Gulf Coast Aerosol Research and Characterization Program (Houston Supersite)

PROGRESS REPORT

EPA Contract No. R-82806201

between the Environmental Protection Agency and the
University of Texas at Austin

Submitted by:

Dr. David Allen
(allen@che.utexas.edu)
512-471-0049

Center for Energy and Environmental Resources
The University of Texas at Austin
10100 Burnet Road, Bldg. 133
MS R7100
Austin, Texas 78758

with contributions from
Gary McGaughey, University of Texas at Austin
Robert Harley, University of California, Berkeley
Matt Fraser, Rice University
William Lonneman, U.S. Environmental Protection Agency

Quarterly progress report for April, 2002

Date of Report: May 13, 2002

EPA Agreement No.: R-82806201

Title: Gulf Coast Aerosol Research and Characterization Study

Investigators: Dr. David Allen (PI) and Dr. Matthew Fraser (Co-PI)

Institutions: University of Texas and Rice University

Research Category: Air Quality/Fine Particulate Matter

Project Period: 01/15/00-11/30/03

Objective of Research: Characterize fine particulate matter and fine particulate matter formation processes in Southeast Texas

Progress Summary/Accomplishments:
Measurements for the Houston fine particulate matter supersite were completed in late 2001. Continuing work is focussing on data analysis and this progress report describes analysis of data collected in the Washburn tunnel during the August – September 2000 intensive sampling period. The goal of the sampling conducted in the Washburn Tunnel was to determine fuel-based emission factors for the Houston on-road fleet; this was accomplished and, in this report, the fuel based emission factors for Houston are compared to emission factors determined in other tunnel studies.

Overview

Measurements collected in a Houston tunnel were used to develop CO, NO_x, and NMHC (non-methane hydrocarbon) emission factors for on-road gasoline vehicles. Samples collected in the tunnel were also used to develop chemical fingerprints of fine particulate matter emitted by on-road diesel vehicles.

Comparison to emission factors reported in previous tunnel studies revealed that the Houston NO_x emission factor was 8% lower than the average emission factor reported in previous tunnel studies while the Houston NMHC emission factor was 50% higher than the average emission factor reported in previous tunnel studies. Emissions of fine particulate matter and fine particle elemental carbon in the tunnel were observed to increase as the fraction of diesel vehicles increased. Surprisingly, ammonia concentrations were also observed to increase as the fraction of diesel vehicles increased. Comparison of individual hydrocarbon ratios based on the tunnel data to ratios based on data obtained by low-level aircraft flying over major transportation corridors showed relatively lower levels of acetylene and MTBE in the ambient environment. Advection of hydrocarbon emissions from industrial sources located to the east and south of Houston may explain the discrepancy between the aircraft and tunnel hydrocarbon ratios.

Background

Vehicular emissions continue to be a major source of air pollutants in the United States; the U.S. Environmental Protection Agency (EPA) estimates that, in 1999, on-road motor vehicles accounted for 29% of total volatile organic compound (VOC) emissions, 34% of total oxides of nitrogen emissions, and 51% of all carbon monoxide emissions nationwide (EPA, 2001).

Estimates of vehicular emissions, such as those reported by the EPA (2001), are typically estimated using emission factor models such as EMFAC (CARB, 1996) or MOBILE (EPA, 2002), together with information on vehicle populations and activity. The emissions factors are often based on dynamometer studies performed in controlled environments. Emission rates derived from these studies are quite precise since the test conditions (e.g., engine type, emissions control technology, fuel composition, vehicle age, etc.) are carefully monitored. However, using the results of dynamometer tests to develop representative emission factors for an entire vehicle fleet is difficult because of the variety of ages, conditions, and maintenance histories associated with on-road fleets. In addition, the driving cycles used in dynamometer tests may not reflect the full range of on-road conditions and this may lead to inaccurate emission estimates (National Research Council, 2000, 2001).

To complement the results of dynamometer studies, vehicle emissions can be determined in on-road settings. For example, remote sensing and tunnel studies have been used to estimate emission factors from thousands of in-use vehicles. Remote sensing is a powerful and inexpensive technique, and can provide accurate CO and NMOC (Non-Methane Organic Compound) measurements. Remote-sensing capabilities for NO_x and $PM_{2.5}$ are more challenging and limited validation studies have been performed to-date

(NRC, 2001). Tunnel air quality measurements are well-suited for measuring vehicle emissions, and have the advantage of sampling a large range of vehicle types under normal operating conditions. In contrast to remote sensing, which samples only exhaust emissions for an operating period less than a second, tunnel studies provide samples that are representative of tailpipe and non-tailpipe (evaporative) emissions during the transit time through the tunnel. In addition, hydrocarbon species are not subject to photochemical degradation and speciation data can be used to estimate both tailpipe and evaporative emissions. Numerous studies have compared measured pollutant concentrations in tunnels to emission factor model predictions (e.g., Pierson et al., 1996; Gertler et al. 1997a; Rogak et al., 1997) and/or have been used to define the detailed chemical composition of mobile source NMOC emissions (e.g., Lonneman et al., 1986; Kirchstetter et al., 1996; Rogak et al., 1997).

During the summer of 2000, a team of investigators collected gas and particle phase measurements in a tunnel in the Houston area. The primary objective of this study was to provide data for estimating vehicular emission factors and composition profiles. A secondary objective was to compare compositions of vehicular emissions obtained in a tunnel to the composition of samples collected during low-level aircraft overflights of major transportation corridors in the Houston area.

Measurements were made in the Washburn Tunnel, which runs under the Houston Ship Channel in highly industrialized eastern Houston, and is the only vehicle tunnel currently in operation in the state of Texas. Hydrocarbon samples were collected over transportation corridors throughout Houston by the Baylor University Twin Otter turbo-prop aircraft.

Data Collection Methods

Tunnel Description

The Washburn Tunnel runs north-south beneath the Houston Ship Channel and connects the cities of Galena Park and Pasadena. The tunnel consists of a single bore, 895 meters in length, with a 6 percent roadway grade outward from the center towards each exit. Forced transverse ventilation is potentially provided by three automatic blower fans located in a tower at the north entrance; however, only one blower fan was in use during this sampling study. Ambient air is drawn through screens on the north and south faces of the fan room and is channeled into a closed-end chamber that runs beneath the vehicle tunnel. This air is forced out of the closed-end chamber through vents located throughout the length of the tunnel at street level along both sides. Additional longitudinal ventilation is induced by the flow of vehicles and by the prevailing winds, which were generally light (2 m/s – 4 m/s) during all sampling periods.

Vehicle traffic typically passes through the Washburn Tunnel at average speeds of 16-20. meters per second (35-45 miles per hour). The vehicle fleet composition varies depending on time of day and day of the week. During the morning and evening rush hours, traffic passing through the tunnel is dominated by light-duty vehicles. At mid-day, a higher proportion of the vehicle fleet is heavy-duty diesel, however, because of height

restrictions in the tunnel, heavy-duty vehicles rarely exceed 10% of the total tunnel traffic.

Measurements were collected on each day during the August 29, 2000 (Tuesday) through September 1, 2000 (Friday) period. Given the potential to isolate the light-duty and heavy-duty vehicle emission signatures based on the expected higher proportion of diesel vehicles during the mid-day period, two-hour tunnel samples were collected from 1200 – 1400 CDT and 1600 – 1800 CDT each day.

Traffic Monitoring

Video cameras were located at multiple locations throughout the Washburn Tunnel. These cameras are used by security personnel for surveillance, and transmit real-time images to the tunnel control room. The video data collected by a wall-mounted surveillance camera located at the north tunnel entrance were recorded during each of the sampling periods on VHS tape. This camera looked directly into the tunnel bore, capturing both lanes of traffic, and provided the video data used to determine traffic volumes and composition.

Table 1 presents the video data capture for each sampling period. Most periods were successfully recorded, with the notable exceptions of the first and last sampling periods. Due to logistical problems, the percent data capture for these periods was 21.7 % and 70.8 %, respectively.

TABLE 1. Percent video data capture by sampling period.

Date	**Sampling Period (CDT)**	**Video Data (CDT)**	**Percent Video Data Capture**
2000/08/29	1200 – 1400	1334 – 1400	21.7
	1600 – 1800	1600 – 1800	100.0
2000/08/30	1200 – 1400	1211 – 1400	90.8
	1600 – 1800	1604 – 1800	96.7
2000/08/31	1200 – 1400	1206 – 1400	95.0
	1600 – 1800	1604 – 1800	96.7
2000/09/01	1200 – 1400	1200 – 1359	99.2
	1600 – 1800	1600 – 1725	70.8

The VHS tapes were viewed in one-half hour to one-hour segments by two observers. One observer was assigned to each lane of traffic (i.e., northbound or southbound). Vehicles were visually classified using the five vehicle type categories listed in Table 2. These vehicle categories were derived from MOBILE5 vehicle classifications (EPA, 1994), which primarily differentiate vehicles based on engine size, fuel usage (gasoline or diesel), and weight. The final classification scheme provided sufficient detail to quantify the traffic stream for the purposes of this study, but did not require observers to be specially trained in vehicle identification.

TABLE 2. Description of vehicle categories used to visually classify vehicles.

Vehicle Category	Description
Cars & Jeeps	Passenger cars and jeeps
Motorcycle	Strictly motorcycles
Light-Duty Trucks	Passenger trucks, SUVs, and vans, regardless of the size of number of doors
Medium-Duty (Six-Wheel) Trucks	Passenger trucks with two axles and six wheels (i.e., four wheels on the rear axle)
Heavy-Duty Vehicles	Trucks with 3 or more axles (includes industrial trucks, transport vehicles, dump trucks, and eighteen wheelers)

Table 3 presents the results of the vehicle traffic counts by vehicle type for each two-hour sampling period by direction. Table 4 presents the total traffic volumes and percent heavy-duty vehicle for each two-hour sampling period by direction. Traffic in the northbound lane is leaving the tunnel on an uphill grade. Traffic in the southbound lane is entering the tunnel on a downhill grade. The vehicle composition was dominated by cars and passenger trucks during all sampling periods. For each sampling period, the traffic volumes and vehicle compositions are similar between lanes. In general, the late afternoon vehicle volumes were more than twice that observed during the mid-day period. The main change from the mid-day (1200 CDT – 1400 CDT) to afternoon rush hour (1600 CDT – 1800 CDT) periods is a large increase in the number of light-duty vehicles (cars and trucks). Therefore, heavy-duty trucks (those with 3 or more axles, expected to be almost all diesel-fueled) comprise a larger fraction of total traffic during the midday sampling periods.

TABLE 3. Traffic counts (total number of vehicles per sampling period) in the Washburn Tunnel by vehicle category and time of day.

		Cars & Jeeps		Light-Duty Trucks		Medium-Duty Trucks[a]		Heavy-Duty Trucks	
Date	Time (CDT)	in[b]	out[c]	in	out	in	out	in	out
8/29/00[d]	1200 – 1400	79	93	107	100	2	1	9	12
	1600 – 1800	1059	1104	1226	1239	19	10	58	51
8/30/00	1200 – 1400	511	468	518	510	7	7	63	68
	1600 – 1800	943	1113	1209	1198	24	27	46	61
8/31/00	1200 – 1400	521	530	539	554	14	17	56	41
	1600 – 1800	1216	1130	1445	1310	27	13	65	38
9/1/00	1200 – 1400	645	638	680	715	11	8	59	59
	1600 – 1800	764	798	810	753	13	2	29	17

[a]Vehicles with two axles and six tires (i.e., four tires on the rear axle) were counted as medium-duty trucks.
[b]Southbound traffic entering the tunnel on a downhill grade.
[c]Northbound traffic leaving the tunnel on an uphill grade.
[d]Traffic counts during the midday sampling period on this day cover only the last 26 minutes of the 2-hour sampling period.

TABLE 4. Traffic volumes (total number of vehicles per sampling period) and percent heavy-duty vehicles in the Washburn Tunnel by time of day.

Date	Time (CDT)	Total Traffic Volume		Percent Heavy-Duty Vehicle	
		in[a]	out[b]	in	out
8/29/00[c]	1200 – 1400	197	206	4.6	5.8
	1600 – 1800	2372	2411	2.4	2.1
8/30/00	1200 – 1400	1100	1056	5.7	6.4
	1600 – 1800	2233	2404	2.1	2.5
8/31/00	1200 – 1400	1133	1144	4.9	3.6
	1600 – 1800	2767	2499	2.3	1.5
9/1/00	1200 – 1400	1395	1420	4.2	4.2
	1600 – 1800	1620	1575	1.8	1.1

[a]Southbound traffic entering the tunnel on a downhill grade. [b]Northbound traffic leaving the tunnel on an uphill grade. [c]Traffic counts during the midday sampling period on this day cover only the last 26 minutes of the 2-hour sampling period.

The Washburn Tunnel has bi-directional and balanced traffic in a single tube, so induced air flow due to motion of vehicles driving through the tunnel is minimal. Therefore, we assume that only emissions from vehicles using the northern half of the tunnel (vehicles leaving the tunnel traveling northbound and uphill, and vehicles entering the tunnel traveling downhill) are captured in the present study. For each sampling period, the fraction of total exhaust carbon emissions in the tunnel coming from heavy-duty diesel engines was estimated using fuel economies measured in a separate on-road study (Pierson et al., 1996). For light-duty vehicles (cars & jeeps, trucks), carbon emission rates of 42 and 65 grams of carbon per vehicle kilometer were used for downhill and uphill traffic, respectively. The corresponding carbon emissions rates for heavy-duty trucks were 154 and 327 g km^{-1}. Medium-duty (six-wheel trucks) vehicles were ignored because their absolute numbers were low, and both gasoline and diesel are used as fuels for these vehicles. By combining carbon emission rates with traffic count data, the percent of total carbon due to heavy-duty diesel engine emissions was estimated, and is shown in the last column of Table 7. The heavy-duty diesel contribution dropped from 19 to 8% of total carbon, on average, in the 1600 – 1800 CDT sampling periods relative to the 1200-1400 CDT periods.

Driving conditions inside the tunnel were periodically monitored by following traffic with a chase car. Since vehicle speeds could be obtained by observing the video data, chase car drive-throughs were limited to one per hour. During these drive-throughs, the traffic speeds were consistently in the 15.7-20.2 meters per second (35-45 miles per hour)

range. Although no formal speed checks have been performed using the video data, video tape observers reported generally steady vehicle speeds during the majority of sampling periods. Variations in traffic flow were, however, periodically observed during the 1600 – 1800 CDT sampling periods, resulting in occasional stop-and-go traffic due to minor bottlenecks.

Pollutant Measurements

Measurements collected during the study included nitrogen oxides, carbon dioxide, carbon monoxide, ammonia, fine particulate matter ($PM_{2.5}$), and individual hydrocarbon species. An integrated sampling interval of two hours was used to ensure that sufficient quantities of particulate matter were collected for composition analysis. Measurements of tunnel air were collected in the tunnel bore, approximately 50 meters from the north entrance. This location was primarily chosen because of its accessibility. In addition, the sampling location should have been relatively unaffected by entrainment of ambient air into the tunnel by vehicles given the predominant winds. Concentrations of ambient (background) air were collected for $PM_{2.5}$ in the fan room. Background concentrations of CO, CO_2, and individual hydrocarbons were collected in the northern portion of the closed-end ventilation chamber. No measurements of background ambient air were collected at the Washburn Tunnel for nitrogen oxides; therefore, data collected at a nearby Continuous Air Monitoring Station (CAMS) were used as a surrogate. This section summarizes the experimental methods used for each measurement type.

Oxides of Nitrogen (NO_x)

NO_x concentrations were measured using a Monitor Labs chemiluminescent continuous emission monitor (CEM). The NO_X CEM was located in the basement of the Washburn Tunnel in an effort to minimize the residence time of the samples. The Teflon® sample line (approximately twelve feet) was passed under a service door and attached to the wall of the tunnel. The sample line inlet was directed towards the interior of the tunnel and positioned approximately 10 inches away from the wall. Due to the frequent change in measured NO_x concentrations in the Washburn Tunnel, 15-minute average concentrations were recorded from the analyzer display.

Since background measurements of NO_x were not collected at the Washburn Tunnel, data from the Continuous Air Monitoring Station (CAMS) site 403, run by the Texas Natural Resource Conservation Commission (TNRCC) were used as a surrogate for background NO_x concentrations. The CAMS 403 station (known as Clinton Drive) is located approximately 5 km west of the Washburn Tunnel in a highly industrialized region similar to that surrounding the Washburn Tunnel. Measurements of NO_x were recorded at CAMS 403 as 5-minute average concentrations and were obtained from the TNRCC website (http://www.tnrcc.state.tx.us) as one-hour averages.

Carbon Dioxide (CO_2), Carbon Monoxide (CO), and Hydrocarbons

Air samples for hydrocarbon analysis were collected over one-hour sampling periods in 6-liter Summa stainless steel canisters. Carbon monoxide and carbon dioxide concentrations were quantified by gas chromatography/flame ionization detection (GC/FID). The GC column consisted of a 180 cm x 0.32 cm stainless steel column packed with 60 – 80 mesh Molecular Sieve 5A (Linde Corp.) maintained at 65 ^{o}C. To detect CO and CO_2 by FID, the column exit flow was mixed with hydrogen and routed through a 30 cm x 0.32 cm stainless steel column packed with 60 – 80 mesh nickel-coated diatomaceous earth substrate maintained at 425 ^{o}C , and was then routed to the FID. In the presence of hydrogen the nickel-coated substrate quantitatively reduced CO and CO_2 to CH_4.

Speciated hydrocarbon concentrations were determined using two GC/FID procedures. The first GC system consisted of a 60 m x 0.32 mm ID fused silica column containing 1 µm DB-1 bonded phase (J&W Scientific, Folsom, California). Column conditions consisted of a –50 ^{o}C initial temperature held for 2 min, followed by temperature programming at 8 ^{o}C min^{-1} to a final temperature of 200 ^{o}C. These column conditions provide resolution of the C_2-C_{12} hydrocarbons, and some oxygenated compounds as well. The second GC system consisted of a 60 m x 0.32 mm ID fused silica column containing a 3 µm DB-1 liquid phase. In addition to temperature programming, flow programming was used to improve the resolution of methyl tert-butyl ether (MTBE) from coeluting paraffinic compounds. Both GC systems required the use of sample preconcentration for quantitative VOC determination. The preconcentration approaches for both systems were identical and consisted of a six-port gas sample valve (Valco, Houston, Texas; Model VIII) configured to use a 25 cm X 0.32 cm stainless steel column packed with 60-80 mesh untreated glass beads as the sample loop. Measured aliquots of sample air were routed through the trap at liquid argon temperature (-187 ^{o}C). A combination of valve switching followed by the replacement of the liquid argon by a dewar flask containing hot water (~99 ^{o}C) resulted in injection of the vaporized VOC into the GC column. More details concerning the GC column and preconcentrations system are provided elsewhere (Lonneman, 1998).

Hydrocarbon Samples obtained aboard the Baylor Twin Otter

The de Havilland DHC-6 Twin Otter turbo-prop aircraft flew multiple missions during the TexAQS program. The Twin Otter is operated by Baylor University and has been instrumented to collect ambient air quality and meteorological data. The aircraft flies at speeds of 40-80 meters per second and typically collects samples at altitudes of 150 - 600 meters above ground level. Further information on the aircraft and TexAQS missions can be found in reports by Sonoma Technologies (2001) and at the TNRCC web site (http://www.tnrcc.state.tx.us).

During a number of the TexAQS flights, the Twin Otter collected instantaneous Summa canister samples over major transportation corridors located throughout the Houston area. The hydrocarbon data obtained in these samples were used to generate an average speciation profile representative of Houston regions dominated by mobile source emissions. Table 5 presents the date, time, and location of samples utilized in this study.

The hydrocarbon analysis performed for these samples was identical to that previously described for the Summa canister samples collected in the Washburn Tunnel.

TABLE 5. Date, time, and location of Baylor Twin Otter hydrocarbon samples obtained over major transportation corridors in the Houston area.

Date	Time (CDT)	Nearest Highway Intersection	Region of Houston
2000/08/18	164540	Loop 610 W at I-10	West
	164840	Hwy 59 at I-10	Downtown
	165110	Loop 610 N at I-10	East
2000/08/19	142530	Loop 610 W at Hwy 59	West
	142650	Loop 610 W at I-10	West
	142855	I-45 at I-10	Downtown
	142950	Hwy 59 at I-10	Downtown
	143125	Loop 610 N at I-10	East
	145150	Loop 610 E at Clinton Dr.	East
	145245	Loop 610 E at Clinton Dr.	East
2000/08/21	22315	Loop 610 W at I-10	West
	22319	Hwy 59 at I-10	Downtown
	30765	Loop 610 W at I-10	West
	144555	Loop 610 N at I-10	East
	150225	Loop 610 E at Clinton Dr.	East
2000/08/25	135920	Loop 610 W at I-10	West
	140215	Hwy 59 at I-10	Downtown
	140515	Loop 610 N at I-10	East
	141745	Loop 610 E at Clinton Dr.	East
2000/08/26	143105	Loop 610 W at Hwy 59	West
	143215	Loop 610 W at I-10	West
	143425	I-45 at I-10	Downtown
	143510	Hwy 59 at I-10	Downtown
	143645	Loop 610 N at I-10	East
	145350	Loop 610 E at Clinton Dr.	East
	145455	Loop 610 E at Clinton Dr.	East
2000/08/29	142525	Loop 610 W at Hwy 59	West
	142655	Loop 610 W at I-10	West
	142850	I-45 at I-10	Downtown
	144750	Loop 610 E at Clinton Dr.	East
2000/08/30	142830	Loop 610 W at Hwy 59	West
	143050	Loop 610 W at I-10	West
	143215	Hwy 59 at I-10	Downtown
	143455	Loop 610 N at I-10	East
2000/09/03	120330	Loop 610 N at I-10	East
	120505	Hwy 59 at I-10	Downtown
	120610	I-45 at I-10	Downtown
	120800	Loop 610 W at I-10	West
	125555	Loop 610 E at Clinton Dr.	East
2000/09/05	152550	Hwy 59 at I-10	Downtown
	152630	I-45 at I-10	Downtown
	152820	Loop 610 W at I-10	West
	152955	Loop 610 W at Hwy 59	West
2000/09/07	151650	Loop 610 N at I-10	East
	151820	Hwy 59 at I-10	Downtown
2000/09/12	140500	Loop 610 W at Hwy 59	West
	140635	Loop 610 W at I-10	West
	140830	I-45 at I-10	Downtown
	140920	Hwy 59 at I-10	Downtown
	142715	Loop 610 E at Clinton Dr.	East
	144145	I-45 at I-10	Downtown
	145130	I-45 at I-10	Downtown
2000/09/15	102215	Loop 610 E at Clinton Dr.	East
	111935	Loop 610 W at Hwy 59	West
	112100	Loop 610 W at I-10	West
	112240	I-45 at I-10	Downtown
	112325	Hwy 59 at I-10	Downtown
	112515	Loop 610 N at I-10	East
	114350	Loop 610 E at Clinton Dr.	East

$PM_{2.5}$

Two identical sets of fine particle composition samplers were used to measure $PM_{2.5}$ mass and composition in the Washburn Tunnel and in the fan room of the air intake building. Particle samplers used Teflon-coated AIHL cyclone separators to remove particles with diameters greater than 2.5 μm. Samples of the remaining fine PM were collected through 3 parallel sampling lines onto two Teflon membrane filters (both with a nominal flow rate of 10 lpm) and one quartz filter (with a nominal flow rate of 5 lpm). Downstream of one of the Teflon filters, oxalic acid coated annular glass denuders were used to sample for gaseous ammonia. For all samples collected in the tunnel, two sequential denuders were used to monitor breakthrough. The flow rates through each sample line was regulated using critical orifice flow devices and verified before and after each sample collection period using a calibrated flow meter at ambient temperature and pressure. The flow meter was calibrated at ambient pressure and a temperature of 22 ^{0}C.

After sample collection, filters were sealed in petri dishes and returned to the laboratory where they were frozen until analyzed. Fine particulate mass concentrations were determined by gravimetric analysis of the Teflon filters. Teflon filters were pre-weighed using an electronic microbalance housed in a climate controlled weighing room. After sampling, filters were equilibrated for a period of 24 hours at 20-22 ^{o}C and 40-50% RH prior to reweighing.

Concentrations of gaseous ammonia were also determined by ion chromatography. After each sampling period, the annular denuders coated with oxalic acid were extracted using 10 ml of dionized water by inverting the denuder at least 50 times. The extract was analyzed for ammonium by ion chromatography as above as a measure of gaseous ammonia. For all tunnel samples, the second, downstream denuder was analyzed to monitor breakthrough. In no cases was the second denuder ammonia concentrations significantly elevated, and the second denuder was used as a method blank.

Organic and elemental carbon were determined from quartz fiber filters using a thermal-optical transmission technique described by Birch and Cary [1996]. Before sampling, the quartz fiber filters were annealed at 550^{o}C for at least 2 hours to remove possible carbon contaminants. After sampling, a 1.45 cm^2 punch was taken from the filter and analyzed for both organic and elemental carbon. First, organic carbon was determined by heating the sample in an oven and analysis of the volatilized material in an oxygen-free helium atmosphere. The carbon was quantified by sequential oxidation to CO_2, reduction to CH_4 and quantification by flame ionization detection. During this heating, pyrolysis of organic material is monitored by light absorption of the sample, and corrected for. Elemental carbon is determined by a similar method but in an atmosphere containing 10% O_2 to oxidize the elemental carbon which is not volatile but is combustible in the presence of oxygen.

Fine particulate matter samples were also collected using a Low Pressure Impactor (LPI) and analyzed using Fourier Transform Infrared spectroscopy (FTIR) (Allen, et al. 1994). The use of a Hering LPI and FTIR spectroscopy to analyze aerosol complements the other methods commonly used in this study to characterize the inorganic, and particularly

the organic fraction of atmospheric aerosol. For the carbonaceous fraction, the FTIR spectroscopy provides data on the relative magnitude of aliphatic carbon, carbonyl groups and organonitrates in the aerosol. Detailed descriptions of the method (Allen, et al, 1994) and its application in air quality field studies have been previously reported (Mylonas, et al, 1991; Pickle, et al, 1990, Blando, et al., 1998).

The results, reported by Laurent (2002) and in the database described below, were consistent with the expected composition of vehicular exhaust. The tunnel samples were enriched in aliphatic carbon (especially in sizes less than 0.26 μm) and depleted in carbonyl groups, relative to the background samples. Both of these findings are characteristic of primary aerosol. Somewhat surprising was the presence, at times, of higher concentrations of organonitrates in the tunnel aerosol than in the background. Garnes et al. (2002) have postulated that these organonitrates may be due to heterogeneous reactions; they represent, however, a small fraction of the total fine particulate matter mass.

NARSTO Data Exchange Standard (DES) Datasets

Data files containing all air pollutant measurements were formatted for submission to the NARSTO Permanent Data Archive (PDA) following the Data Exchange Standard (DES) format. The DES consists of self-documenting ASCII comma-delimited files. The DES was designed to speed the flow of NARSTO data from collection to archival, reduce data processing and re-formatting requirements by users, and enable the NARSTO Quality Systems Science Center (QSSC) to develop tools to automate quality assurance and archival efforts. Further information on NARSTO and the DES can be found at the QSSC website (http://cdiac.esd.ornl.gov/programs/NARSTO/).

Gasoline Sampling and Analysis

Liquid gasoline samples were prepared for analysis by injecting a 0.04 μL aliquot of gasoline into an evacuated SUMMA stainless canister that previously had 80 μL of distilled water injected to passivate inside surfaces of the canister. Canisters were then filled to ~300 kPa absolute pressure using ultrapure helium. Concentrations of individual compounds present in each canister were quantified by GC/FID as described previously, and reported on a percent of total carbon basis.

Canisters containing headspace vapor samples were prepared using the following procedure. Approximately 25 mL of each liquid gasoline sample was pipetted into a 50 mL Erlenmeyer flask, and the flask mouth was closed with a single hole number 1 size Neoprene stopper. A 4 cm X 0.64 cm stainless steel tube closed with a rubber sleeve stopper plug was placed into the hole. Flasks were placed in a constant temperature bath maintained at 25 ^{o}C. After an equilibration period of 20-30 min, a 100 μL aliquot of gasoline headspace vapors was taken from each flask using 250 μL syringes with 5 cm long needles. The headspace vapor samples were injected into evacuated 6-L SUMMA canisters that contained 80 μL of distilled water. The canisters were filled to ~300 kPa

absolute pressure using ultrahigh purity helium. Concentrations of individual compounds present in gasoline headspace vapors were quantified by GC/FID as described previously.

Data Analysis Methods

Emission Factors

The emission factors typically used to estimate vehicle emissions are normalized to vehicle miles traveled (g/mi.). Emission rates derived from data collected during remote sensing and tunnel studies measure emissions relative to the concentration of combustion product carbon dioxide (CO_2). Carbon dioxide is the primary carbon-containing product of fuel combustion and, when combined with a correction for the carbon in the VOC and CO emissions, provides a measure of the amount of fuel burned. The concentrations of VOC, CO, NO_x, and $PM_{2.5}$ measured relative to the corrected CO_2 concentration provide measurements of these emissions per quantity of fuel consumed. These fuel-based emission factors, measured in grams per gallon, have been shown to vary much less over the full range of driving conditions than do the travel-based emission factors (Singer and Harley, 1996). Since the fuel-based emissions approach is less sensitive to the vehicles' operating mode (e.g., speed and acceleration), fuel-based emission factors might be more representative of realistic vehicle operation than those derived from dynamometer studies.

For each 2-hour sampling period, emission factors were calculated from measured tunnel concentrations. By carbon balance, the sum of background-subtracted CO_2 and CO concentrations was used to calculate the amount of carbon present in the fuel that was burned by vehicles traveling through the tunnel. An emission factor for pollutant P was calculated as

$$E_P = \frac{\Delta[P]}{\Delta[CO_2] + \Delta[CO]}$$

where E_P has units of mass of pollutant emitted per mass of carbon in fuel; the background-subtracted concentration of pollutant P is expressed in $\mu g\ m^{-3}$; and the background-subtracted concentrations of CO_2 and CO are in $\mu g\ C\ m^{-3}$ (i.e., when converting concentrations of CO_2 and CO from mol fraction to mass units, a molecular weight of 12 g mol^{-1} was used instead of 44 and 28 g mol^{-1} for CO_2 and CO respectively). Total NO_x concentrations were converted to $\mu g\ m^{-3}$ using a molecular weight of 46 g mol^{-1}, and are reported as NO_2 mass equivalents even though most of the NO_x was emitted in the form of NO. Since measurements of NO_x outside the tunnel were not collected, NO_x data from a nearby ambient monitoring station (CAMS 403) were used as a surrogate for background concentrations.

Both gasoline and diesel engines contributed to the emissions measured during each sampling period. Therefore regression analysis was used to estimate emission factors separately for light-duty (almost all gasoline) and heavy-duty (mostly diesel) vehicles. The independent variable in the regression was the fraction of total carbon (mainly CO_2) emissions coming from diesel engines in each sampling run; this was estimated from traffic counts collected during each sampling period and assumed fuel economies for

each vehicle category. In principle, the y-intercept (i.e., at 0% diesel) from the regression analysis gives an emission factor for gasoline-powered vehicles, and the sum of the slope and the y-intercept gives a diesel exhaust emission factor. Extrapolated emission factors obtained from the regression analysis were multiplied by the appropriate carbon weight fraction, $w_C = 0.85$ for oxygenated gasoline and $w_C = 0.87$ for diesel fuel, to obtain emission factors in units of mass of pollutant emitted per mass of fuel burned. Densities of gasoline and diesel fuel are 740 and 840 g L^{-1} respectively (Kirchstetter et al., 1999).

Volatile Organic Compound Speciation

The organic gas composition for vehicle emissions within the Washburn tunnel was calculated using results from 1600 – 1800 CDT only (eight 1-hour average air samples were collected over 4 days of tunnel sampling at these times). These sampling periods were chosen to minimize the influence of heavy-duty diesel truck emissions on the tunnel measurements. For each 1-hour sample and each organic compound, background concentrations were subtracted from concentrations measured inside the tunnel. Species concentrations were converted to mass units and normalized to total VOC mass measured in each run to obtain mass fractions for each compound.

Analytical results for 15 gasoline samples were combined to develop composite speciation profiles representing liquid gasoline and gasoline vapors. For each of 5 major gasoline brands, regular, mid-, and premium grade samples were combined in a sales-weighted average. The weighting factors (85% regular, 4% mid-grade, and 11% premium) were based on statewide gasoline sales by grade for Texas in August 2000 (EIA, 2001). Results were then averaged across the 5 brands of gasoline that were sampled, with equal weighting on each brand. For each fuel constituent, the relative standard deviation was calculated across five gasoline brands.

Results and Discussion

Tunnel Measurements and Emission Factors

Pollutant concentrations measured inside the tunnel were consistently above background levels for CO_2, CO, NO_x, NMOC, ammonia, and $PM_{2.5}$ as shown in Table 6. The tunnel/background ratios are higher during 1600 – 1800 CDT periods when traffic inside the tunnel is greater. Note however, that tunnel ventilation rates may vary by time of day, so changes in tunnel concentrations are not necessarily proportional to changes in traffic volume.

TABLE 6. Ratios of pollutant concentrations measured inside the tunnel to those measured in ambient air.

Pollutant	**Tunnel/Background concentration Ratio**	
	1200 – 1400 CDT	1600 – 1800 CDT
CO_2	1.69 ± 0.03	2.14 ± 0.12
CO	14.5 ± 1.3	16.8 ± 3.2
NO_x[a]	60.0 ± 17.1	112.5 ± 83.9
NMOC	6.0 ± 0.7	7.7 ± 2.1
$PM_{2.5}$	3.2 ± 1.2	3.1 ± 0.7
NH_3	11.1 ± 4.0	9.6 ± 2.7

[a]No measurements of background ambient air were collected at the Washburn Tunnel for nitrogen oxides; therefore, data collected at a nearby ambient monitoring station (CAMS 403) were used as a surrogate.

Emission factors were calculated by carbon balance for each 2-hour sampling period, and are presented in Table 7. The fraction of carbon (mainly CO_2) inside the tunnel coming from diesel engine exhaust was estimated from traffic counts and fuel consumption by vehicle class based on previous measurements of Pierson et al. (1996). The diesel fractions reported in Table 7 are higher than the corresponding fractions of total traffic counts, because heavy-duty diesel trucks have higher fuel consumption than cars and light-duty trucks per unit distance traveled. Diesel trucks accounted for about 19 and 8% of total carbon emissions inside the tunnel during the 1200 – 1400 CDT and 1600 – 1800 CDT sampling periods, respectively. As expected, CO and NMOC emission factors were higher from 1600 – 1800 CDT when gasoline engine emissions were predominant, and NO_x and PM emission factors were higher earlier in the day when there was more diesel truck traffic. Surprisingly, ammonia measurements showed slightly higher emission rates of ammonia in the 1200 – 1400 CDT sampling period with higher diesel traffic levels. Diesel trucks would be expected to contribute to CO_2 but do not contribute as significantly to emissions of ammonia (Pierson and Brachaczek, 1983). Increased ammonia emissions may result from malfunctioning three-way catalyst-equipped light-duty vehicles running rich (Fraser and Cass, 1998), and it is possible that the mid-day fleet contained a higher proportion of these vehicles.

TABLE 7. Calculated emission factors (g pollutant emitted per kg carbon in fuel) by sampling period

(a) Midday runs (1200 – 1400 CDT)

Date	CO	NMOC	NO_x	$PM_{2.5}$	NH_3	Percent Carbon from HD diesel
Aug 29	59.3	7.11	14.7	0.50	0.32	20.7
Aug 30	57.9	6.60	14.5	0.48	0.29	23.0
Aug 31	47.0	6.80	17.9	0.55	0.39	16.1
Sep 01	62.9	7.97	14.0	0.35	0.38	16.5
Average	57±7	7.1±0.6	15.3±1.8	0.47±0.09	0.35±0.05	19±3

(b) Late afternoon runs (1600 – 1800 CDT)

Date	CO	NMOC	NO_x	$PM_{2.5}$	NH_3	Percent Carbon from HD diesel
Aug 29	82.0	10.85	12.9	n.d.*	n.d.	9.4
Aug 30	79.3	10.27	14.3	0.30	0.29	10.1
Aug 31	78.3	9.45	13.4	0.24	0.26	7.7
Sep 01	73.4	8.30	9.1	n.d.	n.d.	5.7
Average	78±4	9.7±1.1	12.4±2.3	0.27±0.04	0.28±0.02	8±2

* n.d. not determined

In all of the tunnel sampling periods in this study, there was a mix of both light-duty and heavy-duty vehicle emissions. Linear regression analysis was used to extrapolate emission factors for a 100% light-duty vehicle fleet. This corresponds to the y-intercept in a plot of emission factors versus fraction of total carbon attributed to diesel engine exhaust (see Figures 1-5). Results of the regression analysis are summarized in Table 8 for CO, NMOC, NO_x, $PM_{2.5}$ and fine particle elemental carbon. The relative uncertainty in the intercept for NO_x is greater than for the other pollutants, because both gasoline and diesel engines contributed significantly to tunnel concentrations of this pollutant. The contribution of heavy-duty diesel engines to CO and NMOC concentrations was less important, especially during 1600 – 1800 CDT sampling periods, and this makes it easier to extrapolate emission factors to a 100% light-duty vehicle fleet for CO and NMOC. Increasing fine particle and fine particle elemental carbon emissions with increasing fraction of diesel vehicles is as expected (e.g., Pierson and Brachaczek, 1983; Fraser et al., 1998; Kirchstetter et al., 1999; Allen et al., 2001).

TABLE 8. Results of linear regression analysis for emission factors vs. diesel fraction

Pollutant	Intercept	**Slope**	**R^2**
CO	88.2 ± 7.8	-151 ± 52	0.58
NMOC	11.0 ± 1.0	-19 ± 7	0.56
NO_x	10.7 ± 1.8	23 ± 12	0.37
$PM_{2.5}$	0.13 ± 0.10	1.7 ± 0.6	0.64
$PM_{2.5}$ EC	-0.01 ± 0.05	0.87 ± 0.35	0.67

Note the intercept in this table corresponds to the emission factor for a vehicle fleet where the influence of heavy-duty diesel trucks is absent. Regression statistics are shown with associated standard errors of estimate.

The intercepts from the regression analysis (in units of g of pollutant emitted per kg of carbon present in fuel) were converted to emission factors per unit volume of fuel burned; final results are presented in Table 9. As discussed previously, the relative uncertainty in the result for NO_x is greater than for the other pollutants, because the important contribution of heavy-duty diesel engines to emissions of this pollutant was difficult to separate from light-duty vehicle emissions. Emission factors for fine particles are not calculated, as the overall fleet emission rates are dominated by heavy-duty diesel vehicles and not light-duty vehicles.

TABLE 9. Calculated light-duty vehicle emission factors in the Washburn tunnel

Pollutant	**Emission Factor**	
	(g L^{-1})	**(g km^{-1})**
CO	55 ± 5	6.6
NMOC	6.9 ± 0.6	0.83
NO_x	6.7 ± 1.1	0.82

Note emission factors are reported in units of mass of pollutant emitted per unit volume of fuel burned, and are calculated from the intercepts of the regression analysis (see previous table), assuming a carbon mass fraction of 0.85 and a liquid fuel density of 0.74 kg L^{-1} for gasoline. The primary results of this study are expressed per unit of fuel burned. Emission factors per distance traveled are also reported for the reader's convenience, based on assumed fuel economy for the light-duty vehicle fleet (see text).

For comparison with our results, Table 10 presents representative emissions factors for NO_x, NMOC, and CO measured in previous tunnel studies. The sampled fleets for most of these studies were comprised primarily of light-duty gasoline fueled vehicles. The data for the Fort McHenry and Tuscarora tunnels were analyzed to extract the light-duty and heavy-duty components. Note that all but one of these studies were performed at least five years prior to the current study. Given the elapsed time, a newer vehicle fleet with improved emission controls might be expected to contribute to slightly lower emission factors. In fact, between 1994 and 1999, emissions of CO and NO_x in the Caldecott Tunnel decreased by 54% and 41%, respectively. In addition to turnover in the vehicle fleet, Kean et al. (1999) attribute this decrease to impacts of California phase 2 reformulated gasoline. For the Washburn Tunnel, the CO emission rate is comparable to that of the other studies, while a relatively lower NO_x emission rate was observed. Surprisingly, however, the NMOC emission rate for the Washburn Tunnel is among the highest of all NMOC emission factors reported in Table 10.

Table 10. Comparison of emission factors measured during representative tunnel studies. Adapted from Sawyer et al. (2000).

Tunnel	**Roadway grade**	**Year sampled**	**CO (g/L)**	NMOC **(g/L)**	**NO_x (g/L)**
Tuscarora, Pa[a]	Level	1992	48.1	2.89	3.85
Fort McHenry[b] (Baltimore, MD)	Uphill (+3.3%)/ Dnhill (-1.8%)	1992	55.5/47.4	4.88/5.03	7.77/5.55
Caldecott[c] (Oakland, CA)	+4.2%	1994	77.0	3.70	7.47
Callahan[d] (Boston, MA)	Uphill + Dnhill[g]	1995	45.1	4.51	9.32
Lincoln[de] (New York, NY)	Uphill + Dnhill[g]	1995	39.2	5.25	10.95
Deck Park[de] (Phoenix, AZ)	Level	1995	45.1	6.14	8.44
Sepulveda[de] (Los Angeles, CA)	Level	1995	56.2	5.25	7.33
Sherman Way[de] (Van Nuys, CA)	~Level	1995	91.0	6.81	7.55
Caldecott[f] (Oakland, CA)	+4.2%	1999	38.7	1.81	4.85
Washburn (Houston, TX)	Uphill + Dnhill +/- 6%	2000	55	6.9	6.7

[a]Pierson, et al. (1996)
[b]Pierson et al. (1996)
[c]Kirchstetter et al. (1996)
[d]Sagebiel et al. (1996)
[e]Gertler et al. (1997b) [Note: Data from Gertler et al. (1997b) for LD and HD vehicles combined. The HD contribution of Nox is significant, especially in the Lincoln tunnel.
[f]Kean et al. (2000)
[g]Underwater tunnel'; includes both downhill and uphill driving (grade ranges from –3.8% to +3.5%).

Assuming the average fuel consumption of light-duty vehicles is 12 L per 100 km (equivalent fuel economy is about 20 miles per gallon), emission factors can be expressed per km driven (see Table 9). Note however, that the primary results of this study are expressed per unit volume of gasoline burned. Singer and Harley (2000) note that advantages of a fuel-based approach to estimating vehicle emissions include less variation in emission factors with vehicle weight and operating conditions, and ready availability of vehicle activity data (i.e., fuel sales) at the state level from fuel tax records. We caution against extrapolating emission factors derived from the Washburn Tunnel to all of Houston, because emission factors may vary with changes in vehicle age distribution and engine load, and the vehicle fleet and driving conditions inside the tunnel may not represent those of the entire Houston area.

Volatile Organic Compound Speciation

The most abundant organic compounds in Houston gasoline and Washburn Tunnel emissions are listed in Table 11. The ten most abundant species account for about half of total VOC mass in liquid gasoline and tunnel emissions, and about two-thirds of total VOC mass for gasoline vapors. Isopentane, MTBE, toluene, and 2,2,4-trimethylpentane are significant constituents of each of the VOC speciation profiles. As expected, products of incomplete combustion such as ethylene and acetylene are present in tunnel emissions, but are not found in unburned gasoline. Also as expected, gasoline vapors are enriched in lighter low-molecular weight compounds relative to the composition of liquid gasoline. In particular, MTBE and the C_4-C_5 alkanes and alkenes all have high vapor pressures and are more abundant (on a percent of total mass basis) in gasoline vapors than in liquid gasoline.

Tunnel results for propane, methanol, and ethanol suggest low levels of use of these compounds in gasoline and/or as alternative fuels in Houston. Note that reported MTBE mass fractions include a contribution from co-eluting 2,3-dimethylbutane, though MTBE is dominant. A second ether (tert-amyl methyl 1ether or TAME) was identified in the gasoline samples at varying levels depending on the brand. Overall, TAME is present in gasoline at levels that are roughly an order of magnitude lower than MTBE, on average, across the entire pool, though some individual gasoline samples contained up to ~25% of oxygen mass as TAME. There was no significant use of ethanol as a fuel oxygenate in the set of 15 gasoline samples that were collected and analyzed.

TABLE 11. Most abundant volatile organic compounds in Houston gasoline and Washburn Tunnel emissions.

Liquid Gasoline	**wt %**	**rsd**
MTBE	10.9%	0.10
Toluene	7.3%	0.24
Isopentane	6.7%	0.03
2,2,4-TriMethylpentane	5.5%	0.19
2-Methylpentane	4.1%	0.16
m-& p-Xylene	3.9%	0.12
3-Methylpentane	2.7%	0.19
2,3,4-TriMethylpentane	2.6%	0.22
n-Hexane	2.5%	0.24
n-Pentane	2.3%	0.25
subtotal (top 10)	49%	
Gasoline Vapors	**wt %**	**rsd**
Isopentane	23.2%	0.08
MTBE	16.2%	0.13
n-Pentane	6.1%	0.20
2-Methylpentane	5.2%	0.16
n-Butane	5.1%	0.26
3-Methylpentane	3.1%	0.19
2,2,4-TriMethylpentane	2.7%	0.22
Toluene	2.6%	0.21
2-Methyl-2-Butene	2.5%	0.22
n-Hexane	2.5%	0.24
subtotal (top 10)	69%	
Tunnel Emissions	**wt %**	**rsd**
Isopentane	7.7%	0.11
Methane	7.6%	0.37
MTBE	6.5%	0.06
Ethylene	5.4%	0.06
Toluene	5.1%	0.06
2,2,4-TriMethylpentane	3.1%	0.07
Acetylene	3.0%	0.08
2-Methylpentane	2.7%	0.05
m-& p-Xylene	2.7%	0.07
Isobutylene	2.6%	0.08
subtotal (top 10)	46%	

Results for each compound are reported as % of total VOC mass, including oxygen mass where present. Note rsd is relative standard deviation ($s/\bar{x}$) across 5 gasoline brands or 8 one-hour tunnel sampling periods. To minimize the influence of diesel engine emissions, only late afternoon (4-6 PM) tunnel results were selected.

Comparison of Tunnel and Twin Otter Hydrocarbon Speciation Profiles

The sources of hydrocarbon emissions vary considerably across the Houston area. Eastern Houston is heavily industrialized while on-road mobile sources dominate western Houston. Using the canister data obtained during the Baylor University Twin Otter flights (refer to Table 5), average hydrocarbon speciation profiles were developed for samples obtained over transportation corridors located in western, central, and eastern Houston. Ratios of selected hydrocarbon compounds to acetylene, MTBE, and 2-methylpentane were calculated and are presented in Table 12. Acetylene and MTBE are considered tracers of vehicle exhaust emissions, while 2-methylpentane is considered a tracer of both vehicle exhaust and evaporative emissions. Somewhat surprisingly, the ratios are similar across the region for all compounds indicating little variability in the relative ambient concentrations of these compounds across the Houston area on the sampling days reported.

The average hydrocarbon ratios based on the Baylor data are compared to the analogous Washburn Tunnel hydrocarbon ratios in the final two columns of Table 12. This comparison was originally performed to confirm that the Washburn Tunnel hydrocarbon composition for vehicle emissions was similar to that measured in the ambient environment. However, note that the ratios of hydrocarbon concentrations to acetylene and MTBE measured by the Baylor aircraft are lower by factors of 2-3 and 5-8, respectively, compared to those based on the tunnel data. Since acetylene and MTBE are relatively nonreactive in the ambient environment, the relatively lower acetylene and MTBE concentrations suggests that the Houston area is affected by hydrocarbon emissions from sources other than on-road mobile vehicles throughout the urban region. Industrial sources located to the east and south of Houston emit substantial quantities of these compounds. Advection of these emissions across the Houston area may explain the discrepancy between the aircraft and tunnel hydrocarbon ratios.

Table 12. Selected hydrocarbon ratios based on samples obtained aboard the Baylor Twin Otter and in the Washburn Tunnel.

Compound	Baylor Twin Otter Hydrocarbon Ratios				Tunnel Hydrocarbon Ratios
	West Houston	Down-Town	East Houston	Average Houston	
Ratio to acetylene					
2-methyl pentane	3.0	2.2	3.4	2.8	0.9
Toluene	3.9	2.8	n.d.	3.2	1.7
Ethylene	n.d.*	3.2	4.1	3.2	1.8
Isopentane	5.7	5.1	8.9	6.5	2.6
Ratio to 2-methyl pentane					
Acetylene	0.3	0.5	0.2	0.4	1.1
Toluene	1.3	1.3	n.d.	1.2	1.9
Ethylene	n.d.	1.5	1.0	1.1	2.0
Isopentane	1.9	2.3	2.2	2.3	2.9
Ratio to MTBE					
2-methyl pentane	3.9	2.9	3.8	3.5	0.4
Toluene	5.1	3.7	n.d.	4.0	0.8
Ethylene	n.d.	4.2	4.6	4.0	0.8
Isopentane	7.4	6.6	10.0	8.0	1.2
Acetylene	1.3	1.3	1.1	1.2	0.5

* n.d. not determined

References

Allen, D. T., E. J. Palen, M. I. Haimov, S. V. Hering, and J. R. Young, Fourier transform infrared spectroscopy of aerosol collected in a low pressure impactor (LPI/FTIR): method development and field calibration. *Aerosol Sci. and Tech.*, 21, 325-342, 1994.

Allen, J. O., P. R. Mayo, L. S. Hughes, L. G. Salmon, and G. R. Cass, Emissions of size-segregated aerosols from on-road vehicles in the Caldecott Tunnel. *Environ. Sci. Tech.*, 35, 4189-4197, 2001.

Blando, J.D., R. J. Porcja, T-H Li, D. Bowman, P. J. Lioy, and B. J. Turpin, Secondary formation and the Smoky Mountain organic aerosol: an examination of aerosol polarity and functional group composition during SEAVS. *Environ. Sci. Tech.*, 32, 604-613, 1998.

CARB, Methodology for estimating emissions from on-road motor vehicles. Technical support division, Mobile source emission inventory branch, California Environmental Protection Agency, Oct/Nov 1996.

EIA, Refiner motor gasoline volumes by grade, sales type, PAD district, and state (Table 43). *Petroleum Marketing Monthly*. U.S. Energy Information Administration, Department of Energy, Washington, D.C, 2001.

EPA, User's Guide to MOBILE6 (Mobile Source Emission Factor Model). Office of Mobile Sources, Office of Air and Radiation, *EPA420-R-02-001*, Ann Arbor, MI, January 2002.

EPA (2001). National Air Quality and Emission Trends Report, 1999, *EPA-454/R-01-004*, Office of Air Quality Planning and Standards, Research Triangle Park, N. C., March 2001.

EPA, User's Guide to MOBILE5 (Mobile Source Emission Factor Model). Office of Mobile Sources, Office of Air and Radiation, *EPA-AA-TEB-94-01*, Ann Arbor, MI, May 1994.

Fraser, M., G. Cass, and B. Simoneit, Gas-phase and particle-phase organic compounds emitted from motor vehicle in a Los Angeles roadway tunnel. *Environ. Sci. Technol*., 32, 2051-2060, 1998.

Garnes, L.A., Size distributions of organonitrates in ambient aerosol collected in Houston, Texas, M.S. Thesis, Chemical Engineering, University of Texas, Austin, USA, 2001.

Gertler, A. W., D. N. Wittorff, R. McLaren, W. Belzer, and T. Dann, Characterization of vehicle emission in Vancouver BC during the 1993 Lower Fraser Valley Oxidants study. *Atmos. Environ.*, 31, 2107-2112, 1997a.

Gertler, A.W., J. C. Sagebiel, D. N. Wittorff, W. R. Pierson, W. A. Dippel, D. Freeman, and L. Sheetz, Vehicle emissions in five urban tunnels. Desert Research Institute, Reno, NV. Report to the Coordinating Research Council, Atlanta, GA, 1997b.

Hering, S. V., R. C. Flagan, and S. K. Friedlander, Design and evaluation of new low pressure impactor. 1. *Environ. Sci. Tech.*, 12, 667-673, 1978.

Hering, S. V., S. K. Friedlander, J. J. Collings, and L. W. Richards, Design and evaluation of a new low pressure impactor. 2. *Environ. Sci. Tech.*, 13, 184-188, 1979.

Kean, A. J., R. A. Harley, J. D. Little, and G. R. Kendall. On-road measurement of ammonia and other motor vehicle exhaust emissions. *Environ. Sci. Technol*., 34, 3535-3539, 2000.

Kirchstetter, T.W., B. C. Singer, R. A. Harley, G. R. Kendall, and W. Chan, Impact of oxygenated gasoline use on California light-duty vehicle emissions. *Env. Sci. and Tech.*, 30, 661-670, 1996.

Kirchstetter, T. W., R. A. Harley, N. M. Kreisberg, M. R. Stolzenburg, and S. V. Hering, On-road measurement of fine particle and nitrogen oxide emissions from light- and heavy-duty motor vehicles. *Atmos. Environ*., 33, 2955-2968, 1999.

Laurent, J-P., Size-distributions of carbonyl and aliphatic groups in ambient aerosol collected in Houston, Texas, M.S. Thesis, Environmental and Water Resources Engineering, University of Texas, Austin, USA, 2002.

Lonneman, W.A., R. L. Seila, and S. A. Meeks, Non-methane organic composition in the Lincoln tunnel. *Env. Sci. and Tech.*, 20, 790-796, 1986.

Lonneman, W. A., Comparison of hydrocarbon composition in Los Angeles for the years 1968 and 1997, paper presented at Conference on Measurement of Toxic and Related Pollutants, Air and Waste Manage. Assoc., Cary, N. C., Sept. 1-3, 1998.

Mylonas, D. T., D. T. Allen, S. H. Ehrman, and S. E. Pratsinis, The sources and size distributions of organonitrates in Los Angeles aerosol. *Atmos. Environ.*, 25, 2855-2861, 1991.

NRC. Modeling Mobile-Source Emissions. National Academy Press, Washington, D. C., 2000.

NRC. Emerging Emissions Testing Technologies in Evaluating Vehicle Emissions Inspection and Maintenance Programs. National Academy Press, Washington, D. C., 2001.

Pierson, W. R., A. W. Gertler, N. F. Robinson, J. C. Sagebiel, B. Zielinska, G. A. Bishop, D. H. Stedman, R. B. Zweidinger, and W. D. Ray, Real-world automotive emissions—summary of recent tunnel studies in the Fort McHenry and Tuscarora Mountain tunnels, *Atmos. Environ.*, 30, 2233-2256, 1996.

Pickle, T., D. T. Allen, and S. E. Pratsinis, The sources and size distributions of aliphatic and carbonyl carbon in Los Angeles aerosol. *Atmos. Environ.*, 24, 2221-2228, 1990.

Pierson, W. R. and W. W. Brackaczek, Particulate matter associated with vehicles on the road. II. *Aerosol Sci. Technol.*, 2, 1-40, 1983.

Rogak, S.N., U. Pott, T. Dann, and E. Wang. Gaseous emissions from vehicles in a traffic tunnel in Vancouver, BC. *Air Waste Manage. Assoc.*, 47, 1997.

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

Sayer, R. F., R. A. Harley, S. H. Cadle, J. M. Norbeck, R. Slott, and H. A. Bravo, Mobile sources critical review. *Atmos. Environ.*, 34, 2161-2181, 2000.

Singer, B.C., and R. A. Harley, A fuel-based inventory of motor vehicle exhaust emissions in the Los Angeles area during summer 1997. *Atmos. Environ.*, 34, 1783-1795, 2000.

Singer, B. C., and R. A. Harley. A fuel-based motor vehicle emission inventory, *Air Waste Manage. Assoc*., 46, 581-593, 1996.

Sonoma (2001). Analysis of year 2000 air quality data collected by the Baylor University aircraft: final report, Sonoma Technology, Inc, STI-900930-2096-FR, Petaluma, CA, July 2001.

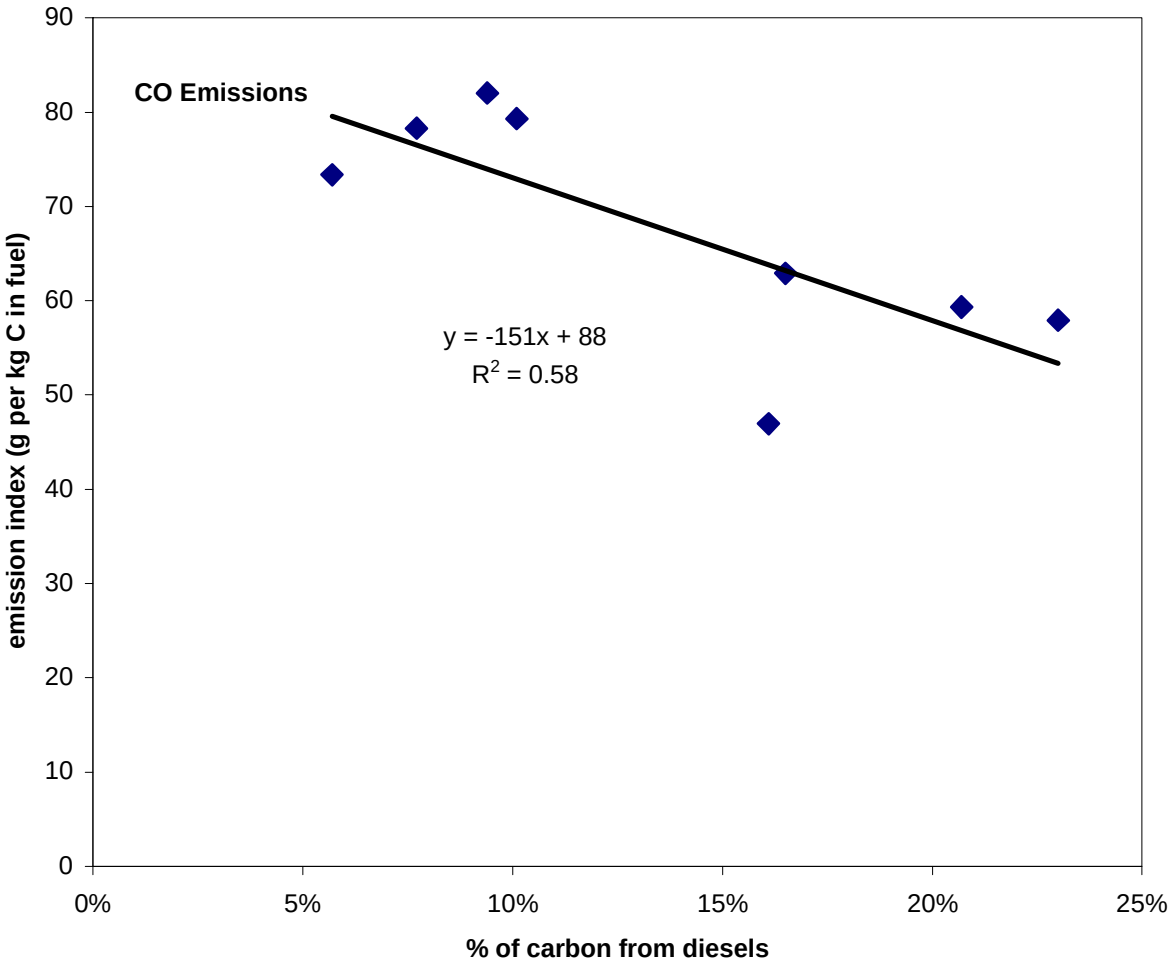

Figure 1. Carbon monoxide emission factors versus diesel contribution to total carbon emissions in the Washburn tunnel.

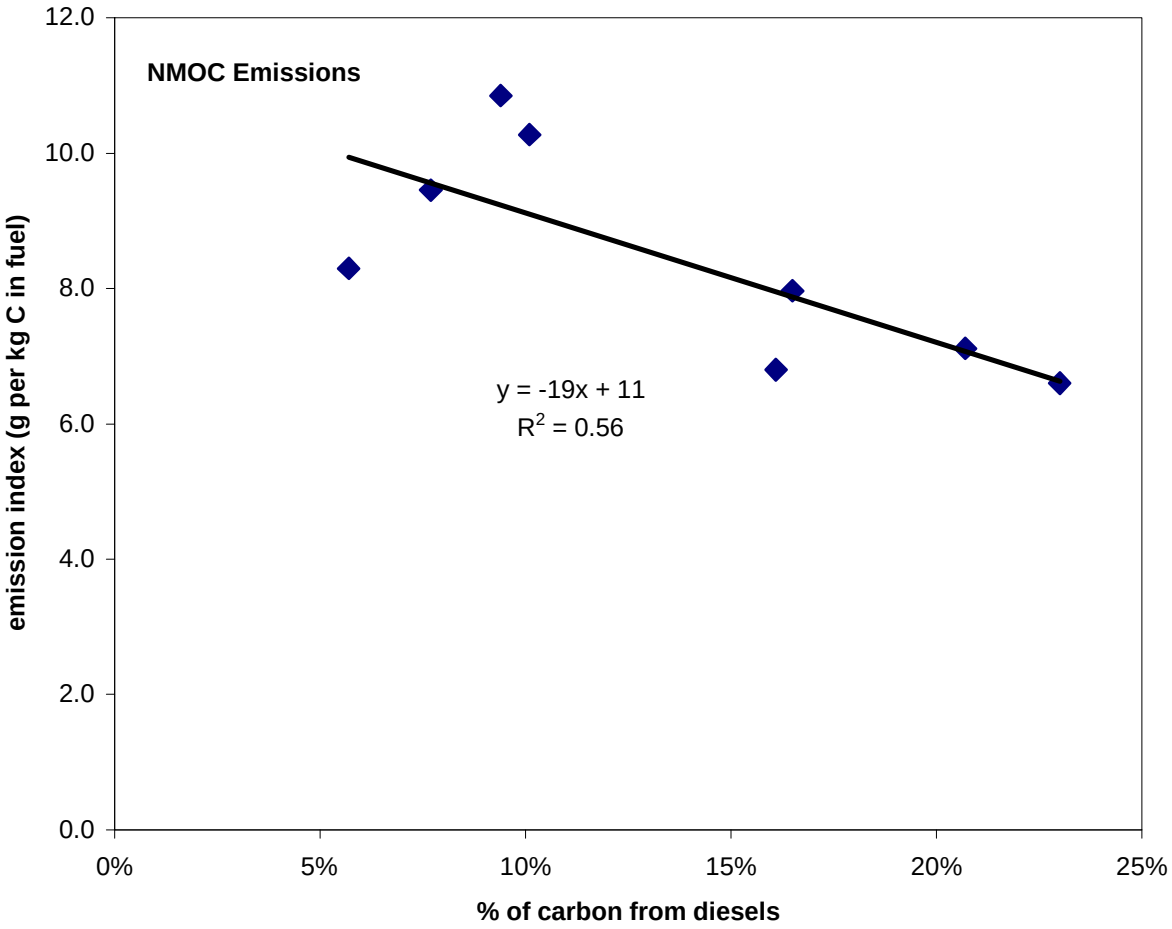

Figure 2. Non-methane organic compound emission factors versus diesel contribution to total carbon emissions in the Washburn tunnel.

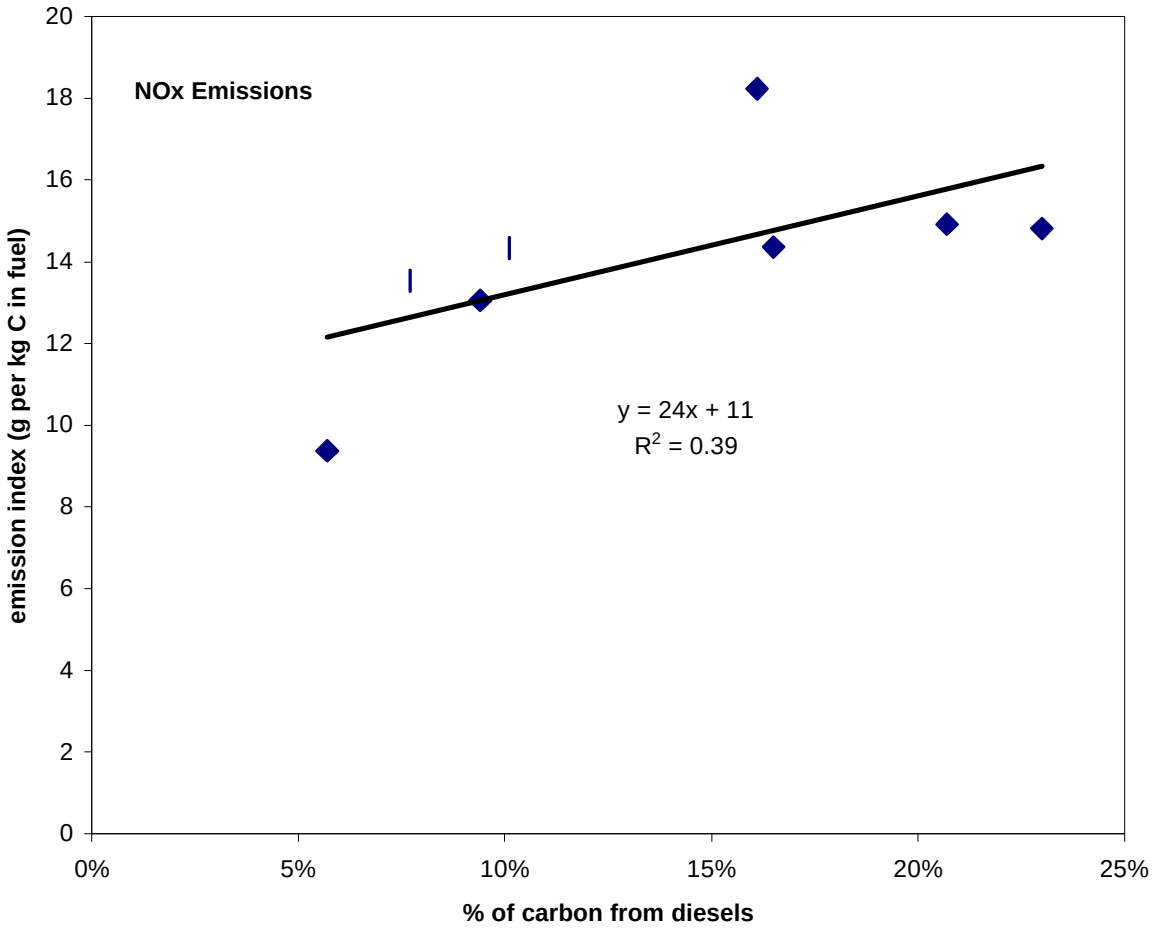

Figure 3. Nitrogen oxide emission factors versus diesel contribution to total carbon emissions in the Washburn tunnel.

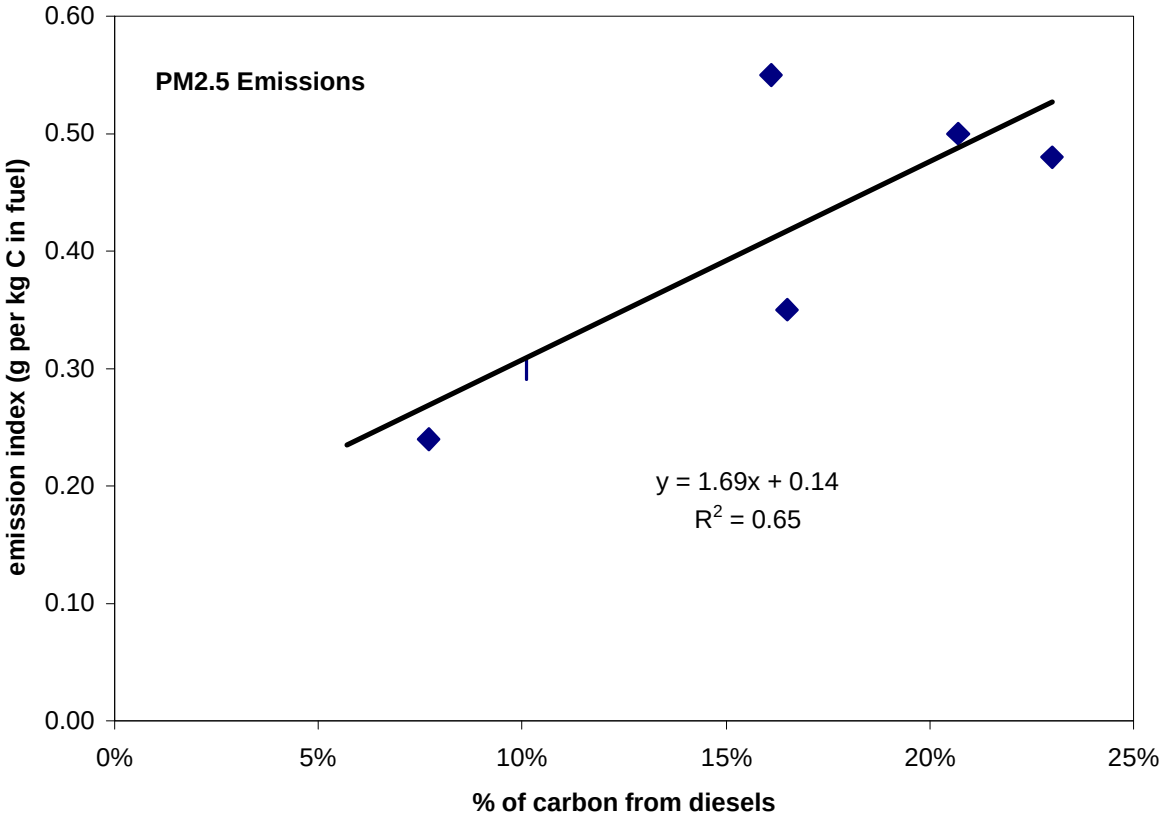

Figure 4. Fine particle emission factors versus diesel contribution to total carbon emissions in the Washburn tunnel.

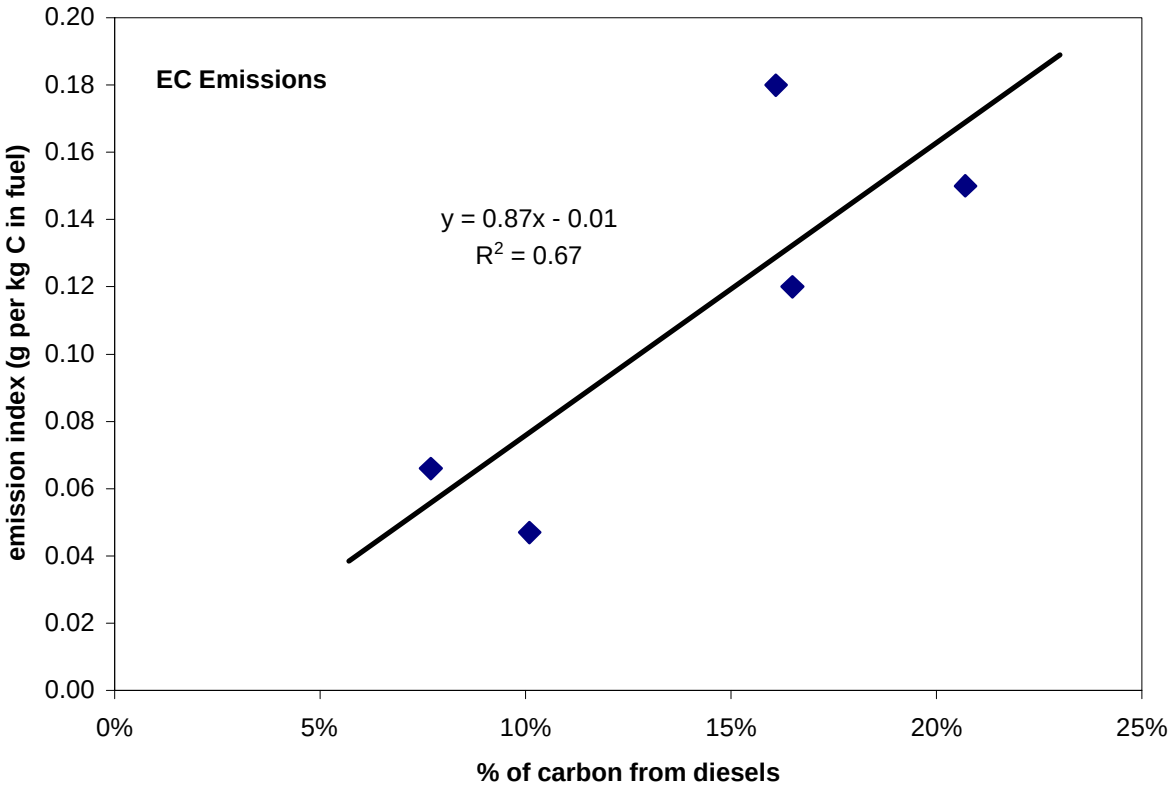

Figure 5. Fine particle elemental carbon emission factors versus diesel contribution to total carbon emissions in the Washburn tunnel.