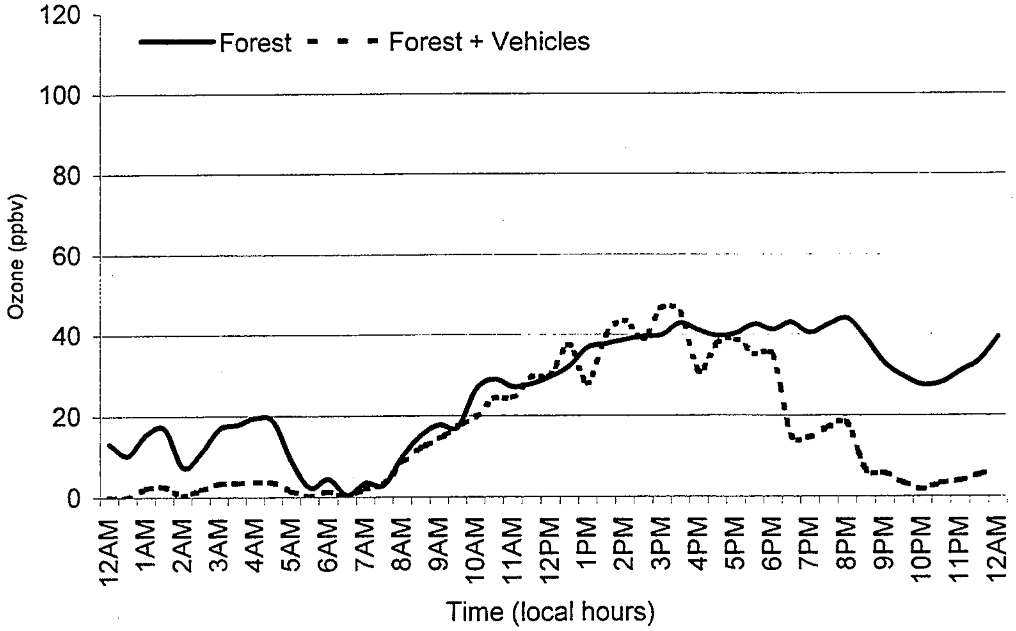

Figure 27. Ozone formation over simulation period at a height of 10m (Forest versus Forest+Vehicles).

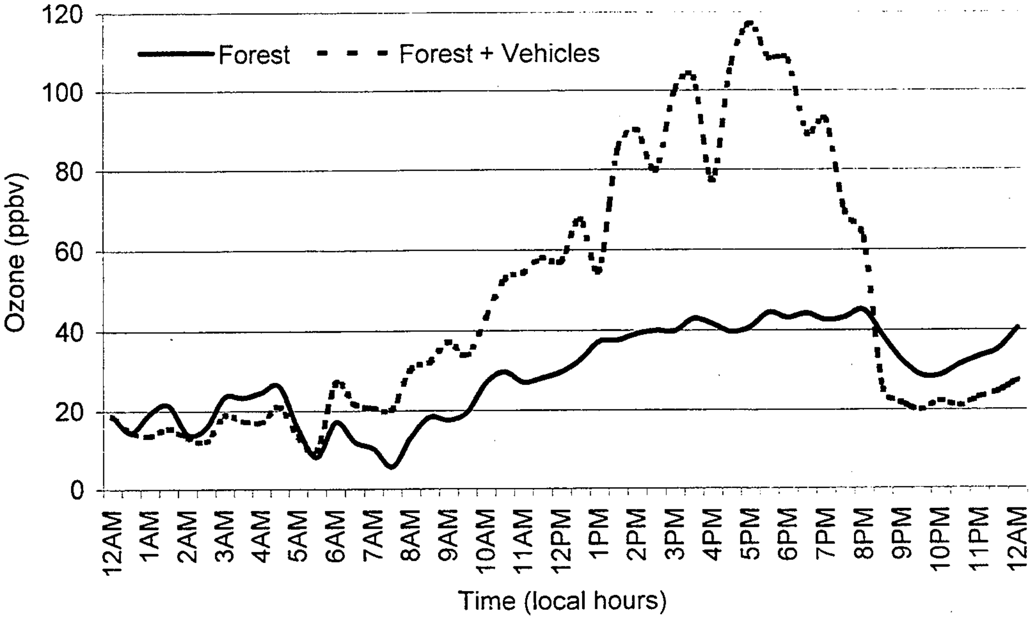

Figure 28. Ozone formation over simulation period at a height of 22m (Forest versus Forest+Vehicles).

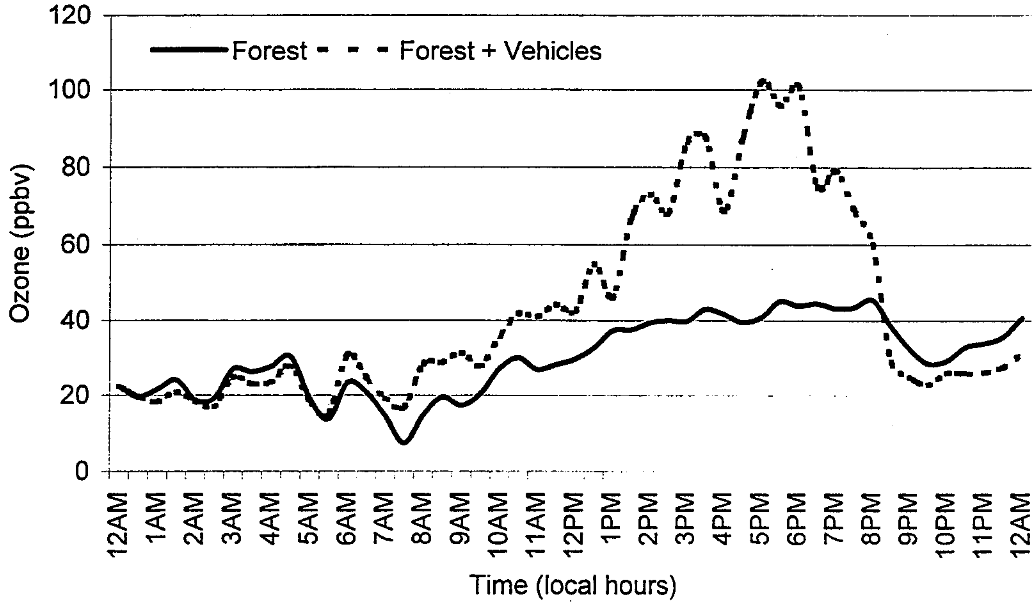

Figure 29. Ozone formation over simulation period at a height of 30m (Forest versus Forest+Vehicles).

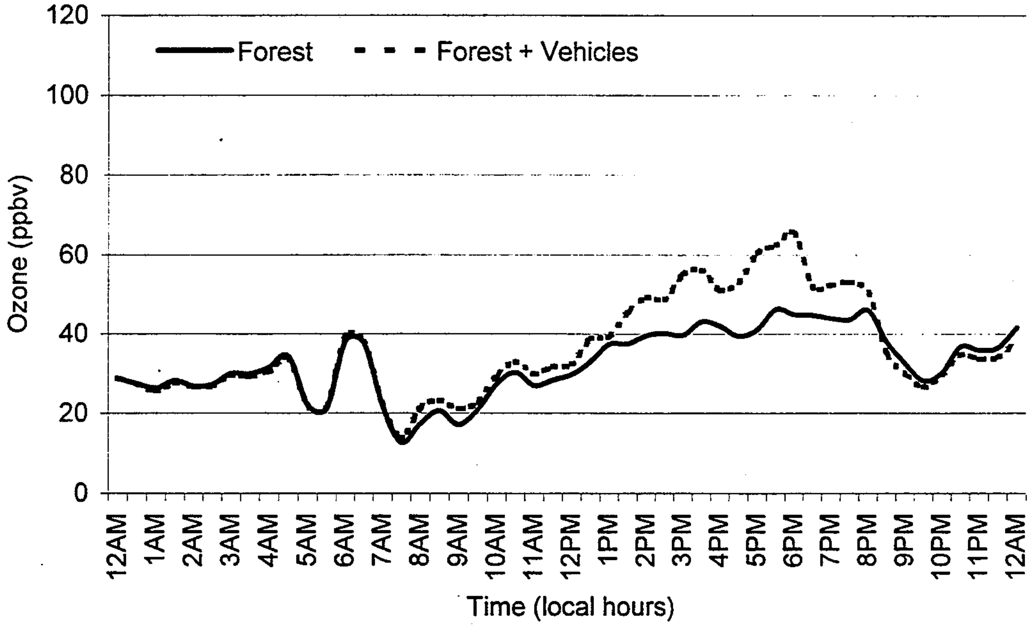

Figure 30. Ozone formation over simulation period at a height of 50m (Forest versus Forest+Vehicles).

Figures 27 through 30 clearly indicate that the addition of the vehicle emissions to the rural environment substantially increases ozone formation. In fact, the peak ozone formation at the 22 meter level (Figure 28) is more than twice that formed in the absence of the vehicle emissions. It is also worth noting that the resultant ozone levels are well above the 80 ppbv threshold set in the 1997 revisions to the *NAAQS*. At the 50 meter level (Figure 30) the ozone mixing ratios for both scenarios begin to converge somewhat but the contribution of the vehicles emissions to peak ozone formation are still evident at this height. This is further evidence of the localized effect of the vehicle emissions and supports the assertion that ozone formation in rural areas is generally formed rapidly and close to the source of NO_x emissions (Trainer et al., 1993). It is also observed from the above figures that peak ozone formation occurs in the late afternoon when traffic volumes are at their highest (between 4PM and 6PM).

Figures 31 and 32 are vertical profiles of ozone mixing ratios at 6:00 AM and 5:30 PM (period of peak ozone formation), respectively. At 6:00 AM, solar activity is sufficient to support some photochemistry and ozone mixing ratios begin to rise as indicated in Figures 27through 30. At this point in the day the ozone formed in the presence of the vehicle emissions is less than that formed for the *Forest* scenario. During the late afternoon, when photochemical activity is more prominent and traffic volumes have increased, the difference in the ozone profiles is substantial as shown in Figure 32. Figure 32 shows ozone levels in the first 10 meters of the atmosphere to be very low. This is a results of the ozone being "scavenged" by the NO emitted from the interstate traffic. The scavenging of ozone by vehicle-emitted NO will be explored in more detail in Section 4.5. Figure 32 also indicates the peak ozone formation occurring at roughly 22 meters which corresponds to the top of the canopy.

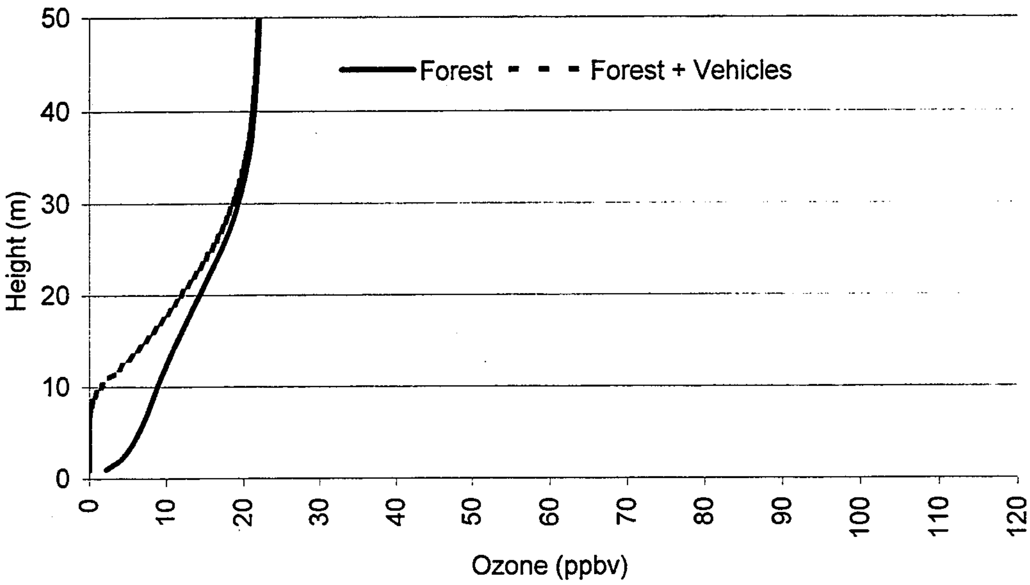

Figure 31. Vertical profile of ozone formation at 6:00 AM (Forest versus Forest+Vehicles).

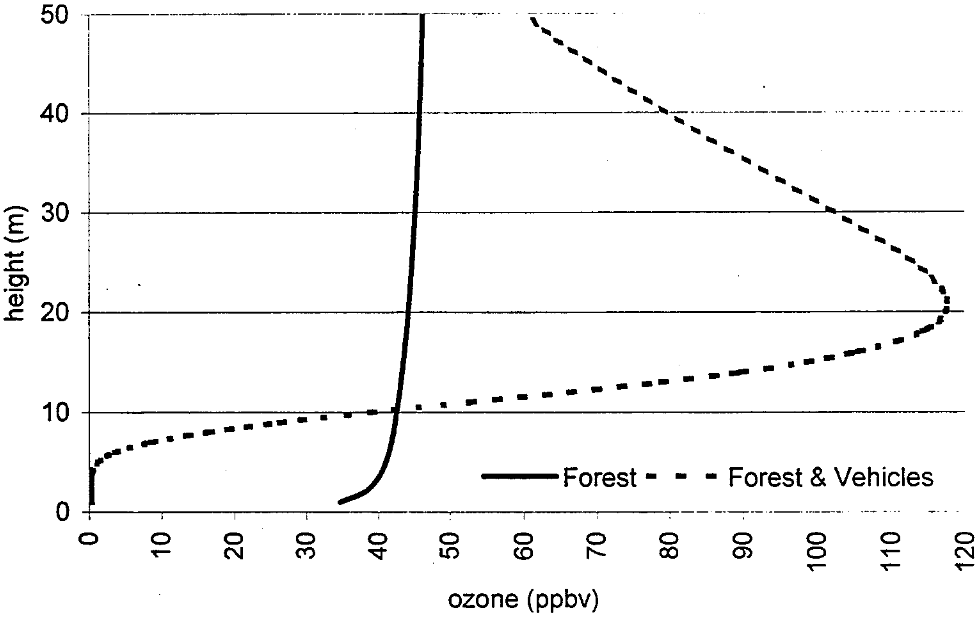

Figure 32. Vertical profile of ozone formation at 5:30 PM (Forest versus Forest+Vehicles).

4.2. Forest+Vehicles Versus Vehicles Only

The next comparison involved the *Forest+Vehicles* scenario and a scenario with only vehicle emissions. By comparing scenarios with and without biogenic emissions the contribution to ozone formation from the vehicle-emitted precursors was isolated. The results of these comparisons are shown as vertical profiles at 6:00 AM and 5:30 PM in Figures 33 and 34, respectively.

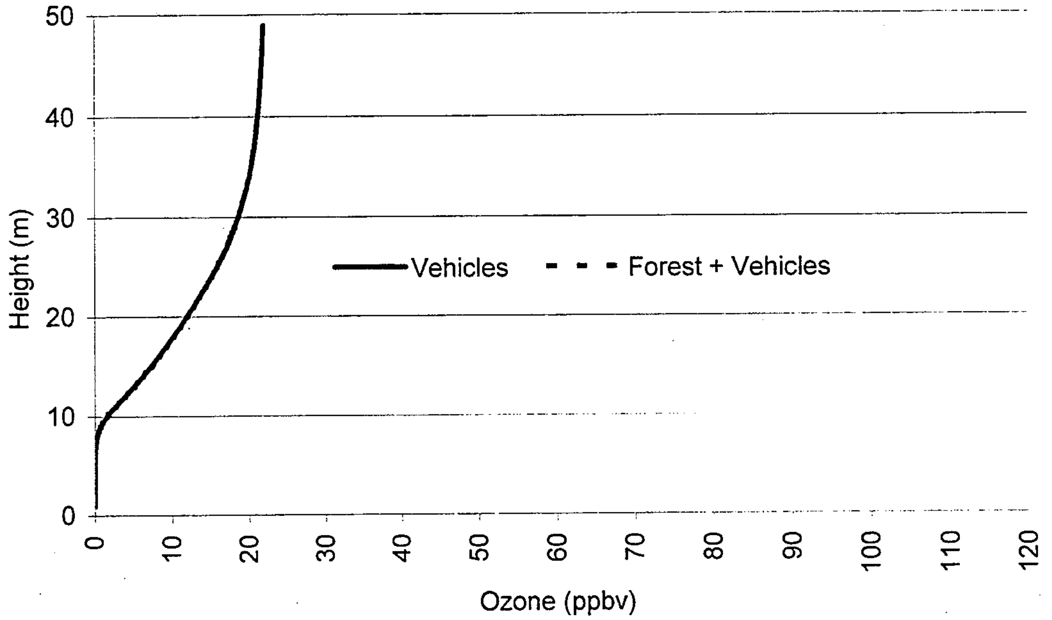

Figure 33. Vertical profile of ozone formation at 6:00 AM (Vehicles versus Forest+Vehicles).

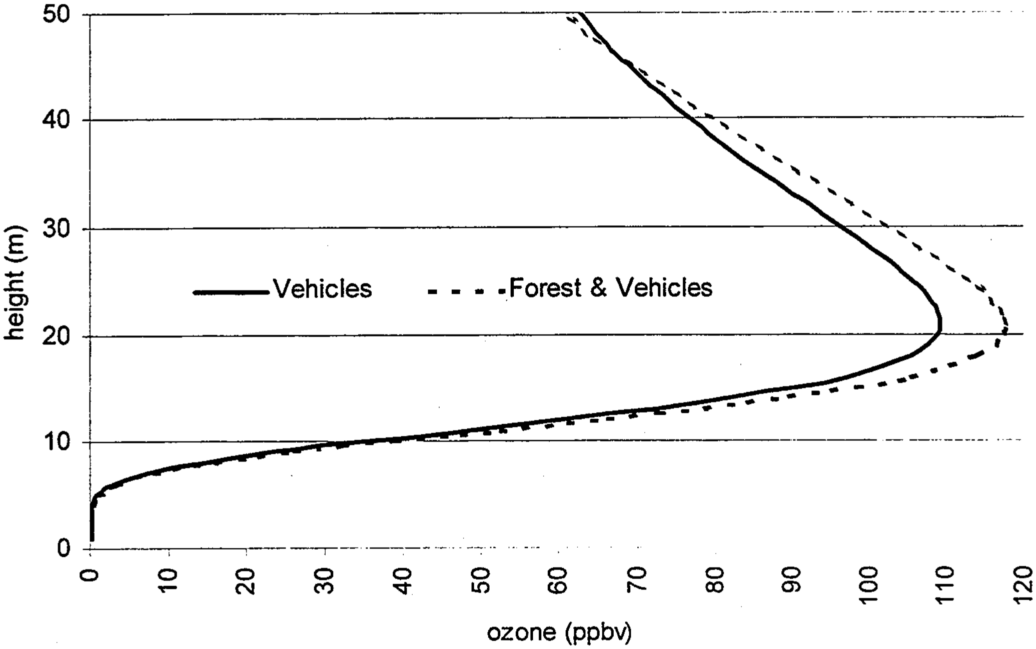

Figure 34. Vertical profile of ozone formation at 5:30 PM
(Vehicles versus Forest+Vehicles).

As indicated in Figure 33, there was no difference between the scenarios with and without biogenic emissions during the morning hours. Figure 34 indicates less ozone formation for the *Vehicles* case than for the case that includes biogenic emissions. This result agrees with the evidence presented in the literature that suggests the that biogenic HC contribute to ozone formation in the presence of anthropogenic NO_x (Trainer et al., 1993; Sillman, 1999).

Recall that Figure 32 (*Forest versus Forest+Vehicles* comparison) indicates the potential for peak ozone formation approaching 120 ppbv for the *Forest+Vehicles* scenario and only slightly above 40 ppbv for the *Forest* scenario. Figure 29 (*Forest+Vehicles* vs. *Vehicles*) indicates peak ozone formation around 120 ppbv when the biogenic emissions are present and just under 110 ppbv when no biogenic emissions are present. These results suggest that introducing vehicle emissions does not have an "additive effect" on ozone formation. Rather, the vehicle emissions and the chemical processes in which they participate "dominate" local ozone formation. This result agrees with the observation from the original study of the Canadian forest where on the second day of measurements NO_x was advected into the study area and substantially increased ozone production. From this the authors concluded that ozone formation in and above the forest canopy was indeed NO_x-limited (Makar et al., 1999).

4.3. Vehicles Versus Vehicles with No NO_x Emissions

Since the previous comparisons indicate the dominance of the vehicle emissions in local ozone formation in the rural interstate environment and all of the literature suggested the importance of NO_x, a comparison between the *Vehicle* scenario and one including *Vehicle* emissions without NO_x was performed. The results of these simulations are compared with the original *Forest* scenario in the vertical profiles at 6:00 AM and 5:30 PM shown in Figures 35 and 36, respectively.

Figure 36 indicates that the *Vehicle* scenario results in lower ozone levels than either the *Vehicles with no NO_x emissions* or the *Forest* scenarios. This result is expected as the NO_x emitted by the vehicles scavenges the ozone via reactions *NOX1* and *NOX2* (Atkinson et al., 1997).

(*NOX1*) $NO + O_3 \rightarrow NO_2$

(*NOX2*) $NO_2 + O_3 \rightarrow NO_3$

At this time of the day, available sunlight is not sufficient to produce ozone faster than the vehicle-emitted NO_x scavenges it.

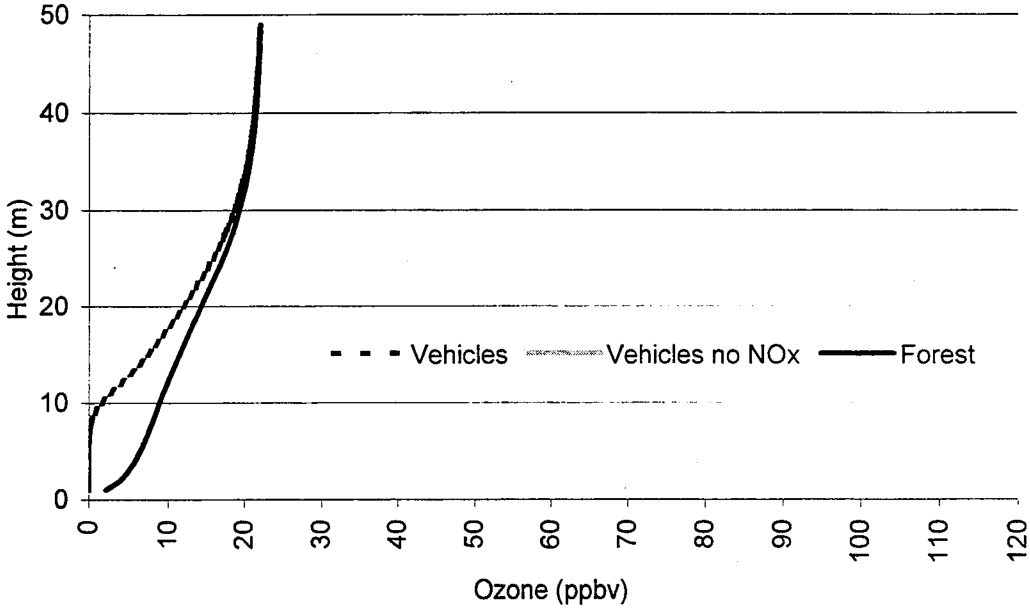

Figure 35. Vertical profile of ozone formation at 6:00 AM (Vehicles versus Vehicles with no NO_x).

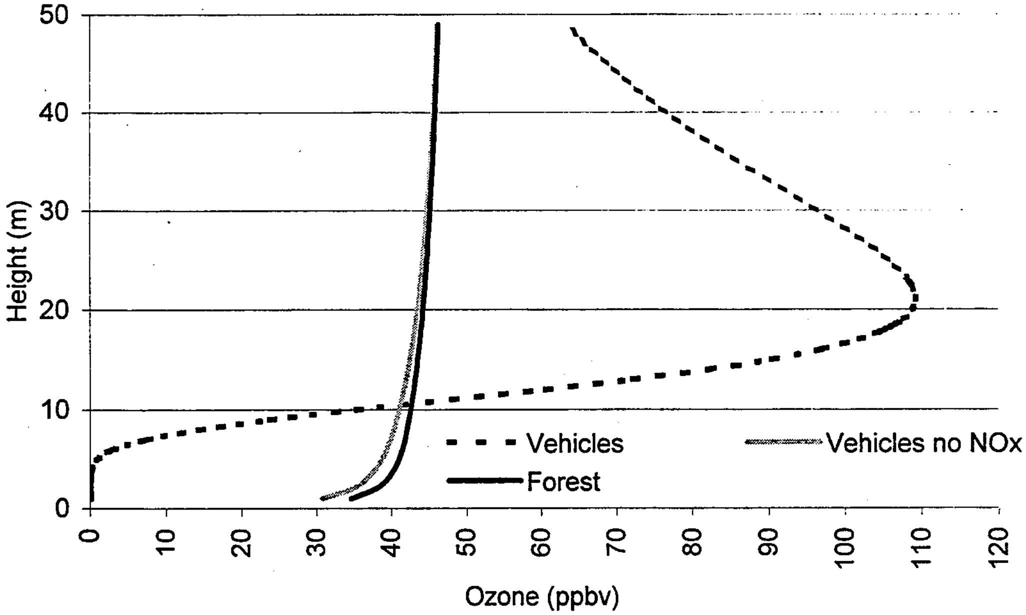

Figure 36. Vertical profile of ozone formation at 5:30 PM (Vehicles versus Vehicles with no NO_x).

The ozone produced in the *Vehicles with no NO_x emissions* and *Forest* scenarios is nearly identical. During the afternoon period of peak ozone production, however, the *Forest* scenario actually results in slightly higher ozone levels than the *Vehicles with no NO_x emissions* scenario as observed in Figure 36. This result suggests that in the absence of ozone-forming NO_x, other vehicle emissions scavenge ozone. Past research has indeed shown that HC attributable to vehicle emissions such as ethane and various alkenes do react with ozone, thereby scavenging it from the atmosphere (Atkinson, 1994).

4.4. Vehicles Versus Vehicles with 50% NO_x

A final comparison was performed between the scenario containing only vehicle emissions and one containing vehicle emissions with the total NO_x emissions reduced by 50%. This comparison was performed to further elucidate the effects of vehicle-emitted NO_x on rural ozone formation and corresponds to the current plans to cut heavy duty vehicle NO_x emissions by half between 1998 and 2004 (EPA, 1997). The vertical profile for this comparison is presented in Figure 37. Figure 37 shows that the new ozone threshold, 80 ppbv, is exceeded even with the total NO_x emissions reduced by 50%.

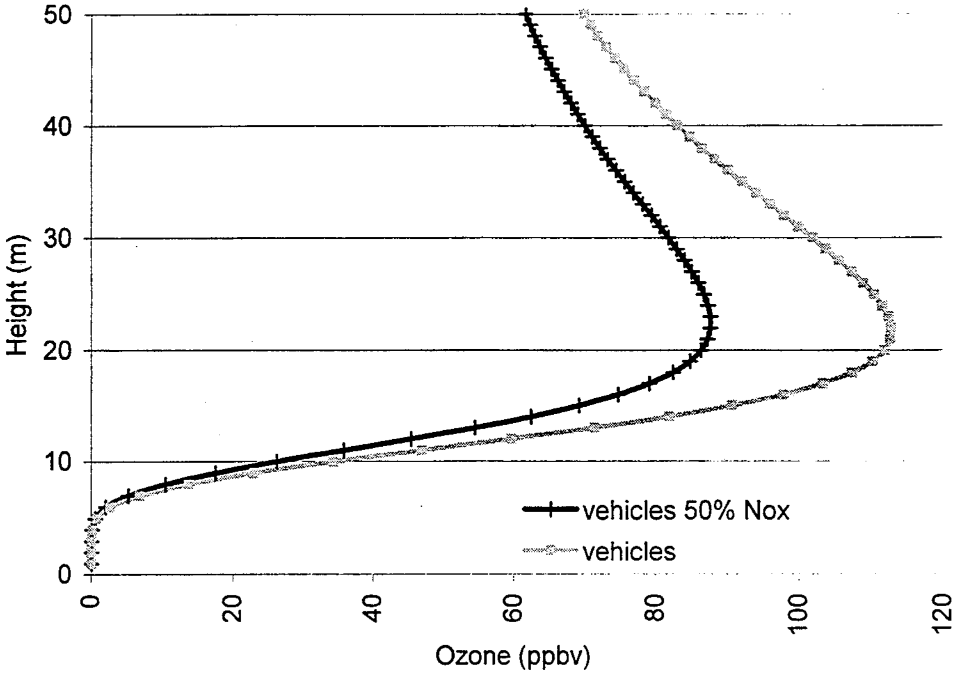

Figure 37. Vertical profile of ozone formation at 5:30 PM (Vehicles versus Vehicles with 50% NO_x).

4.5. Discussion of Results

Additional scenarios were performed in which all biogenic HC species (including CH_4 and background HC-oxidation products) as well as background levels of CO were "zeroed-out." The resultant ozone formation was similar to that of the other scenarios analyzed. These additional results further suggested the dominance of vehicle-emitted NO_x on ozone formation in the rural interstate environment. Again, these results were unexpected in that the literature suggested it was the combination of biogenic HC and anthropogenic NO_x in the rural environment that could lead to substantial ozone formation. The following sections present some analyses of ozone precursors formed in different scenarios to examine the underlying reasons for the dominance of the NO_x emissions in the rural interstate environment.

4.5.1. Chemical Analysis

Ozone formation is a very complex, non-linear process. In its simplest formation, as was evidenced in reactions *O1* through *O2*, it is clear that one of the principal factors controlling ozone formation is the availability of nitrogen dioxide (NO_2).

$$(O1)\quad HO_2 + NO \rightarrow NO_2 + OH$$

$$(O2)\quad NO_2 + h\nu \rightarrow NO + O$$

$$(O3)\quad O + O_2 + M \rightarrow O_3 + M$$

These reactions indicate that the hydroperoxyl radical (HO_2) and NO play a direct role in ozone formation. It is the photolysis of NO_2 (reaction *O2*) that produces the oxygen atom, O, which is then available to combine with an oxygen molecule, O_2 (reaction *O3*), to form ozone. There are two important mechanisms by which NO_2 is formed in the rural interstate atmosphere:

- Reaction of vehicle-emitted NO via reactions *NO1*, *NO2*, *NO3*, and *NO4*:

$$(NO1)\quad NO + O_3 \rightarrow NO_2$$

$$(NO2)\quad NO + NO_3 \rightarrow 2NO_2$$

$$(NO3)\quad NO + NO + O \rightarrow 2NO_2$$

$$(NO4)\quad HO_2 + NO \rightarrow NO_2 + OH$$

- Reaction of HC-oxidation products with vehicle-emitted NO such as reaction (*NO5*):

(*NO5*) $RO_2 + NO \rightarrow RO + NO_2$

Another important component of the ozone formation process is HO_2. Formation of HO_2 is facilitated by the oxidation of HC by the OH-radical as shown in reactions *R1* through *R4.*

(*R1*) $RH + OH \rightarrow R + H_2O$

(*R2*) $R + O_2 + M \rightarrow RO_2 + M$

(*R3*) $RO_2 + NO \rightarrow RO + NO_2$

(*R4*) $RO + O_2 + M \rightarrow HCHO + HO_2 + M$

4.5.2. Chemical Comparisons

In the condensed chemical mechanism employed in the model used in this research there are nearly 270 reactions occurring at different rates, many of which are competing reactions (i.e, a substance is formed in one reaction while the same substance is consumed in another reaction) (Makar et al., 1999). In the scenarios simulated in this study, the vehicles, particularly trucks, are a major source of NO_x. As discussed above, this NO_x plays an important role in the ozone formation process. In order to investigate the role of vehicle-emitted NO_x in further detail, more simulations were run with varying emissions parameters and a second set of comparisons was performed. Table 10 presents a summary of the scenarios analyzed in more chemical detail. Comparisons among these scenarios were performed to evaluate the effects of the various emissions on the formation of the ozone precursors, OH, HO_2, and NO_2. The results of these comparisons are presented as vertical profiles during peak ozone formation (5:30 PM) in Figures 38 through 39. The vertical profiles are shown between 0 and 30 m to provide greater detail in the range where the vehicle emissions have the greatest effect.

Table 10. Summary of Scenarios Analyzed in Chemical Detail [10].

Scenario	Background Emissions		Biogenic Emissions		Anthropogenic Emissions		
	CO	Oxidized HC	CH_4	NMHC	NO_x	CO	HC
Baseline	+	+	+	+	-	-	-
Vehicles-NMHC	+	+	+	-	+	+	+
Vehicles-background	-	-	-	-	+	+	+

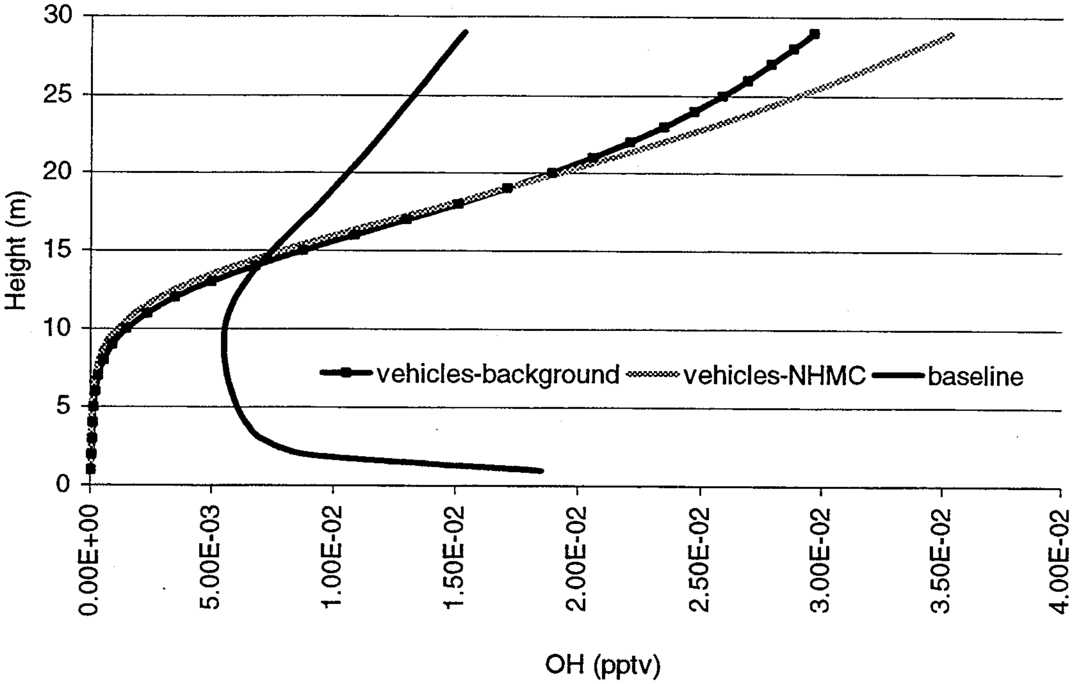

Figure 38. Vertical profile of OH at 5:30 PM.

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[10] + indicates the compound(s) (column) was used in that run (row). – indicates that the compound(s) was not used in the run identified by the row. NMHC is used to represent all non-methane based hydrocarbons.

It is observed from figure 38 that introduction of vehicle-emitted NO results in OH being scavenged near the roadway by the NO and related species formed through NO-derived reactions (e.g., nitric acid – HNO_3, pernitric acid – HNO_4, nitrous acid –HONO, and NO_2). These OH-reactions result in both HO_2 and NO_2, ultimately elevating their levels.

The resultant elevated HO_2 is shown in Figure 39. Figure 39 shows that HO_2 is scavenged by vehicle-emitted NO similarly to OH. Recalling reaction *O1*, $HO_2 + NO \rightarrow NO_2 + OH$, we would then expect elevated NO_2 concentrations as a result of the HO_2-NO reaction. Figure 40 indicates that this indeed is the case and that vehicle-emitted NO results in elevated NO_2 that is then available to be photolyzed and ultimately contributes to ozone formation (reactions *O1* through *O2*).

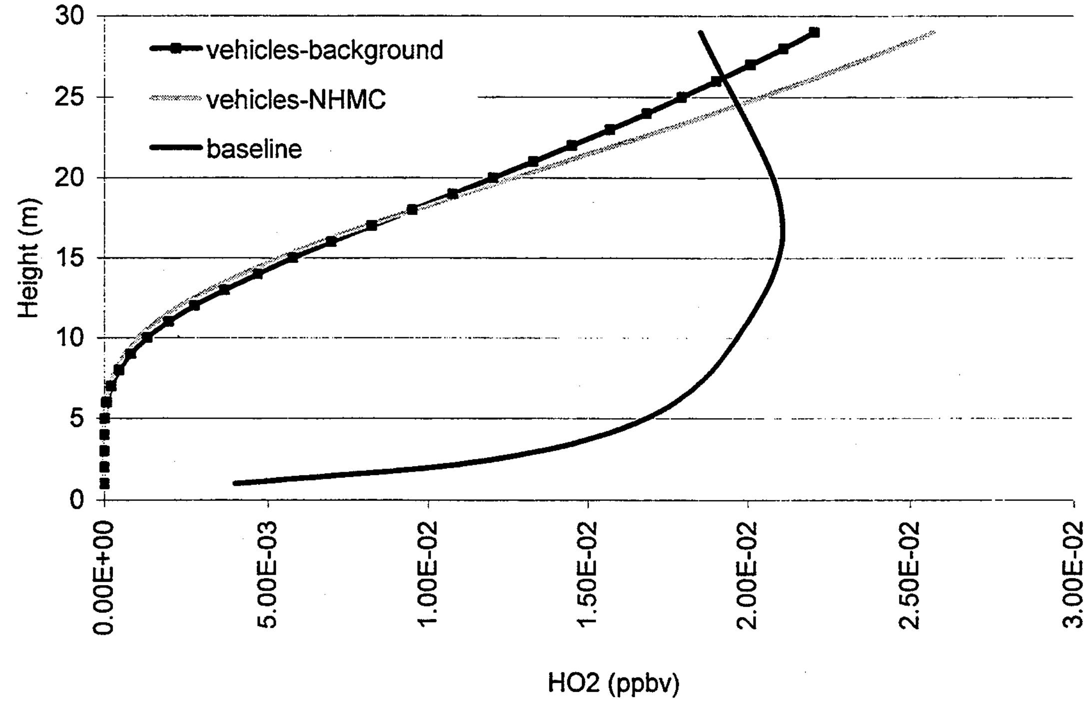

Figure 39. Vertical profile of HO_2 at 5:30 PM.

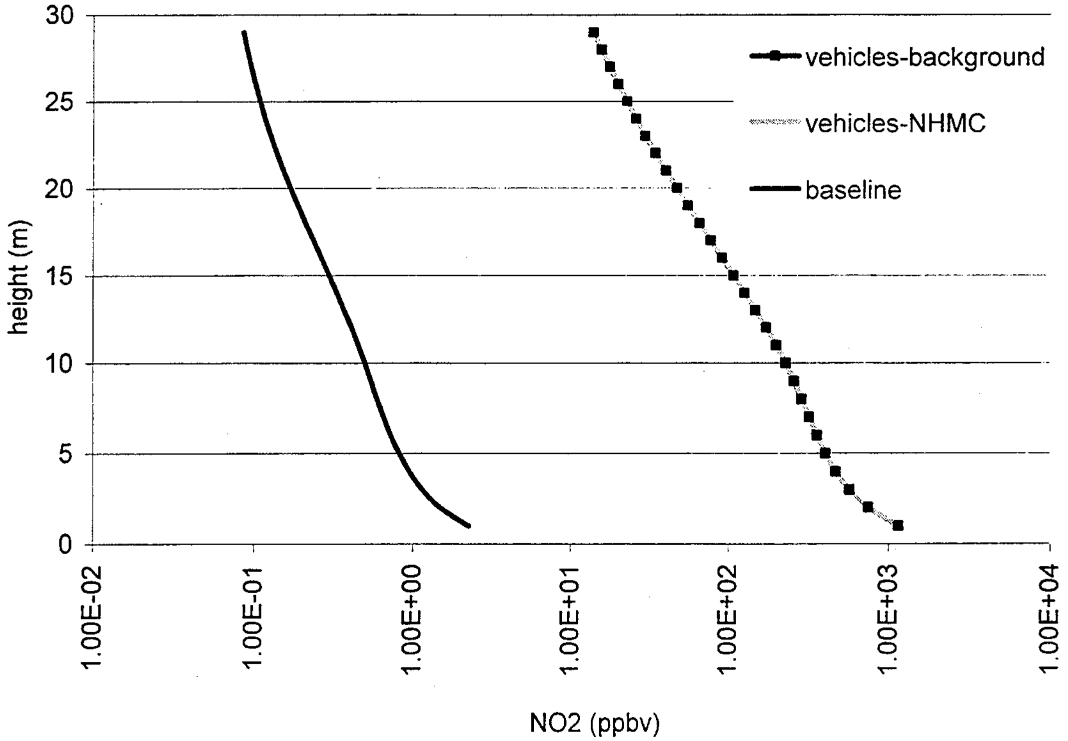

Figure 40. Vertical profile of NO_2 at 5:30 PM.

The *Vehicles-Background* and *Vehicles-NMHC* scenarios shown in Figure 40 include NO_x emissions from vehicles. Therefore, it can be concluded that the elevated NO_2 levels shown in Figure 40 are due solely to the NO emissions from vehicles.

4.5.3. Summary

The additional analyses presented in the previous section provide some insight into the dominance of the vehicle-emitted NO in ozone formation in the rural interstate environment. Even in the absence of any OH produced via the oxidation of biogenic or anthropogenic HC, the NO contributes enough OH to drive the OH-HO_2-NO_2 reaction pathways that lead to net ozone formation. This is an important conclusion in that there is considerable debate in both the scientific and regulatory communities as to the relative value of implementing policies on NO_x- as opposed to HC-controls for motor vehicles. In many urban areas such as Los Angeles, it has been shown that HC controls would be most effective in limiting ozone production and that NO_x controls may actually contribute to higher ozone levels (Finlayson-Pitts, 1993). In southeastern cities such as Atlanta and in rural areas where ozone formation is considered to be NO_x-limited most of the time, HC controls are considered to be less effective than NO_x controls in limiting ozone formation (Sillman, 1999). The research present herein has shown that in the case of the rural interstate environment NO_x is the dominant factor controlling ozone formation. Therefore, as shown in the 50% NO_x scenario, a reduction in the amount of NO_x emitted along the roadway would reduce ozone formation in the rural interstate environment.

4.6. Sensitivity Analyses

There were two primary assumptions made during the development of the modeling procedure to analyze the scenarios presented in the previous section. These assumptions pertain to the dispersion of vehicle emissions via the box model described in Section 3.3. The first assumption was made in the choice of the mixing height of the box model. The second was the choice of a resultant wind speed to represent the total effects of the ambient wind and the turbulence generated by traffic passing through the box. Simulations using different values for these parameters are presented in the following sections.

4.6.1. Mixing Height

The height of the box was assumed to be 10 meters to account for the effects of vehicle wakes on the dispersion of pollutants. In order to examine the effect of this assumption on resultant ozone levels, two variations of the *Forest+Vehicles* scenario were simulated with different mixing cell heights. The other heights were arbitrarily chosen as 8 meters and 12 meters to illustrate the effects of allowing less (h = 8 m) volume and more volume (h = 12 m) in which the vehicle-emitted pollutants mix. Obviously, the same level of pollutant dispersed throughout a larger volume will result in lower concentrations and the converse would also be expected to hold true. Figures 41 and 42 show the resultant ozone levels at the 10 meter (assumed height of original box model) and 22 meters (height of forest canopy) over the simulation period. A Vertical profile of the of resultant ozone at 5:30 PM is shown in Figure 43.

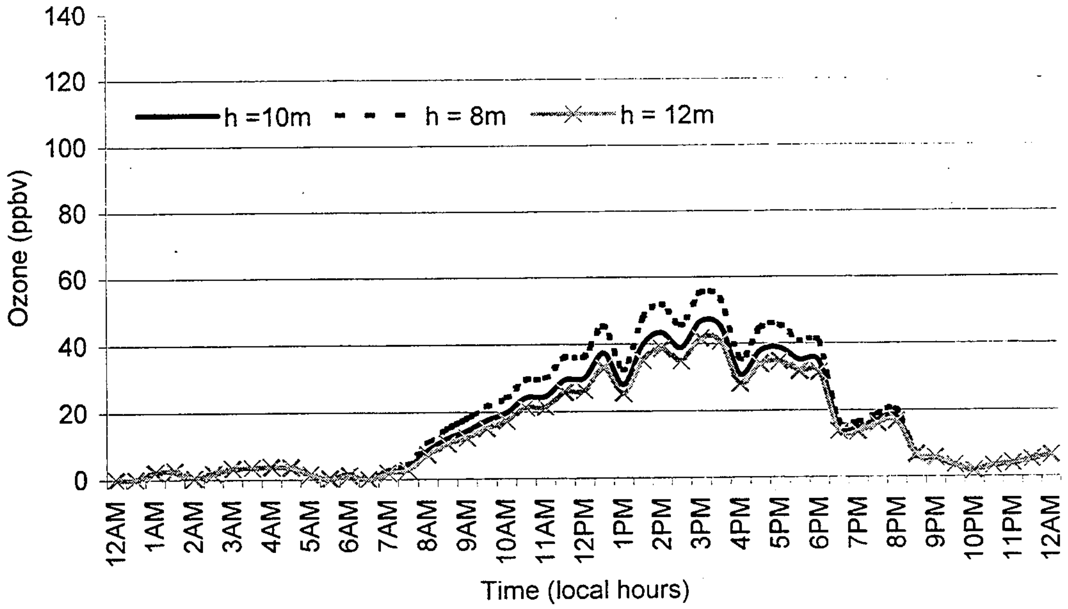

Figure 41. Ozone formation over simulation period at a height of 10 m (Varied mixing height).

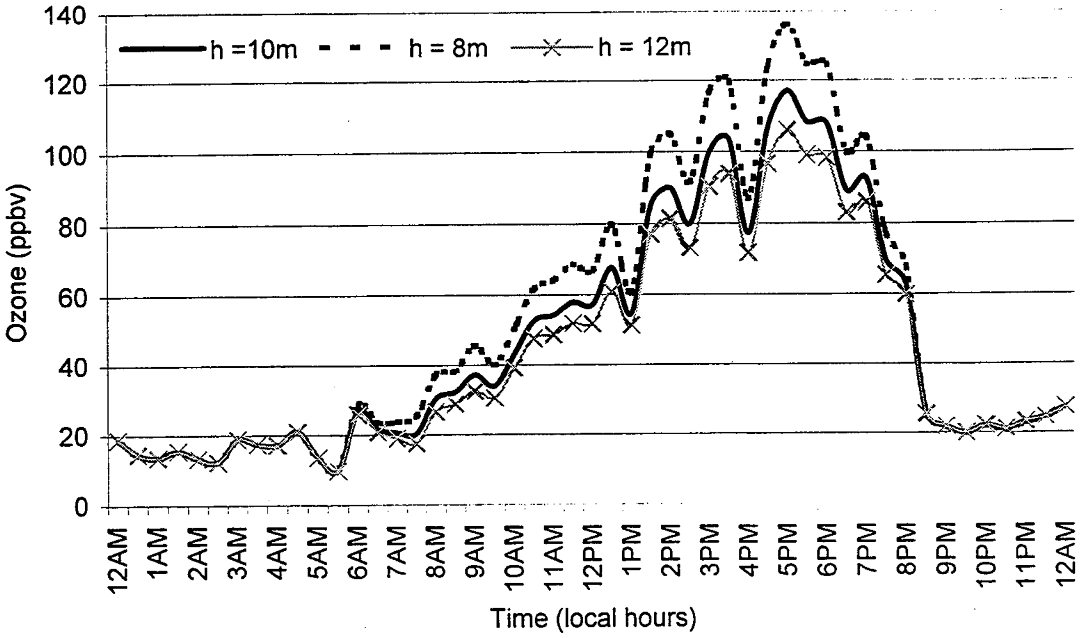

Figure 42. Ozone formation over simulation period at a height of 22 m (Varied mixing height).

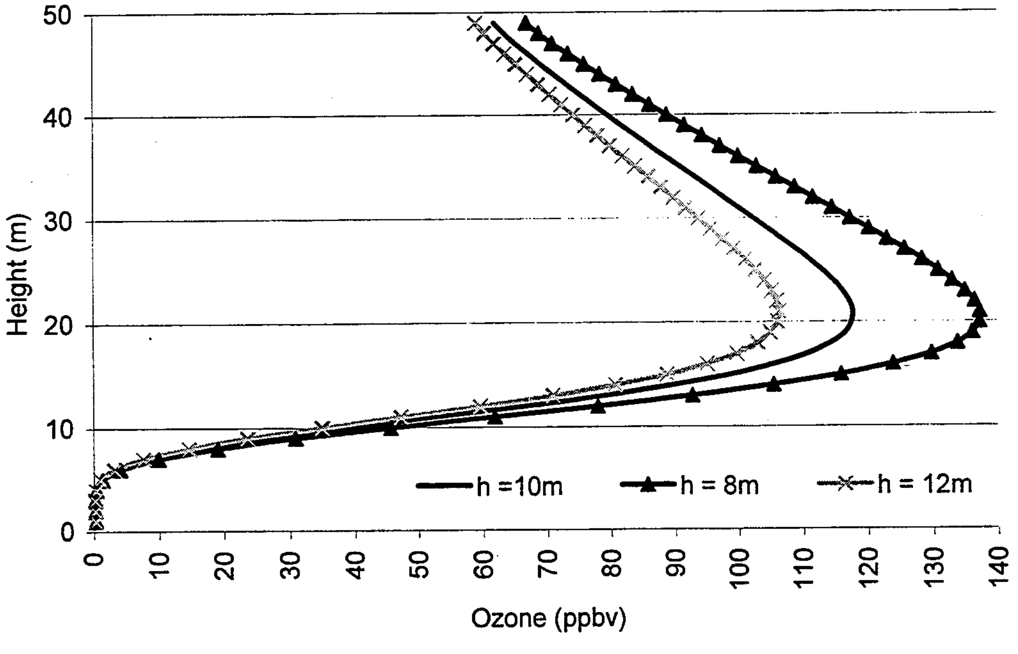

Figure 43. Vertical profile of ozone formation at 5:30 PM (Varied mixing height).

The results in Figures 41 through 43 are expected in that the h = 8 meters scenario implies that the same amount of NO_x emitted from the exhaust of the vehicles in traffic is initially mixed in a smaller volume resulting in higher concentrations. Since ozone formation has been shown to be NO_x-dependent, it satisfies expectations that the resultant ozone is large for smaller mixing cells and vice versa. The affects of the varying the height of the mixing cell are summarized in Table 11. It should be noted that the h = 8 meters scenario seems unlikely in the presence of significant truck traffic based on the fact that most pollutants from large trucks are emitted from exhaust stacks at heights up to 3.6 meters and then immediately dispersed by the truck's trailer which may be as high as 4.3 meters (Jimenez et al., 2000).

Table 11. Summary of Effects of Varying Mixing Cell Height.

Height (m)	% Change in pollutant concentration in box	% Change in ozone 10 meters above roadway	% Change in ozone at top of canopy (22 m)
8	+ 25	+ 16	+ 15
12	- 17	- 9	- 9

4.6.2. Wind Speed in Mixing Cell

The wind speed within the mixing cell was assumed to be 6 m/sec. The effect on ozone production of higher wind speeds resulting from traffic-generated turbulence was examined using two cases with higher wind speeds; 8 m/sec and 12 m/sec. Intuitively, higher wind speeds will increase mixing within the box and result in lower pollutant concentrations.

Figures, 44 through 46 indicate that this is indeed the case and that the lower concentration of vehicle-emitted pollutants results in lower ozone levels. No smaller wind speeds were examined as the literature suggested that traffic-induced wind speeds were above 6 m/sec for most cases involving large trucks (Karim et al, 1998). The effects of the varying the wind speed are summarized in Table 12.

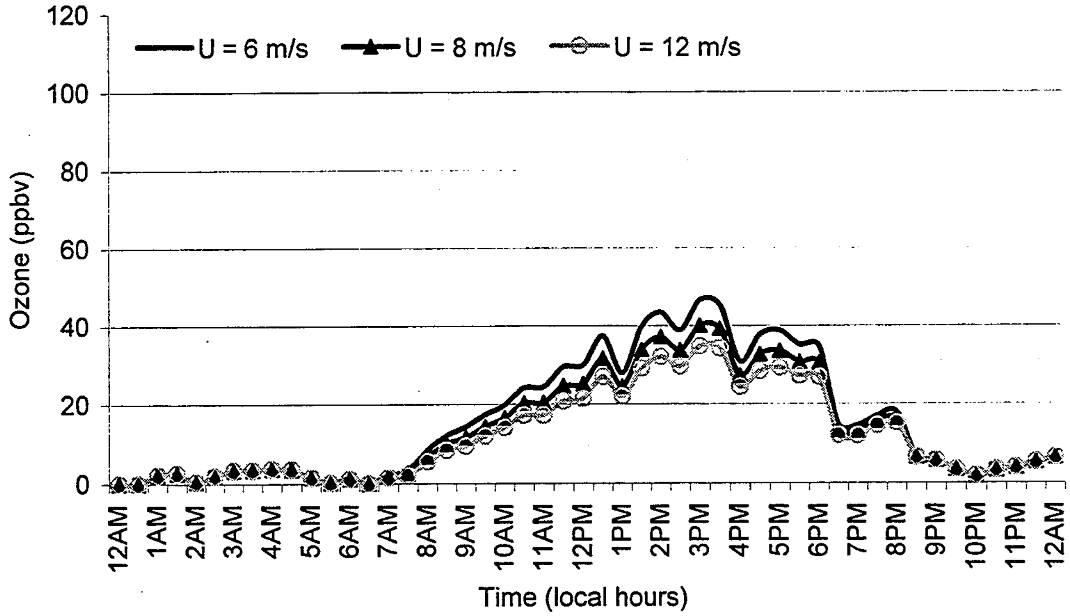

Figure 44. Ozone formation over simulation period at a height of 10 m (Varied wind speed).

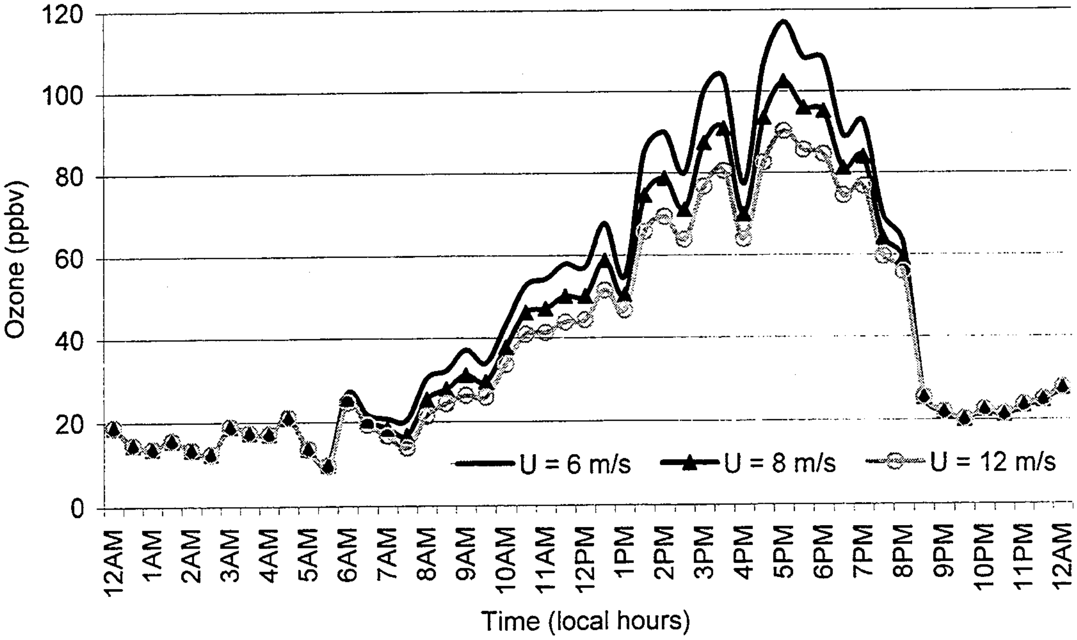

Figure 45. Ozone formation over simulation period at a height of 22 m (Varied wind speed).

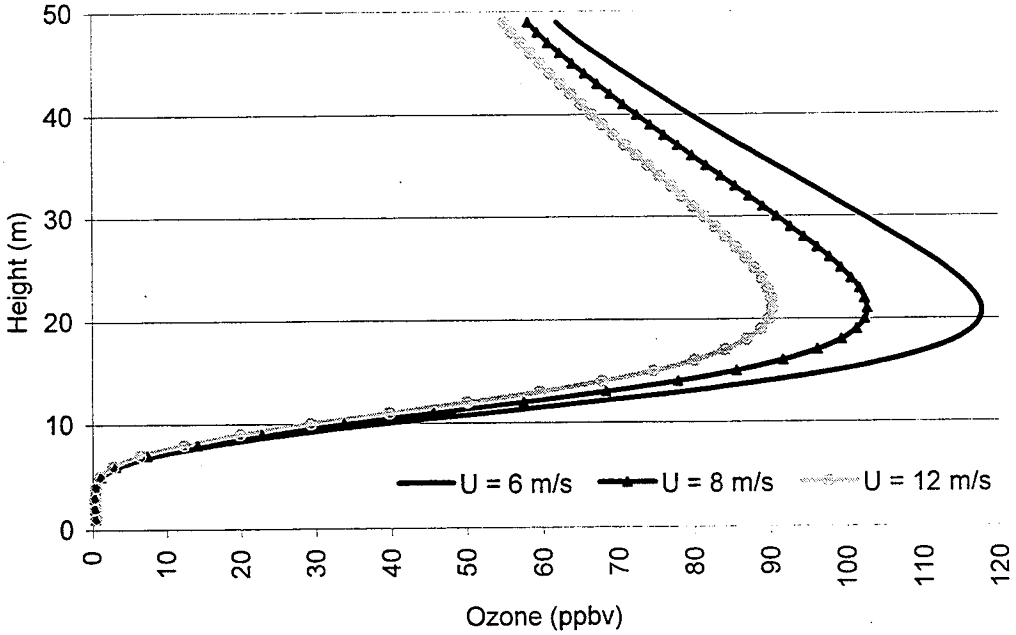

Figure 46. Vertical profile of ozone formation at 5:30 PM (Varied wind speed).

Table 12. Summary of Effects of Varying Wind Speed within Mixing Cell.

Wind Speed (m/sec)	% Change in pollutant concentration in box	% Change in ozone 10 meters above roadway	% Change in ozone at top of canopy (22 m)
8	- 23	- 12	- 11
12	-48	- 23	- 21

4.6.3. Discussion

Clearly, varying model parameters affects resultant ozone levels. In both cases (varying wind speed and varying box height) it was shown that estimates of pollutant concentrations within the mixing cell are more sensitive to these changes than are the resultant ozone concentrations. The original assumptions used to formulate the box model calculations were based on evidence presented in the literature and are considered reasonable. It should be noted that none of the results produced ozone levels below the *NAAQS*.

4.7. Traffic Effects

After conducting the various scenarios with varied chemical parameters and those presented in the sensitivity analyses, another set of scenarios were examined to ascertain the effects of varying traffic parameters on resultant ozone levels. Variations in traffic speed over ranges realistic for a rural interstate (50 mph to 70 mph) were also simulated using FRESIM. The results, however, indicated little change in the emission rate over this speed range (recall that acceleration was the controlling factor with respect to emission rate as was discussed in Chapter 3). For this reason, no photochemical analyses was performed for the varying speed scenarios as it was not expected that the results would differ much from the baseline case.

was performed for the varying speed scenarios as it was not expected that the results would differ much from the baseline case.

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In addition the scenarios using the I-81 traffic data, three more simulations were performed: 10% more traffic; 10% more trucks; and 10% less trucks [11]. The resultant ozone for these scenarios were compared with the "baseline" containing the original I-81 traffic volumes. The results of the comparisons are presented in Figure 47.

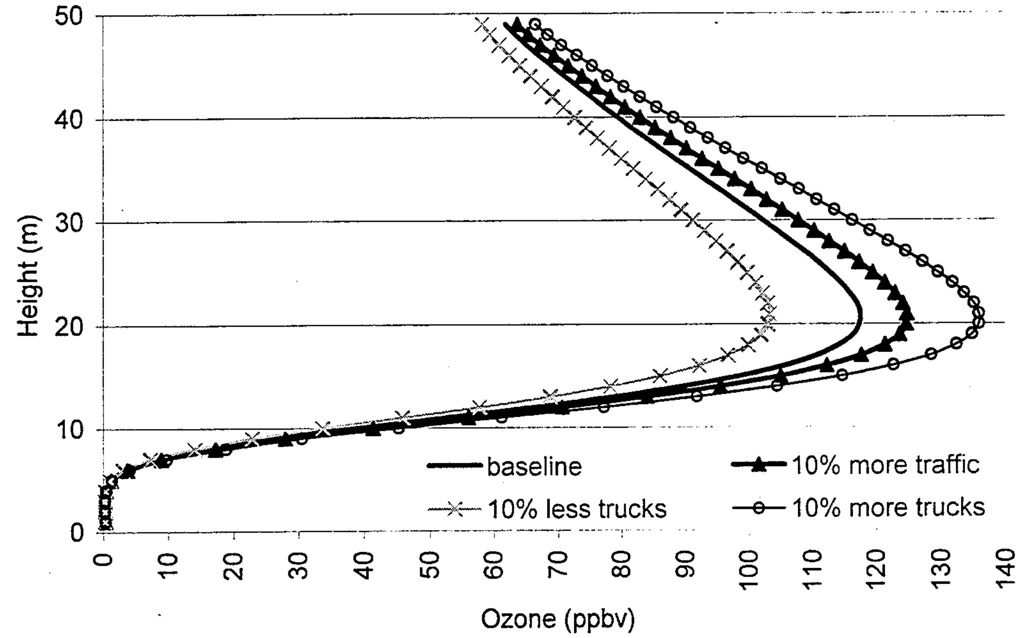

Figure 47. Vertical profile of ozone formation at 5:30 PM (Varied traffic).

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[11] 10% more traffic implies that each hourly volume in the I-81 data was increased by 10% with percentage trucks held constant. The 10% more trucks scenario was developed by simply adding 10% to the total truck percentage from the I-81 data. Similarly, for the 10% less trucks scenario.

The results in Figure 47 reemphasizes the importance of NO_x emitted from heavy duty vehicles in ozone production. Although the *10% more traffic* scenario represents larger traffic volumes than any of the other scenarios, it produces less ozone than the scenario where only the percentage of trucks in increased. Conversely, the *10% less traffic* scenario results in much lower ozone levels. Table 13 summarizes the effects of varying the traffic on peak ozone formation at 10 meters above the roadway and at the top of the forest canopy (22 m).

Table 13. Summary of Effects of Traffic Variation on Ozone Production.

Traffic	Percent Change in Ozone formation	
	10 m	22 m
10 % more traffic	+ 6	+ 7
10 % more trucks	+ 15	+ 16
10 % less trucks	- 12	- 13

These results are very interesting in terms of the development of transportation polices to mitigate ozone formation. NO_x emissions from truck traffic are clearly implicated. This implies that any strategies to reduce the traffic contribution to rural ozone formation would focus on interstate truck traffic. Several studies have concluded that freight moved by train results in less NO_x emitted per unit freight transported than for freight moved by truck (Barth and Tadi, 1996; Hutchins, 1994). This would suggest that a modal shift of freight from truck to rail for long hauls through rural areas characterized by NO_x-limited ozone formation would result in less ozone formed per unit freight moved. These results also support the aggressive measures taken to control NO_x

emissions from heavy duty vehicles and even lends support to alternative fuel initiatives intended to replace diesel-power with power sources that produce less emissions (e.g. hydrogen fuel cells).

4.8. Vehicle Emissions Modeling Effects

The emission rate estimates used in all of the previous scenarios were determined using the FRESIM look-up tables developed in this research using the Colorado truck emissions data (Section 3.1.2.). This was done because the original FRESIM look-up tables for truck emissions were shown to overestimate emission rates considerably when compared to field and laboratory studies. A final sensitivity analysis was performed to assess the impact of using the new FRESIM tables on the ozone production in lieu of the original FRESIM tables [12]. The results are presented in Figures 48 through 52.

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[12] The scenario with the updated FRESIM values corresponds to the *Forest+Vehicles* scenario presented in Section 4.1.

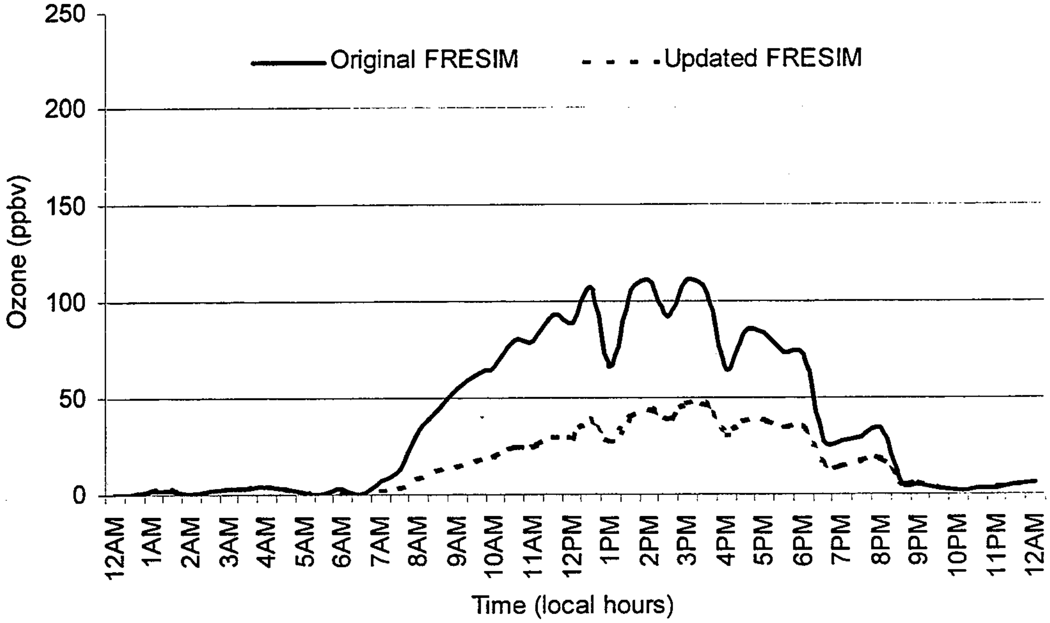

Figure 48. Ozone formation over simulation period at a height of 10 m (Varied emissions estimates).

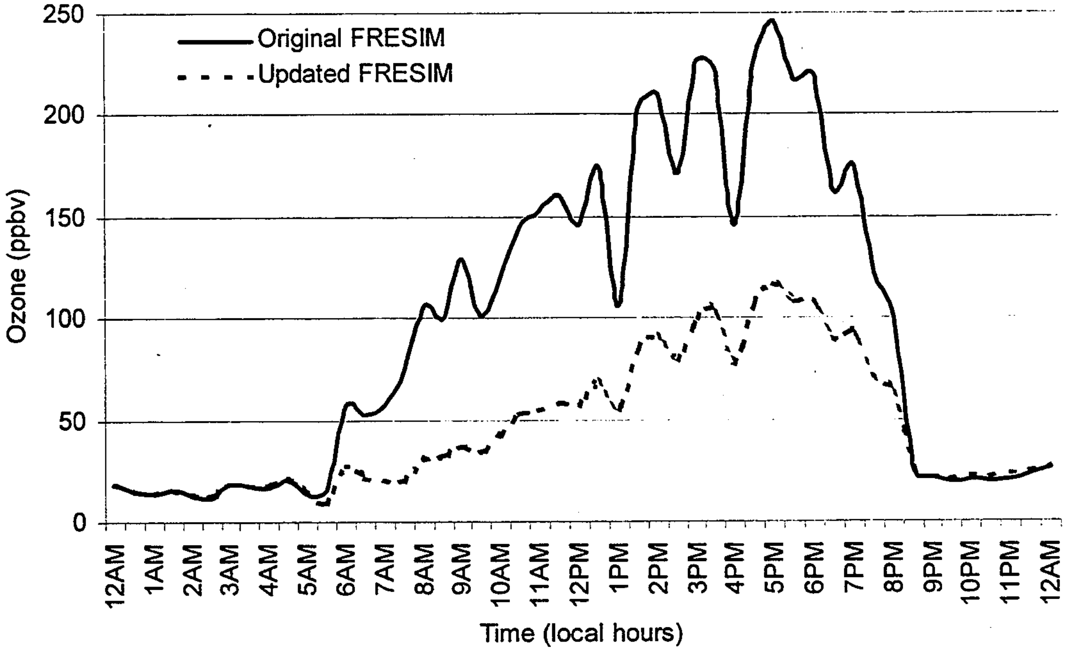

Figure 49. Ozone formation over simulation period at a height of 22 m (Varied emissions estimates).

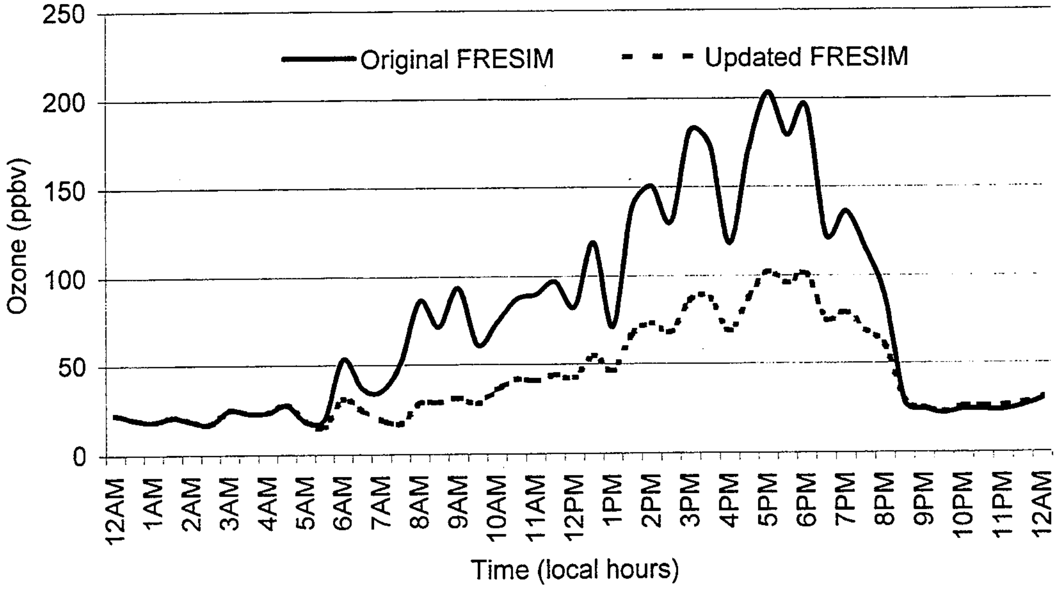

Figure 50. Ozone formation over simulation period at a height of 30 m (Varied emissions estimates).

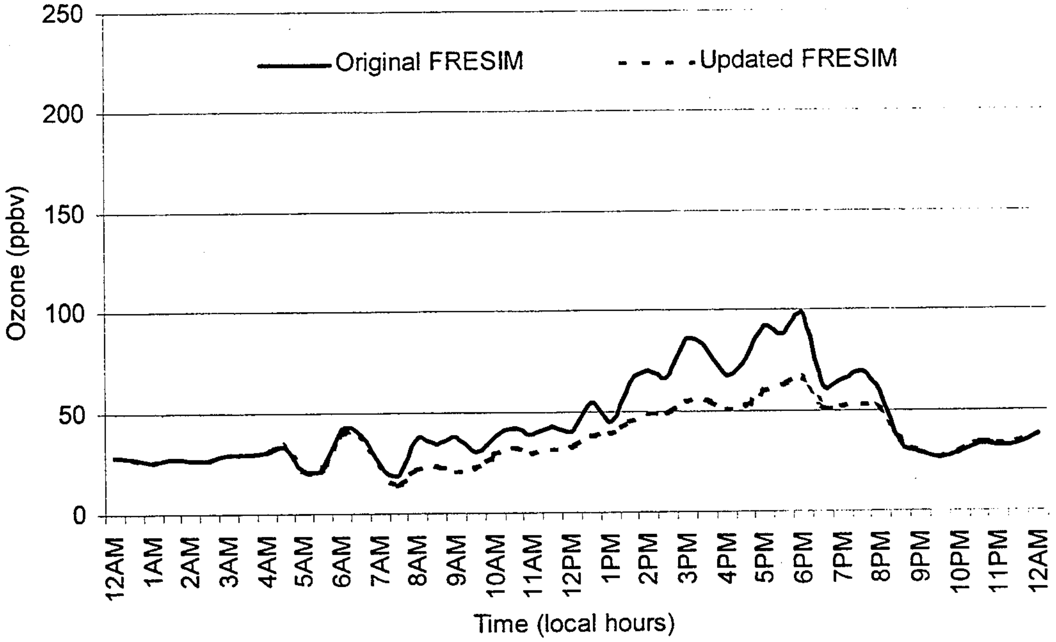

Figure 51. Ozone formation over simulation period at a height of 50 m (Varied emissions estimates).

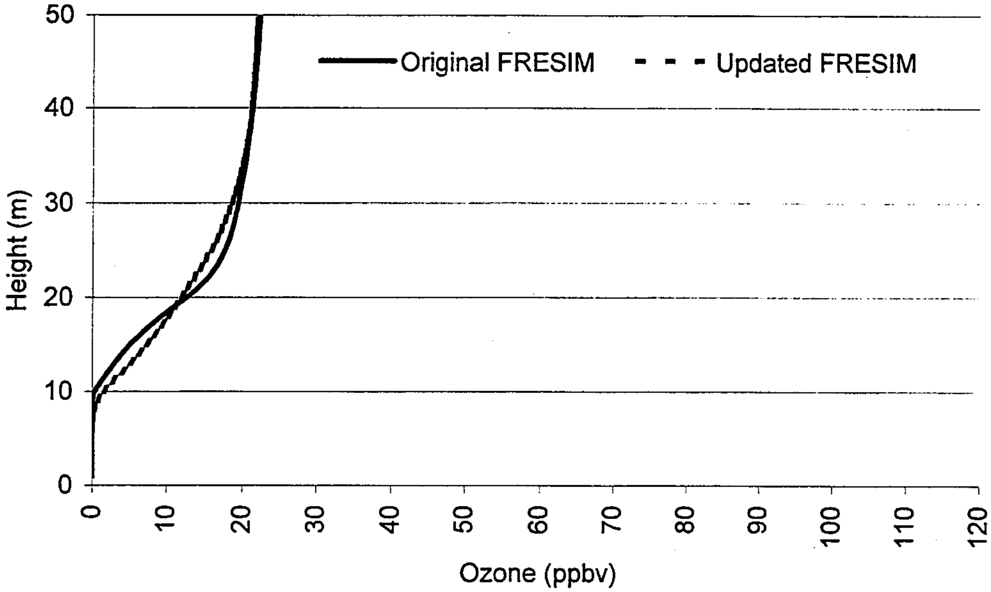

Figure 52. Vertical profile of ozone formation at 6:00 AM (Varied emissions estimates).

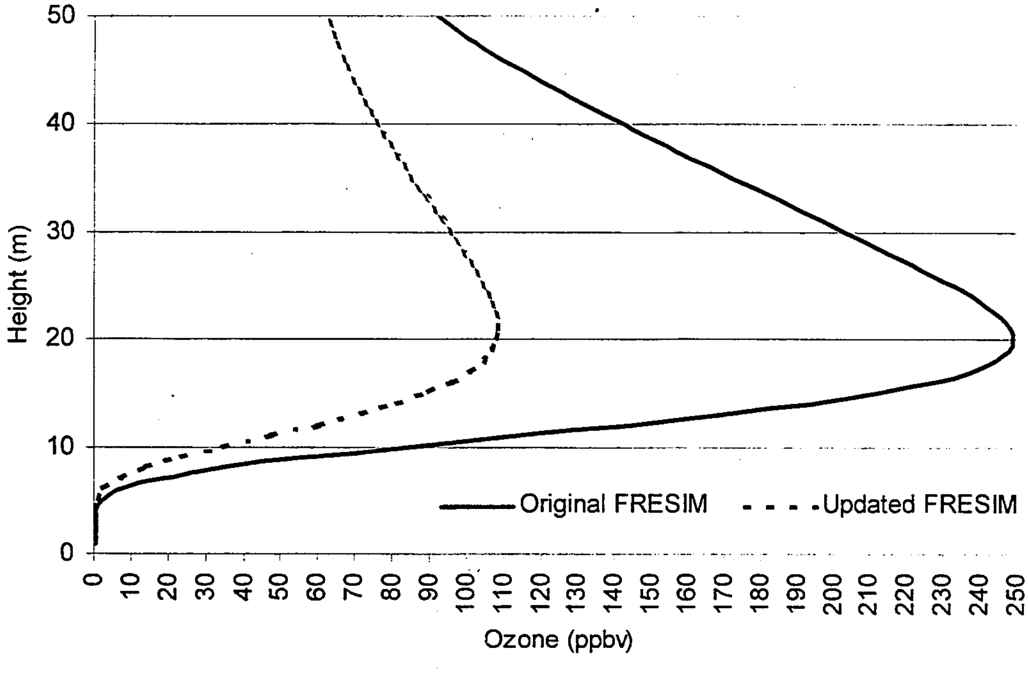

Figure 53. Vertical profile of ozone formation at 5:30 PM (Varied emissions estimates).

Figures 48 through 53 show that the original FRESIM resulted in substantially high ozone formation. The peak ozone formation was more than twice that attributable to the updated FRESIM emission estimates suggesting ozone levels of nearly 250 ppbv. Such a high ozone level was considered very unrealistic and no evidence in the literature could be found to support the notion that vehicles could be responsible for that magnitude of ozone formation. Over the period from 1986 to 1995, the EPA reported maximum ozone level averaged from 174 monitoring sites of no more than 120 ppbv (EPA, 1996). Whereas heavily polluted urban areas in California and Texas did report ozone levels in the range of 250 ppbv on several occasions during the 1995 high ozone season (EPA, 1996). These results further support the suitability of the emissions estimating procedure developed in this research.

4.9. Summary of Photochemical Modeling

Several scenarios and sensitivity analyses are presented that examine the relationship between emissions from rural interstate traffic and ozone formation. The results suggest that NO_x emitted from vehicles traveling along the interstate can contribute to substantial ozone formation – resulting in ozone levels ranging from 80 ppbv to 140 ppbv (generally around 120 ppbv). The scenarios examined suggest resultant ozone levels in excess of the 80 ppbv standard recently put forth by the EPA. The ozone mixing ratios reported for the scenarios agree well with ozone levels (measured and modeled) associated with motor vehicle emissions presented in the literature (Toll and Baldasano, 2000; Brücher et al., 2000; Winner et al., 2000; Proyou et al., 1998; Harley et al., 1997; Dunker et al., 1996). In particular, two European studies indicated ozone levels outside urban areas in the range of 100 ppbv to 120 ppbv attributable to mobile sources (Toll and Baldasano, 2000; Brücher et al., 2000). Neither of these studies explicitly indicate whether truck traffic was a factor but the German study (Brücher et al., 2000) presented measured and modeled NO_x levels that were lower than those and did not suggest substantial truck traffic. All of the previous studies and the work presented herein clearly indicate that emissions from roadway traffic, when isolated from other sources, can result in substantial ozone formation.

Chapter 5. APPLICATION TO ANOTHER FOREST

5.1. Background

The development of the modeling procedure, the analyses of the various scenarios, and the sensitivity analyses all utilized microclimate and meteorological data collected from the Borden forest in Ontario, Canada. The following section presents an effort to collect and utilize data from a lower latitude forest where the occurrence of rural interstate traffic is more common. A site near Oak Ridge, Tennessee was chosen as much of the microclimate data has been published (Baldocchi et al., 1999) and the meteorological data was readily available from the National Oceanic and Air Administration (NOAA)[12]. Differences in the forest canopies and meteorological conditions between the Borden and Oak Ridge forests result in very different HC emissions capabilities. Table 14 shows the information relevant to the capacity for biogenic emissions of both the Borden and Oak Ridge forests. The meteorological and microclimate data required to run the photochemical model, particular location/forest specific parameters such as foliage type and distribution, HC emission rates from foliage species, and leaf area index, come from field measurements designed to collect these parameters and are described in detail elsewhere (Fuentes et al.,1995; Baldocchi et al., 1999).

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[12] The meteorological data is available for download on the website of the Atmospheric Turbulence and Diffusion Division of NOAA at http://www.atdd.noaa.gov/ and the NCDC at http://www.ncdc.noaa.gov/.

Table 14. Summary of Biogenic Emissions Parameters.

Parameter	Forest	
	Borden	Oak Ridge
Latitude/ Longitude (degrees)	44.32/ 80.93	35.96/ 84.29
Forest canopy height (meters)	22	22
Leaf area index (m^2/m^2)	4.1	5.0
Isoprene emission rates (μg/g/hr)	17.5	147.7
Tree species	Aspen	Red Oak

An additional photochemical simulation was conducted for a data set describing conditions for a forest near Oak Ridge, Tennessee. Figures 54 and 55 contrast the parameters affecting HC emissions (solar radiation, temperature, and humidity) in the photochemical model for both the Borden forest and the Oak Ridge forest. The data reported in the NCDC data sets are collected at various heights above the ground. Some of these data (e.g., temperature, water vapor pressure) vary with height throughout a forest canopy and must be scaled for use in the different levels of the model. Relationships presented in the literature for scaling these parameters were applied to the Oak Ridge data. (Lamb et al., 1993; Fuentes et al., 1995; Baldocchi et al., 1999).

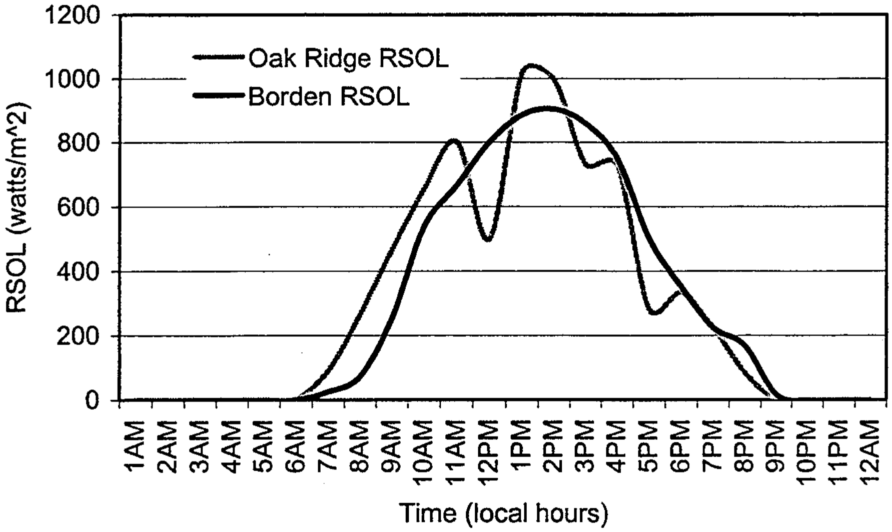

Figure 54. Comparison of solar radiation at Borden and Oak Ridge.

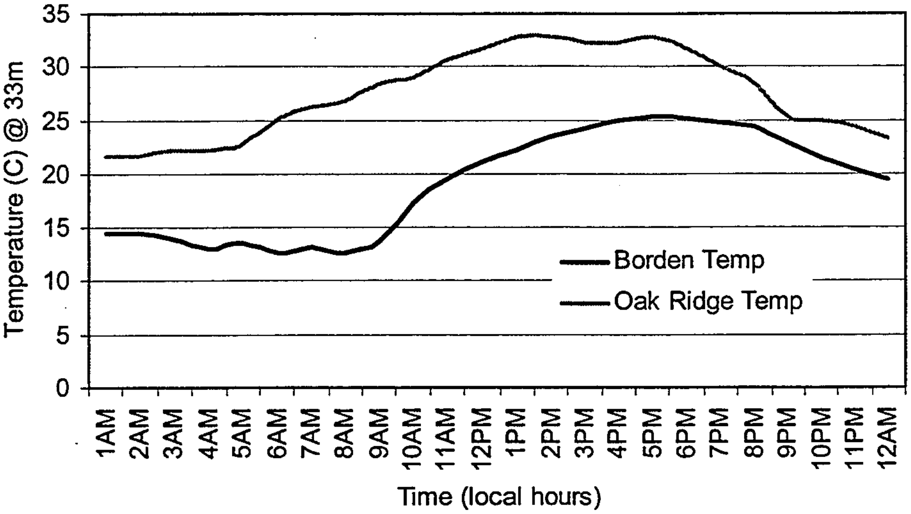

Figure 55. Comparison of temperature at Borden and Oak Ridge.

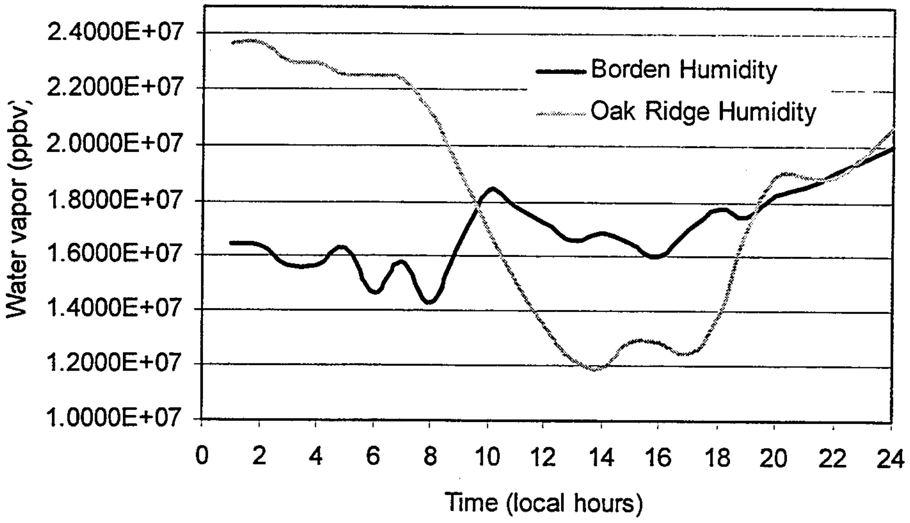

Figure 56. Comparison of humidity (water vapor)at Borden and Oak Ridge.

The photochemical model was used to simulate the chemical and physical processes in the Oak Ridge forest. Figure 57 contrasts the isoprene produced at the top of the Borden canopy (22 meters) with that produced in by Oak Ridge forest canopy. It is observed from Figure 57 that the Oak Ridge forest emits much more isoprene than does the Borden forest. This result is expected and is attributable to the difference in climate and tree species present at the two sites.

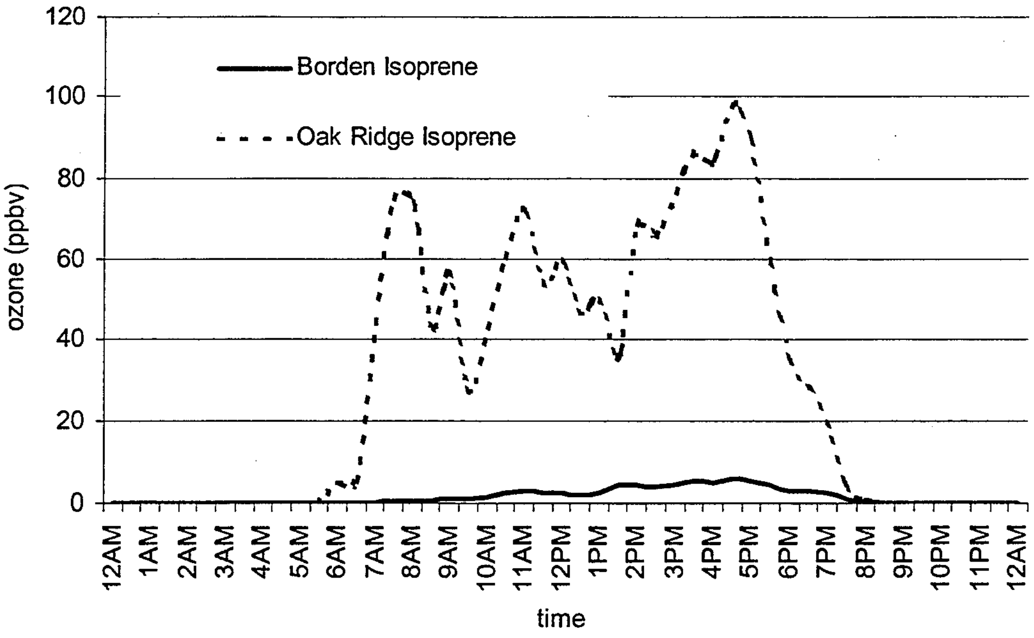

Figure 57. Comparison of isoprene emitted at Borden and Oak Ridge.

5.2. Results

The same I-81 traffic data was simulated and the estimated emissions were processed using the procedure previously described. The resultant pollutant mixing ratios were placed in an input file and the photochemical model was run with the new microclimate and meteorological parameters. The results of the photochemical simulation for the Oak Ridge forest are presented in Figure 58.

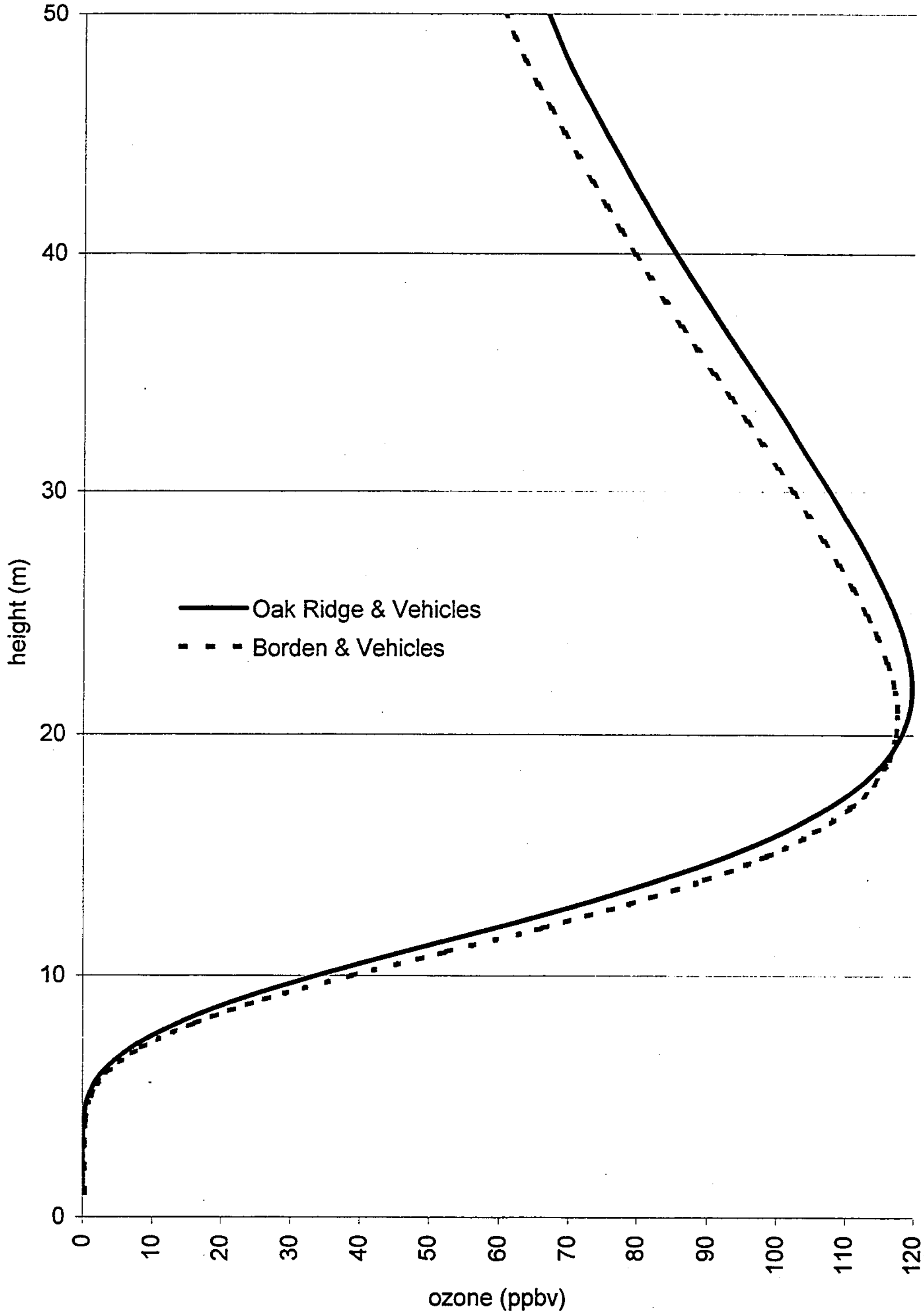

Figure 58. Comparison of ozone profiles at 5:30 PM for Borden and Oak Ridge.

5.3. Discussion

As indicated in Figure 58, the resultant ozone levels are predicted to be higher in the Oak Ridge forest than in the Borden forest. These results are expected as the higher temperatures and, thus, greater photochemical activity would be expected. Figure 58 indicates the potential for peak ozone formation in the Oak Ridge, Tennessee, region attributable to emissions from rural interstate traffic to be around 120 ppbv. Measurements taken during the Southern Oxidants Study and the East Tennessee Ozone Study reported peak ozone levels in rural areas of Tennessee ranging from 80 ppbv to 110 ppbv (Cowling and Furiness, 2001). Measurements taken downwind from Nashville, showed peak ozone levels in excess of 120 ppbv. Although there are no available data that show the ozone formation in the immediate vicinity of the rural interstate, the results reported in rural areas underscore the importance of NO_x in ozone formation and suggest that the levels predicted in the current research are within the range of expected values.

Chapter 6. CONCLUSIONS AND IMPLICATIONS

6.1. Conclusions

The previous sections have presented an analysis of the relationship between emissions from traffic traveling along a rural interstate and local ozone formation. The research was based on a modeling procedure developed to incorporate the emission estimates developed through traffic operations simulation into a photochemical model. Test scenarios were examined to evaluate the effects of different emissions conditions on ozone formation. The following conclusions were gleaned from this research:

- Traffic emissions along a rural interstate contribute to substantial ozone formation in the rural environment when compared to ozone formation in the absence of vehicle emissions.
- Ozone levels immediately above the roadway (22 m) were estimated to be around 120 ppbv.
- The large amounts of anthropogenic NO_x emitted from traffic, particularly heavy-duty vehicles, dominate the ozone formation in the immediate vicinity of the rural interstate. This finding supports earlier assertions that NO_x-limited ozone formation occurs rapidly and close to the NO_x source.
- The contribution of the other traffic-emitted ozone precursors, HC and CO, was shown to be negligible when compared to the effects of the NO_x emissions from the heavy-duty vehicles again confirming the NO_x-limited ozone formation regime of rural environments.

- The research supported the assertion that biogenic HC do contribute to elevated ozone levels in the presence of anthropogenic NO_x emissions. The research showed that the majority of the elevated ozone levels in the immediate vicinity of the roadway, however, were attributable to traffic-emitted NO_x.
- The dominance of the NO_x emissions was shown by examination of their effects on important ozone precursors. It was shown that the vehicle-emitted NO_x resulted in elevated levels of the hydroxyl radical (OH), hydroperoxy radical (HO_2), and, as expected, nitrogen dioxide (NO_2). Elevation of these important precursors resulted in elevated ozone levels as expected.
- The heavy-duty vehicle emission rate estimates for HC and CO currently produced by FRESIM are inaccurate. Some improvement in FRESIM's ability to produce reasonable emission estimates was achieved through the use of recent laboratory-derived emissions data.
- The updated FRESIM emissions estimates predicted maximum ozone levels around 120 ppbv, which agreed well with other studies of traffic-induced ozone formation.
- The original FRESIM emissions estimates predicted peak ozone levels near 250 ppbv, which is more along, the lines of that produced in very polluted urban areas in California and Texas.
- The photochemical model predicted higher isoprene mixing ratios for a forest and climate conditions representative of the Oak Ridge, Tennessee area over

those predicted for the Borden forest in Ontario, Canada. As expected for the hotter climate, the resultant ozone levels were higher for the Oak Ridge forest.

- Measurement studies reported for rural areas underscore the imnprotance of NO_x in ozone formation and suggest that ozone levels predicted in the current research are within the range of expected values.

6.2. Implications

It was shown that emissions from rural interstate traffic, particularly the NO_x emitted from trucks, contribute to substantial ozone formation. These results constitute a contribution to both the atmospheric science and transportation communities for the following primary reasons:

1. The ozone levels in the immediate vicinity of the interstate are above the acceptable thresholds put forth in both the primary and secondary standards of the revised *NAAQS*. This suggests that the estimated ozone levels are sufficient to create unhealthy conditions and damage vegetation.
2. The results indicate that rural interstate traffic is a significant source of ozone and ozone precursors. Beyond their local effects, the traffic-generated ozone and precursors are available for downwind transport where they may contribute to unacceptable ozone levels in other areas.
3. By describing the relationship between ozone formation and NO_x emitted from a rural interstate and its significance, the results support the most recent emission standards imposed on the trucking industry that require NO_x

emissions for vehicles manufactured after 2004 to be reduced to half of their 1998 values.

4. The results also support technologies and alternative fuels that further reduce NO_x emissions from heavy duty vehicles.
5. The research suggests that rural interstates may be a significant local source of photochemical pollutants that requires explicit treatment in regional scale analyses.

6.3. Recommendations

The research presented herein has fulfilled its purpose of examining the relationship between rural ozone formation and emissions from interstate traffic. It has also presented a methodology for future investigations. Several recommendations regarding potential applications, extensions, and improvements to this research are presented below.

- Additional efforts to collect and compile more reliable vehicle emission rate estimates are currently being conducted. The results of these studies should be incorporated into traffic simulation models to improve modeled emissions estimates so that they more closely resemble real world emissions.
- Once existing emissions are adequately described, it would be informative to use the procedure to examine the photochemical effects of alternative fuels rather than just their effect on inventories of emitted pollutants.

- The box model formulation used to describe the initial dispersion of vehicle-emitted pollutants required several assumptions. Integration of a more robust, deterministic dispersion methodology such as that presented by Karim et al. might improve the modeling procedure (Karim et al., 1998). At the least, it would obviate the mixing height and resultant wind speed assumptions described in Section 3.3.
- The modeling procedure presented herein describes ozone formation directly over the roadway only. It would be useful to develop a methodology to disperse the vehicle-emitted pollutants, the resultant oxidation products, and the oxidation processes themselves downwind to estimate the effects of the roadway emissions on the local environment.
- It would be informative to setup a simulation experiment where a grid-based regional model is run for a rural area containing an interstate facility. The baseline run could show how the large-scale model processes the traffic emissions (determined on a VMT/average speed basis) within the affected model grids. The second run could utilize the results of this research to develop emissions and photochemical descriptions nested within affected grids and specify their input into the model. This type of exercise would examine the effects of explicitly treating interstates and other major roadways as sub-grid features within regional models.
- It would also be useful to explore the effects the various traffic and emissions scenarios have on the formation of other harmful oxidation products such as

peryoxyacetylnitrate (PAN) and nitric acid (HNO_3) which contributes to acidification in the environment (NRC, 1991).

CITATIONS

Ahn, K. 1998. *Microscopic Fuel Consumption and Emission Modeling.* Masters. Thesis. Virginia Polytechnic Institute and State University. Blacksburg, VA.

AL-Omishy, H.K. and Al-Samarrai, H.S. 1988. Road traffic simulation model for predicting pollutant emissions. *Atmospheric Environment.* 22, No. 4, 769-774.

Atkinson, R. Gas-phase troposheric chemistry of organic compounds. *Journal of Physical Chemistry Reference Data Monograph*, 2, 1-216.

Atkinson R., Baulch, D.L., Cox, R.A., Hampson, R.F., Kerr, J.A., Rossi, M.J., Troe, J. 1997. Evaluated kinetic, photochemical and heterogeneous data for atmospheric chemistry: Supplement V, IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry. *Journal of Physical Chemistry Reference Data*, 26, 521-1012.

Automotive Environmental Systems. 1973. *A Study of Emission from Light Duty Vehicles in Six Cities*. PB220142.

Baldocchi, D.D., Fuentes, J.D., Bowling, D.R., Turnipseed, A.A., Monson, R.K. 1999. Sacling isoprene fluxes from leaves to canopies: test cases over a Boreal aspen forest and a mixed species deciduous forest. *Journal of Applied Meteorology.* 38, 885-898.

Barkawi, A. 1997. *An Evaluation of Modal and Average Speed Approaches for Mobile Source Emissions Estimation*. Ph.D. Thesis. University of Tennessee. Knoxville, TN.

Barkawi, A. 1998. Telephone conversation May 1998.

Barth, M.J and Tadi, R.R. 1996. Emissions comparison between truck and rail: Study of California I-40. *Transportation Research Record No. 1520.* Washington, DC: Transportation Research Board.

Baumgardner, R. E. and Edgerton, E. S. 1998. Rural ozone across the Eastern United States: Analysis of CASTNet data, 1988-1995. *Journal of Air & Waste Management*, 48, 674-688.

Bellomo, S. J. and Liff, S. D. 1984. *Fundamentals of Air Quality for Highway Planning and Project Development*. Publication No. DTFH61-83-C-00077. Washington, DC: Federal Highway Administration.

Blanchard, C.L. and Stoeckenius, T. 2001. Ozone response to precursor controls: comparison of data analysis methods with the predictions of photochemical air quality simulation models. *Atmospheric Environment*, 35, 1203-1215.

Brücher, W., Kessler, C., Kerschgens, M.J., Ebel, A. 2000. Simulation of traffic-induced air pollution on regional to local scales. *Atmospheric Environment*, 34, 4675-4681.

Bureau of Transportation Statistics. 1998. National Transportation Statistics – Highway Profile. Washington, DC: U.S. Department of Transportation.

Carpenter, W.A., Clemena, G.G., Heisler, R.L. 1976. *Introduction to AIRPOL-4A: An Introduction ands User's Guide.* Charlottesville, VA: Virginia Highway and Transportation Research Council. Report No. 76-R38.

Carter, W.P. and Lurmann, F.W. 1990. *Evaluation Of The RADM Gas-Phase Chemical Mechanism.* Research Triangle Park, NC: U.S. Environmental Protection Agency.

Chameides W., et al. 1987. Net ozone photochemical production over the eastern and central north Pacific as inferred from CTE/CITE 1 observations during fall 1983. *Journal of Geophysical Research* 92, 2131-2152.

Chameides W., Fehsenfeld, F., Rodger, M.O., Cardelino, C. Martinez, J., Parish, D., Lonneman, W., Lawson, D.R., Rasmussen, R.A., Zimmerman, P., Greenberg, J., Middleton, P., Wang, T. 1992. Ozone precursor relationships in the ambient atmosphere. *Journal of Geophysical Research* 97, 6037-6055.

Chameides, W.L. and Cowling, E.B. 1995. *The State Of The Southern Oxidants Study: Policy-Relevant Findings in Ozone Pollution Research 1988 - 1994.* Raleigh, NC: Southern Oxidants Study Science Team, North Carolina State University.

Cowling, E.B. and Furiness, C. 2001. *The State Of The Southern Oxidants Study: Policy-Relevant Findings in Ozone Pollution Research 19994 - 2001.* Raleigh, NC: Southern Oxidants Study Science Team, North Carolina State University.

Chang, M.E., Hartley D.E., Cardelino C., Chang W.L. 1996. *Inverse modeling of biogenic isoprene emissions.* Geophysical Research Letters. 96GL02370 Vol. 23 , No. 21: 3007.

Childress, J.P. and Wilson, J.H. 1994. *Analysis of Real-time Vehicle Hydrocarbon Emissions Data.* EPA/600/SR-94/059. Research Triangle Park, NC: U.S. Environmental Protection Agency.

Chin, M., Jacob, D.J., Munger, J.W., Parish, D.D., and Dodridge, B.G. 1994. Relationship of ozone and carbon monoxide over North America. *Journal of Geophysical Research.* 99, 14565-14573.

Ciciero-Fernandez, P., Long, J.R., and Winer, A.M. 1997. effects of Grades and Other Loads on On-Road Emissions of Hydrocarbons and Carbon Monoxide. *Journal of Air & Waste Management*, 47, 898-904.

Clean Air Act of 1990,. Section 107. 1990. Washington, DC: Office of the Federal Register.

Clean Air Act of 1990, Section 108. 1990. Washington, DC: Office of the Federal Register.

Devore, J.L. *Probability and Statistics for Engineering and the Sciences, Fifth Edition.* Pacific Grove, CA: Duxbury.

DOE. 1998. *Heavy Duty Vehicle Test Fact Sheet: Heavy-Duty Vehicle Emissions Testing Program – Giving Fleet Operators Access to a Convenient Mobile Testing Lab.* Washington, DC: U.S. Department of Energy.

Dunker, A.M., Morris, R.E., Pollack, A.K., Schleyer, C.H., and Yarwood, G. 1996. Photochemical modeling of the impact of fuels and vehicles on urban ozone using auto/oil program data. *Environmental Science & Technology.* 30, 787-807.

EPA. 1986. *Air Quality Criteria for Ozone and Other Photochemical Oxidants: Vols. 2 and 3.* EPA-600/8-84-020bF and EPA-600/8-84/020bF-cF. Research Triangle Park, NC: U.S. Environmental Protection Agency.

EPA. 1986. *Preliminary Evaluation Studies With The Regional Acid Deposition Model (RADM).* Research Triangle Park, NC: U.S. Environmental Protection Agency.

EPA. 1992. *Procedures for the Preparation of Emission Inventories for Carbon Monoxide and Precursors of Ozone. Volume II: Emission Inventory Requirments for*

Photochemical Air Quality Models (REVISED). EPA 454/R-92-026. Research Triangle Park, NC: U.S. Environmental Protection Agency.

EPA. 1996. *National Air Quality and Emissions Trends report, 1995*. EPA 454/R-96-005. Research Triangle Park, NC: U.S. Environmental Protection Agency.

EPA. 1997. *Fact Sheet: EPA's Revised Ozone Standard Technology.* Washington, DC: U.S. Environmental Protection Agency.

EPA. 1997. *Final Regulatory Impact Analysis: Control of Emissions of Air Pollution from Highway Heavy-Duty Engines.* Washington, DC: U. S. Environmental Protection Agency.

EPA. 1998. *EPA Third-Generation Air Quality Modeling System. Models-3 Volume 9B: User Manual.* EPA-600/R-98-069(a). Washington, DC: U.S. Environmental Protection Agency.

EPA. 1998. *Fact Sheet: Policy to Provide for Extending the Date to Meet Ground-level Ozone Air Quality Standards for Areas Affected by Transport of Pollutants from Upwind Areas.* Washington, DC: U.S. Environmental Protection Agency.

Federal Test Procedure. 1989. Code of Federal Regulations, Title 40, Parts 89-99. Washington, DC: Office of the Federal Register.

Fehsenfeld, F., Calvert, J., Fall, R., Goldan, P., Guenther, A.B., Hewitt, C.N., Lamb, B., Shaw, L., Trainer, M., Westberg, H., Zimmerman, P. 1992. Emissions of volatile organic compounds from vegetation and the implications for atmospheric chemistry. *Global Biogeochemical Cycles*, 6, 389-430.

FHWA. 1976. *Fundamentals of Air Quality.* Information Package No. 76-5. Washington, DC: Federal Highway Administration.

FHWA. 1994. *Evaluation of MOBILE Vehicle Emission Model.* DOT-VNTSC-FHWA-94-8. Washington, DC: Federal Highway Administration.

FHWA. 1994. *A Summary: Air Quality Provisions of the Intermodal Surface Transportation Efficiency Act of 1991.* Washington, DC: Federal Highway Administration.

FHWA. 1994. *FRESIM User Guide, Version 4.5.* Mclean, VA: Research, Development, and Technology, Federal Highway Administration.

Finlayson-Pitts B. and Pitts J. 1993. Atmospheric chemistry of tropospheric formation: scientific and regulatory implications. *Journal of Air & Waste Management*, 43, 1091-1100.

Fishman J., Seiler W., Gregory G., Sachse G., Beck S., and Hill G. 1987. Vertical profiles of ozone, carbon monoxide, and dew point temperature obtained during GTE/CITE 1, October to November 1983. *Journal of Geophysical Research*, 92, 2083-2094.

Fuentes, J.D., Wang, D., Den Hartog, G., Neumann, H.H., Dann, T.F., Puckett, K.J. 1995 Modeled and field measurements of biogenic hydrocarbon emissions from a Canadian deciduous forest. *Atmospheric Environment.* 29, 3003-3017.

Gertler, A.W., Fujita, E.M., Pierson, W.R., and Wittorff, D.N. 1996. Apportionment of NMHC tailpipe vs. non-tailpipe emissions in the Fort McHenry and Tuscarora Mountain Tunnels. *Atmospheric Environment.* 30, 2297-2305.

Guensler R. 1991. *Uncertainty in the Emission Inventory for Heavy-Duty Diesel-Powered Trucks*. UCD-ITS-RR-91-02. Davis, CA: Institute of Transportation Studies, University of California, Davis.

Guensler R. 1993. *Transportation Data Needs for Evolving Emissions Inventory Models.* UCD-ITS-RR-93-XX. Davis, CA: Institute of Transportation Studies, University of California, Davis.

Guenther, A. B., Zimmerman, P., and Harley, P. 1994. Natural volatile organic compound emission rates for U.S. woodland landscapes. *Atmospheric Environment.* 28, 1197-1210.

Guenther, A. B., Hewitt, C. N., Erickson, D. Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J. and Zimmerman, P. 1995. A global model of natural volatile organic compound emissions. *Journal of Geophysical Research.* 100, 8873-8892.

Gillani, N.V. 1987. *Ozone Formation in Pollutant Plumes: A Reactive Plume Model with Arbitrary Crosswind Resolution.* Research Triangle Park, NC: U.S. Environmental Protection Agency.

Gillani, N.V. and Pleim, J.E. 1996. Sub-grid scale features of anthropogenic emissions of NO_x and VOC in the context of regional Eulerian models. *Atmospheric Environment.* 30, 2043-2059.

HPMS. 1997. Data received from Federal Highway Administration.

Harley, R.A., Sawyer, R.F., and Milford, J.B. 1997. Updated photochemical modeling for California's South Coast Air Basin: Comparison of chemical mechanisms and motor vehicle emission inventories. *Environmental Science & Technology.* 31, 2829-2839.

Harvey, G. and Deakin, E. 1992. *Transportation and Air Quality. Searching for Solutions. A Policy Discussion Series, Number 5.* Washington, D.C: Federal Highway Administration.

Ho, J. and Winer, A.M. 1998. Effects of Fuel Type, Driving Cycle, and Emission Status on In-Use Vehicle Exhaust Reactivity. *Journal of Air & Waste Management*, 48, 592-603.

Hov O., Hesstvedt, E., and Isaksen, I. 1978. Long-range transport of tropospheric ozone. *Nature*. *273*, 341-344.

Hutchins, F.P. 1994. *Estimate of Relative NO_x Emissions Resulting from Movement of Freight by Truck and by Train*. Washington, DC: U.S. Environmental Protection Agency.

Isaksen, I., Hov, O., and Hesstvedt, E. 1978. Ozone generation of rural areas. *Environmental. Science & Technology*. 12, 1279-1284.

Jacob, D.J, Horowitz, L.W., Munger, J.W., Heikes, B.G., Dickerson, R.R., Artz, R.S., and Keene, W.C. 1995. Seasonal transition from NO_x- to hydrocarbon-limited conditions for ozone production over the eastern United States in September. *Journal of Geophysical Research*. 100, 9315-9324.

Jenkin, M.E. and Clemitshaw, K.C. 2000. Ozone and other secondary photochemical pollutants: chemical processes governing their formation in the planetary boundary layer. *Atmospheric Environment*. 34, 2499-2527.

Jimenez, J.L., McRae, G.J., Nelson, D.D., Zahinser, M.S., and Kolb, C.E. 2000. Remote sensing of NO and NO_2 emissions from heavy-duty diesel vehicles using tunable diode lasers. *Environmental Science & Technology*. 34, 2380-2387.

Karim, M.D. and Hiroshi, M. 1998. A mathematical model of wind flow, vehicle wake, and pollutant concentration in urban road microenvironments. Part I: Model Description. *Transportation Research, Part D: Transport and Environment*. Vol. 3D, No. 2, 81-92.

Karim, M.D. Hiroshi, M., and Guensler, R. 1998. A mathematical model of wind flow, vehicle wake, and pollutant concentration in urban road microenvironments. Part II: Model Results. *Transportation Research, Part D: Transport and Environment*. Vol. 3D, No. 3, 171-191.

Kunsleman, P. 1974. *Automobile Exhaust Emission Model Analysis Model*. EPA-460/3-74-005. Washington, DC: U.S. Environmental Protection Agency.

Lamb, R.G. 1983. *A Regional Scale (1000 km) Model of Photochemical Air Pollution. Part 1. Theoretical Formulation.* EPA-600/3-83-035. Research Triangle Park, NC: U.S. Environmental Protection Agency.

Lamb, B., Guenther, A., Gay, D., and Westberg, H. 1987. A national inventory of biogenic hydrocarbon emissions. *Atmospheric Environment*. 21, 1695-1705.

Lamb, B., Gay, D. Westberg, H. 1993 A biogenic hydrocarbon emission inventory for the U.S.A. using a simple forest canopy model. *Atmospheric Environment.* 27A, 1673-1690.

Leppard, W.R., Rapp, L.A., Burns, V.R., Gorse, R.A., Knepper, J.C., Koehl, W.J. 1992 Effects of gasoline composition on vehicle engine-out and tailpipe hydrocarbon emissions. SAE Technical Series No. 920329. Society of Automobile Engineers.

Liang, J. and Jacobson, M.Z. 2000. Effects of subgrid segregation on ozone production efficiency in a chemical model. *Atmospheric Environment*, 34, 2975-2982.

Lieberman, E., Rosenfield, N. 1977. *Network Flow Simulation for Urban Trafic Control System – Phase II. Vol. 5 Extension of NETSIM Simulation Model to Incorporate Vehicle Fuel Consumption and Emissions.* FHWA-RD-77-45. Washington, DC: Federal Highway Administration.

Lopez, A., Barthomeuf, M.O., Huertas, M.L. 1989. Simulation of chemical processes occurring in an atmospheric boundary layer. Influence of light and biogenic hydrocarbons on the formation of oxidants. *Atmospheric Environment*, 23, 1465-1478.

Makar, P.A., Fuentes, J.D., Wang, D., Staebler, R.M., and Wiebe, H.A. 1999. Chemical processing of biogenic hydrocarbons within and above a temperate deciduous forest. *Journal of Geophysical Research.* 104, 3581-3603.

Martinez, J.R., and H.B. Singh. 1979. Survey of The Role of NO_x in Non-urban Ozone Formation. EPA-450/4-79-035. , Research Triangle Park, NC: U.S. Environmental Protection Agency.

Masters, G.M. 1998. *Introduction to Environmental Engineering and Science, Second Edition*. Englewood Cliffs, NJ: Prentice Hall.

McGill, R. *Fuel Consumption and Emissions Values for Traffic Models*. FHWA-85-053. Washington, DC: Federal Highway Administration.

McLaren, R. Gertler, A.W., Wittorff, D.N., Belzer, W., Dann, T., Singleton, D.L. 1996. Real-world measurements of exhaust and evaporative emissions in the Cassar Tunnel predicted by chemical mass balance modeling. *Environmental Science & Technology*. 30, 3001-3009.

Middleton P., Stockwell W., and Carter W. 1990. Aggregation and analysis of volatile organic compound emissions for regional modeling. *Atmospheric Environment*, 24A, 1107-1134.

Montzka, S. 1993. Isoprene and its oxidation products, methyl vinyl ketone and methacrolein, in the rural troposphere. *Journal of Geophysical Research*, 98D, 1101-1111.

Morris, R.E. and Myers, T.C. 1990. *User's Guide for the Urban Airshed Model, Volume I: User's Manual for UAM (CB-IV).* EPA-450/4-90-007A. Research Triangle Park, NC: U.S. Environmental Protection Agency.

Nelson, C., Siwek, S., Guensler, R., and Michelson, K. 1991. *Managing Trucks for Air Quality: Current Work in Progress.* Transportation Research Record No. 1312. Washington, DC: Transportation Research Board.

NRC. 1981. *NO_x Emission Controls for Heavy-Duty Vehicles: Towards Meeting a 1986 Standard.* Washington, DC: National Research Council.

NRC. 1991. *Rethinking the Ozone Problem in Urban and Regional Air Pollution.* Washington, DC: National Research Councils.

Nizich S., McMullen T., and Misenheimer D. 1994. *National Air Pollutant Emission Trends, 1900-1993.* EPA-454-R-94-027. Research Triangle Park, NC: U.S. Environmental Protection Agency.

Olszyna, K. J., Bailey, E. M., Meagher, J. F. 1993. O_3 and NO_y relationships at a rural site in Tennessee. *Eos Transactions*. American Geophysical Union. 74.

Ostria, S.J. 1996. *Assessing Emissions Contribution of Intercity Trucking.* Transportation Research Record No. 1312. Washington, DC: Transportation Research Board.

Papacostas, C.S. and Prevedouros, P.D. 1993. *Transportation Engineering and Planning, Second Edition.* Englewood Cliffs, NJ: Prentice Hall.

Perkins, H. 1974. *Air Pollution.* New York, NY: McGraw-Hill Book Company.

Petersen, W.B. 1980. *User's Guide for HIWAY 2. A Highway Air Pollution Model.* EPA-600/18-80-018. Washington, DC: U.S. Environmental Protection Agency.

Pierotti, D., Wopsy, S., Jacob, D., and Rasmussen, R. 1990. Isoprene and its oxidation products: methacrolein and methyl vinyl ketone. *Journal of Geophysical Research*, 95, 1871-1881.

Pierson, W.R., Gertler, A.W., Robinson, N.F., Sagebiel, J.C., Zielinzka, B., Bishop, G.A., Stedman, D.H., Zweidinger, R.B., and Ray, W.D. 1996. Real-world automotive emissions – Summary of studies in the Fort McHenry and Tuscarora Mountain tunnels. *Atmospheric Environment*, 30, 2233-2256.

Proyou, A.G., Ziomas, I.C., and Stathopoulos, A. 1998. Application of a three-layer photochemical box model in an Athens street canyon. *Journal of Air & Waste Management*, 48, 427-433.

Rogak, S.N., Pott, U., Dann, T., Wang, D. 1998. Gaseous emissions from vehicles in a traffic tunnel in Vancouver, British Columbia. *Journal of Air & Waste Management*, 48, 604-615.

Russell, A. and Dennis, R. 2000. NARSTO critical review of photochemical models and modeling. *Atmospheric Environment*, 34. 2283-2324.

Sagebiel, J. C., Zielinska, B., Pierson, W. R., and Gertler, A. W. 1996. Real-world emissions and calculated reactivities of organic species from motor vehicles. *Atmospheric Environment*, 30, 2287-2296.

Sawyer, R.F., Harley, R.A., Cadle, S.H., Norbeck, J.M., Slott, and Bravo, H.A. 2000. Mobile sources critical review: 1998 NARSTO assessment. *Atmospheric Environment.* 34, 2161-2181.

Schafer, F. and van Basshuyen, R. 1995. *Reduced Emissions and Fuel Consumption in Automobile Engines*. New York: Springer-Verlag.

Schimek, P. 1998. *Reducing PM and NO_x Emissions from Heavy-Duty Vehicles: The Urban Bus Case.* Proceedings from the 77th Annual Transportation Research Board. Washington, DC: Transportation Research Board.

Sedifan, L., Rao, T.S., and Czapski, U. 1981. Effect of traffic-generated turbulence on near-field dispersion. *Atmospheric Environment*, 15, 527-536.

Selph, M.A., Dietzmann, H.E. 1984. *Characterization of Heavy-Duty Motor Vehicle Emissions Under Transient Driving Conditions.* EPA-600/S3-84-104. Washington, DC: U.S. Environmental Protection Agency.

Sharkey, T. and Loreto, F. 1993. Water stress, temperature, and light effects on the capacity for isoprene emission and photosynthesis of kudzu leaves. *Oecologia*. 95, 238-333.

Sillman, S., Logan, J.A., and Wofsy, S.C. 1990. A regional scale model for ozone in the United States with subgrid representation of urban and power plant plumes. *Journal of Geophysical Research*, 95, 5731-5748.

Sillman, S. 1999. The relation between ozone, NO_x and hydrocarbons in urban and polluted rural environments. *Atmospheric Environment*, 33, 1821- 1845.

Smith, P. 1998. Blowing in the wind. *ITS International.* September/October. p. 86.

Sportisse, Bruno. 2001. Box model versus Eulerian models in air pollution modeling. *Atmospheric Environment*, 35, 173-178.

Sturm, P.J., Almbauer, R., Sudy, C., and Pucher, K. 1997. Application of Computational Methods for the Determination of Traffic Emissions. *Journal of Air & Waste Management*, 48, 674-688.

Teets, M.K. 1996. *Highway Statistics 1996.* Washington, DC: U.S. Department of Transportation.

Toll, I. and Baldasano, J.M. 2000. Modleing of photochemical air pollution in the Barcelona area with highly disaggregated anthropogenic and biogenic emissions. *Atmospheric Environment.* 35, 3069-3084.

TRB. 1995. *Expanding Metropolitan Highways: Implications for Air Quality and Energy Use*. Washington, DC: Transportation Research Board.

Trainer, M., Williams, E., Parrish, D., Buhr, M., Allwine, E., Westberg, H., Fehsenfeld, F., and Liu, S. 1987. Models and observations of the impact of natural hydrocarbons on rural ozone. *Nature*, 329: 705-707.

Trainer, M., et al. 1993. Correlation of ozone with NO_y in photochemically aged air. *Journal of Geophysical Research*, 98, 2917-2925.

Van Aerde, M. 1998. *INTEGRATION Release 2.10 for Windows: User's Guide-Volume I, Fundamental Model Features*. Backsburg, VA.

Wayson, R.L. 1999. *Dispersion Modeling at Intersections: An Overview.* Lecture given at the Microscale Air Quality Impact Assessment for Transportation Projects. Sponsored by the Committee on Transportation and Air Quality (AF103). 78th Annual Transportation Research Board Meeting.

White, L.J. 1982. *The Regulation of Air Pollutant Emissions from Motor Vehicles.* Washington, DC: American Enterprise Institute for Public Policy Research.

Whitten, G.Z., Johnson, R.G., and Killus, J.P. 1985. *Development Of A Chemical Kinetic Mechanism For The U.S. EPA Regional Oxidant Model.* Research Triangle Park, NC: U.S. Environmental Protection Agency.

Winner, D.A. and Cass, G.R. 2000. Effect of emissions control on the long-term frequency distribution of regional ozone concentrations. *Environmental Science & Technology.* 34, 2612-2617.

Wu, B., Miller, J.S., and Demetsky, M.J. 1996. *Sensitivity of the Urban Airshed Model to Ozone Precursor Vehicular Emissions: Volume I – Sensitivity Analysis for a Specific Geographical Location.* Charlottesville: University of Virginia, School of Engineering and Applied Science.

USDOT. 1998. *A Summary: Transportation Equity Act for the 21st Century.* Washington, DC: U.S. Department of Transportation

Yanowitz, J., Graboski, M.S., Ryan, L.B.A., Alleman, T.A., McCormick, R.L. 1999. Chassis dynamometer study of emissions from 21 in-use heavy-duty vehicles. *Environmental Science & Technology*, 33, 209-216.

Zielinska, B., Sagebiel, J. C., Harshfield, G., Gertler, A. W., and Pierson, W. R. 1996. Volatile organic compounds up to C_{20} emitted from motor vehicles; measurement methods. *Atmospheric Environment*, 30, 2269-2286.

REFERENCES

Aneja, V.P., Mathur, R., Arya, S.P., Li, Y., Murray, G.C., Manuszak, T.L. 2000. Coupling the vertical distribution of ozone in the atmospheric boundary layer. *Environmental Science & Technology*, 34, 2324-2329.

Arya, S.P. *Air Pollution Meteorology and Dispersion*. 1999. Oxford, England: Oxfurd University Press.

Atkinson, R. 1990. Gas-phase tropospheric chemistry of organic compounds: A review. *Atmospheric Environment,* 24A, 1-41.

Atkinson, R. and Carter, W. 1990. Kinetics and mechanisms of the gas-phase reactions of ozone with organic compounds under atmospheric conditions. *Chemical Review*, 84, 437-470.

Atkinson, R. Atmpsoheric chemistry of VOCs and NO_X. 2000. *Atmospheric Environment*, 34, 2063-2101.

Baldocchi, D., Guenther, A., Harley, P., Klinger, L., Zimmerman, Lamb, B., Westberg, H. 1995. The fluxes and air chemistry of isoprene above a deciduous hardwood forest. *Philosophical Transactions of the Royal Society of London*, 350, 279-296.

Barkawi, A. 1997. An Evaluation of Modal and Average Speed Approaches for Mobile Source Emissions Estimation. Ph.D. Thesis. University of Tennessee. Knoxville, TN.

Black, F., Tejada, S., and Kleindienst, T. 1998. Preparation of Automobile Organic Emission Surrogates for Photochemical Model Validation. *Atmospheric Environment*, 32, 2443-2451.

Cadle, S.H., Gorse, R.A., Belian, T.C., and Lawson, D.R. 1997. Real-World Vehicle Emissions: A Summary of the Seventeenth Coordinating Research Council On-Road Vehicle Emissions Workshop. *Journal of Air & Waste Management*, 48, 174-185.

Chameides W., et al. 1989. Ozone precursors and photochemistry over the eastern North Pacific during the spring of 1984 based on the NASA GTE/CITE 1 airborne observations. *Journal of Geophysical Research* 94, 9799-9808.

Colville, R.N., Hutchinson, E.J., Mindell, J.S., and Warren, R.F. 2001. The transport sector as a source of air pollution. *Atmospheric Environment.* 35, 1537-1565.

Dodge, M.C. 2000. Chemical oxidant mechanisms for air quality modeling: critical review. *Atmospheric Environment.* 34, 2103-2130.

Goa W., Wesely M., and Doskey P. (1993). Numerical modeling of the turbulent diffusion chemistry of NO_x, O_3, isoprene, and other reactive trace gases in and above a forest canopy. *Journal of Geophysical Research,* 98, 18339-18353.

Gilliam, F.S. and Turil, N.L. 1995. Temporal Patterns of ozone pollution in West Virginia: Implications for high-elevation hardwood forests. *Journal of Air & Waste Management*, 4, 621-626.

Gillani, N.V. 1987. *Ozone Formation in Pollutant Plumes: A Reactive Plume Model with Arbitrary Crosswind Resolution.* Research Triangle Park, NC: U.S. Environmental Protection Agency.

Fuentes, J.D., Wang, D., Neumann, H.H., Gillespie, T.J., Den Hartod, G., Dann, T.F. 1996. Ambient biogenic hydrocarbons and isoprene emissions from a mixed deciduous forest. *Journal of Atmospheric Chemistry*, 25, 67-95.

Fuentes, J.D., Wang, D., Gu, L. 1999. Seasonal variations in isoprene emissions from a Boreal aspen forest. *Journal of Applied Meteorology*, 38, 855-869.

Fuentes, J.D. and Wang,D. 1999. On the seasonality of isoprene emissions from a mixed temperate forest. *Ecological Applications*, 9(4), 1118-1131.

Duffy, B.L., Nelson, P.F., Ye, Y., and Weeks, I.A. 1999. Speciated Hydrocarbon Profiles and Calculated Reactivities of Exhaust and Evaporative emissions for 82 In-Use Light-Duty Australian Vehicles. *Atmospheric Environment*, 33, 291-307.

Harris, G.W., Carter, W.P., Winer, A.M., Pitts, J.N. 1982. Ozone generation of rural areas. *Environ. Science & Technolology*, 12, 1279-1284.

Haszpra, L. and Szilagyi, I. 1994. Non-Methane Hydrocarbon Composition of Car Exhaust in Hungary. *Atmospheric Environment*, 28, 2609-2614.

Hidy, G.M. 2000. Ozone process insights from field experiments Part I: Overview. *Atmospheric Environment*, 34, 2001-2022.

Huber, L., Laville, P., Fuentes, J.D. 1999. Uncertainties in isoprene emissions from a mixed deciduous forest estimated using a canopy microclimate model. *Journal of Applied Meteorology*, 38, 899-912.

Kaharabata, S.K., Schuepp, P.H., Fuentes, J.D. 1999. Source footprint considerations in the determination of volatile organic compound fluxes from forest canopies. *Journal of Applied Meteorology*, 38, 878-884.

Karamchandani, P., Koo, A., and Seigneur, C. 1998. Reduced gas-phase kinetic mechanism for atmospheric plume chemistry. *Environmental Science & Technology*, 32, 1709-1720.

Killus, J., and Whitten, G. 1984. Isoprene: A photochemical kinetic mechanism. *Environmental. Science & Technology*. 18, 142-148.

Kirchstetter, T.W., Harley, R.A., and Littlejohn, D. 1996. Measurement of nitrous acid in motor vehicle exhaust. *Environmental. Science & Technology*. 30, 2843-2849.

Kleinman, L.I.. 2000. Ozone process insights from field experiments Part I: Observation-based analysis for ozone production. *Atmospheric Environment*, 34, 2023-2033.

Klingenberg, H. 1996. *Automobile Exhaust Emission Testing: Measurement of Regulated and Unregulated Exhaust Gas Components, Exhausts Emission Tests*. Berlin: Springer.

Lamb, B., Pierce, T., Baldocchi, D., Allwine, E., Dilts, S., Westberg, H., Geron, C., Guenther, A., Klinger, L., Harley, P., Zimmerman, P. 1996. Evaluation of forest canopy models for estimating isoprene emissions. *Journal of Geophysical Research*, 101, 22,787-22,797.

Lefohn, A.S., Edwards, P.J., and Adams, M.B. 1994. The characterization of ozone exposures in rural West Virginia and Virginia. *Journal of Air & Waste Management*, 44. 1276-1283.

Logan, J. 1985. Tropospheric ozone: Seasonal behavior, trends and anthropogenic influence. *Journal of Geophysical Research*, 90, 10463-10482.

Lowenthal, D.H., Zelinska, B., Chow, J.C., Watson, J.G., Gautam, M., Ferguuson, D.H., Neuroth, G.R., and Stevens, K.D. 1994. Characterization of Heavy-Duty Diesel Vehicle Emissions. *Atmospheric Environment*, 28, 731-743.

Loyd, A., Atkinson, R., Lurman, R., Nitta, B. 1983. Modeling potential ozone impacts from natural hydrocarbon emissions - I. *Atmospheric Environment*, 17, 1931-1950.

Modica, L.G., et al. 1989. *Flexible Regional Emissions Data System (FREDS), documentation for the 1985 NAPAP emissions inventory: Project summary.* Research Triangle Park, NC: U.S. Environmental Protection Agency.

Musselman, R.C., McCool, P.M., and Lefohn, A.S. 1994. Ozone descriptors for an air quality standard to protect vegetation. *Journal of Air & Waste Management*, 44, 1383 – 1390.

Oettl, D. Kukkonen, J., Albauer, R.A., Sturm, P.J., Pohjola, M., and Harkonen, J. 2001. Evaluation of Gaussian and a Lagrangian model against a roadside data set, with emphasis on low wind speed conditions. *Atmospheric Environment*, 24A, 1107-1134.

OTAG recommends ozone controls tailored to pollution transport. 1997. *Environmental Science & Technology*, 31, 352A-353A.

Pierce, T.E. and Baugues, K.A. 1991. *User's guide to the personal computer version of the biogenic emissions inventory system (PC-BEIS).* Research Triangle Park, NC: U.S. Environmental Protection Agency.

Prinn R., Cunnold D., Rasmussen R., Simmonds P., Alyea F., Crawford A., Fraser P., and Rosen R. 1987. Atmospheric trends in methylchloroform and the global for the hydroxyl radical. *Science*, 238, 945-950.

Roth, P.M. 1999. A qualitative approach to evaluating the anticipated reliability of a photochemical air quality simulation model for a selected application. *Journal of Air & Waste Management*, 49, 1050-1059.

Shunk, G.A., 1994. *TRANSIMS Project Description Model Improvement Program.* Arlington, TX: Texas Transportation Institute.

Stasiuk, W.N. and P.E. Coffey. 1974. Rural and Urban Ozone Relationships in New York State. *Journal of the Air Pollution Control Association*, 24, 564-568.

Zannetti, P. *Air Pollution Modeling: Theories, Computational Methods and Available Software.* New York, NY: Van Nostrand Reinhold.