Section 211(B) Tier 2 High End Exposure Study of Conventional and Oxygenated Gasoline

COMPILED FINAL REPORT

Prepared for

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EXECUTIVE SUMMARY

This study evaluated the upper-end distribution of inhalation exposures to evaporative and combustion emissions from conventional and oxygenated-gasoline. This final report describes the measurement methods and protocol used in the study and summarizes the validation and initial analysis of the assembled database. The main findings and conclusions are emphasized in this final report and additional details and descriptions of the data are provided in several supporting appendices.

Introduction and Background

The 211b Research Group is an unincorporated group of USA fuel and fuel additive manufacturers affiliated by contractual obligation to meet the testing requirements of Section 211(b) (2) and 211(e) of Clean Air Act. The American Petroleum Institute (API) manages the required work on behalf of the 211b Research Group.

Mobile source air toxics (MSAT) may pose an adverse health risk, especially in microenvironments with high exposures to vehicle exhaust or evaporative emissions. Although programs such as reformulated gasoline (RFG) are intended to reduce the emissions of MSAT and ozone precursors, uncertainties remain regarding population exposures associated with both oxygenate-gasoline blends and conventional gasoline. Accordingly, the EPA issued requirements for a test program in accordance with the Alternative Tier 2 provisions of the fuels and fuel additives (F/FA) regulations, which are required pursuant to Section 211 of the Clean Air Act. To satisfy those testing requirements, API contracted with a research team consisting of the Desert Research Institute (DRI), Southwest Research Institute (SwRI), Lovelace Respiratory Research Institute (LRRI), and TRJ Environmental, Inc (TRJ) to conduct a study of the high-end distribution of inhalation exposures to evaporative and combustion emissions of conventional and oxygenated-gasoline (MTBE-gasoline, and ethanol-gasoline).

The results of this study provide data that will allow estimation of the upper-end of the frequency of annual average inhalation exposures to evaporative and combustion emissions of gasoline and oxygenated-gasoline. EPA may accomplish this by using the scripted exposures in high-end microenvironments with EPA regulatory exposure models, such as the Hazardous Air Pollutant Exposure Model (HAPEM). HAPEM is a screening-level exposure model for assessing average long-term inhalation exposure of the general population, or specific sub-populations, over spatial scales ranging from urban to national. The information from this study will permit sensitivity analyses to determine the range of these exposures, especially during heavy traffic, in residential and public parking garages and during refueling. The study also provides data for determining the relative proportion of evaporative versus combustion emissions in higher exposure microenvironments.

The specific objectives of the study are to provide information allowing EPA to:

- Quantify personal exposures to motor vehicle gasoline evaporative and combustion emissions in microenvironments (MEs) representing the upper end of the population exposure frequency distribution (99th + percentile) of such exposures;

- Determine quantitative relationships between personal exposures in selected MEs and fixed site measurements in these MEs and at nearby air monitoring stations;

- Determine how personal exposures differ among cities and seasons in which methyl t-butyl ether (MTBE)- and ethanol (EtOH)-gasolines are used compared with a city where oxygenated fuels are not used.;

- Extrapolate study data to other cities and other oxygenated fuels;

- Apportion the relative contributions of vehicle fuel combustion versus evaporative emissions to personal exposures in high-end MEs;

- Determine the relationship between vehicle tailpipe and evaporative emissions and exposure levels in a trailing vehicle cabin and in a residence with an attached garage.

Experimental Methods and Approach

The study was conducted in several phases. First, DRI evaluated the suitability of available measurement methods for meeting the technical objectives of the study. These methods included continuous and time-integrated measurements of carbon monoxide (CO), total volatile organic compounds (VOC), and the following MSAT species: benzene, toluene, ethylbenzene and xylenes (BTEX), 1,3-butadiene (1,3-BD), methyl tertiary butyl ether (MTBE), formaldehyde and acetaldehyde. Exposure measurements included well-established time-integrated methods for measurements of hydrocarbons and carbonyl compounds. These samples provide data of known precision and accuracy for each chemical species of interest during each exposure measurement, which typically covered a 20 to 40 min period. Several continuous and semi-continuous methods were used to provide time-resolved data ranging from 1 to 10 minutes. Continuous exposure measurements included benzene, toluene, ethylbenzene, and xylenes (BTEX) by a portable mass spectrometer (MS), carbon monoxide (CO) by a portable electrochemical analyzer and by a nondispersive infrared (NDIR) analyzer, and estimates of total volatile organic compounds by a portable photoionization detector (PID). Semi-continuous measurements of BTEX were also obtained from analysis of solid phase microextraction (SPME) fibers.

Because exposure levels in most microenvironments were expected to vary with time, the measurement protocol included continuous measurements of target species with time resolution of 1 minute or less. This requirement necessitated the use of instruments such as the Kore MS200 and the Alpha Omega formaldehyde analyzer, which have not previously been proven for such application and did not perform sufficiently well in field conditions during the pilot studies. Furthermore, there are no acceptable continuous methods for 1,3-butadiene, MTBE, ethanol, acetaldehyde or nonmethane hydrocarbons (NMHC) that could be used in portable modes of operation with adequate sensitivity. Therefore, our sampling strategy consists of a three-tier approach shown in Table E-1, which lists the overlapping measurement methods used in the Section 211(B) Tier 2 High-End Exposure Screening Study and their intended application.

Table E-1. Measurement methods used in the Section 211(B) Tier 2 High-End Exposure Screening Study. Data applications for specific methods are classified as reference, confirmatory, and surrogate.

	Continuous					Semi-Cont	Integrated		
Method	T15 CO	NDIR CO	ppbRAE	MS200	HCHO	SPME	Canister	DNPH	Adsorbent
Applicable Environments	outdoor and in-cabin	all	outdoor and in-cabin	higher end MEs	outdoor	All	all	all	all
Time Resolution	1 min	seconds	seconds	1 min	1 min	10 min	20-40&5 min	20-40 min	20-40 min
Detection Limits	0.1 ppm	0.04 ppm	1 ppb	1-3 ppbv	1 ppbv	0.2 ppbv	0.05 ppbC	0.1 ppbv	0.2 ppbv
Data Application [1]	S	S	S	C	C	C	R	R	R
CO	SC	SC					R		
PID [2]			SC						
BTEX	S (a)	S (a)	SC (c)	C		C	R		
1,3-Butadiene	S (a)	S (a)	S (c)				R		
MTBE	S (a)	S (a)	S (c)			C	R		
Formaldehyde	S (b)	S (b)	S (d)		C			R	
Acetaldehye	S (b)	S (b)	S (d)					R	
Ethanol	S (e)	S (e)	S (f)						R
NMHC	S (a)	S (a)	S (c)				R		

1. Category of data application include surrogate (S), confirmatory (C) reference (R), and surrogate compounds or signal (SC)
2. Sum of molecules ionizable at 10.6 eV and detected by photoionization detector.
S (a). Time series will be reconstructed from the canister/CO ratio for exhaust-dominated samples.
S (b). Time series will be reconstructed from the DNPH/CO ratio for exhaust-dominated samples except outdoor daytime samples.
S (c). Time series will be reconstructed from the canister/PID ratio for exhaust- or evap-dominated samples in outdoor MEs.
S (d). Time series will be reconstructed from the DNPH/PID ratio for exhaust-dominated samples except outdoor daytime samples.
S (e). Time series will be reconstructed from the solid adsorbent/CO ratio for exhaust-dominated samples.
S (f). Time series will be reconstructed from the solid adsorbent/PID ratio for exhaust and evap-dominated samples.

The measurements are classified in one of three tiers: reference, surrogate, and confirmatory. The base set or "reference" (R) measurements consist of three well-established time-integrated measurements. These include: canister sampling and analysis by gas chromatography with flame ionization detection for CO, BTEX, 1,3-butadiene, MTBE, and nonmethane hydrocarbons (NMHC); 2,4-dinitrophenylhydrazine (DNPH) cartridge sampling and analysis by high performance liquid chromatography with UV detection for formaldehyde and acetaldehyde; and solid adsorbent sampling and analysis of ethanol by gas chromatography with mass spectrometry. These three methods combined measure all species of interest over the entire sampling period within each microenvironment. Although these integrated methods do not characterize peak exposures in microenvironments with highly varying exposure levels, they serve several other purposes. They provide a basis for validating continuous and semi-continuous data. They also provide a basis for deriving correlations between the time-integrated values with time averages of continuous data from the CO and PID instruments. Thus the continuous data were used as "surrogates" (S) for reconstructing the time series of specific MSAT based on these correlations. For example, data for BTEX, 1,3-butadiene, and MTBE from the canister measurements were correlated to continuous CO and PID data to reconstruct their time series in exhaust-dominated environments. In a similar manner, the time series of formaldehyde was reconstructed from the correlation of the integrated DNPH samples with CO. Outdoor afternoon samples were excluded due to potential contributions of carbonyl compounds formed from atmospheric reactions of hydrocarbons. Table E-1 shows other correlations that can be used in this manner. Two pilot studies were conducted in Reno, NV to test the proposed measurement methods under field conditions and to refine the exposure protocols. Two experimental approaches were used in the main study.

Controlled Exposure Measurements in San Antonio

First, DRI and SwRI conducted exposure measurements in San Antonio under controlled conditions to establish quantitative relationships between vehicle tailpipe and evaporative emissions and exposure levels in two specific microenvironments, a trailing vehicle cabin and in a residence with an attached garage. The two vehicles (2.2L 4-cylinder 1993 Toyota Camry and a 5.0L V8 1995 Ford F150 Pickup truck) used in these controlled exposure experiments were tested at the SwRI laboratory for FTP (Federal Test Procedure) exhaust and hot soak evaporative emissions (Merritt, 2005). The tests were performed with the vehicles in normal and in malfunction condition while operating on summer and winter grade fuels from Houston, Atlanta and Chicago in summer 2002 and winter 2005. Measured FTP exhaust NMHC emission rates for the sedan and truck averaged 0.21 and 0.31 g/mi, respectively, in normal mode. Both emission rates are below the certified emission standards. The induced malfunctions raised NMHC emission rates by a factor of 16.7 for the sedan to 3.58 g/mi and factor of 7.0 for the truck to 2.20 g/mi. Differences in NMHC emission rates among the three regional fuels were not significant. The p values of the regression between Atlanta and Houston and Atlanta and Chicago fuels were 0.07 and 0.08, respectively for normal mode and 0.01 and 0.04, respectively for malfunction mode. The percent relative standard deviations of the NMHC emission rates for the sedan and truck were 15% and 14%, respectively, in normal mode and 3% and 6%, respectively with the induced malfunctions.

The two test vehicles in normal operation and with induced malfunction were used to determine exposure in a cabin of a third vehicle which trailed the test vehicle. During each test, the trailing vehicle was driven behind the test vehicle over a travel loop of several miles in a

rural area south of San Antonio. Measurements were made during the first 10 minutes without the test vehicle in order to established background exposure levels. Each trailing vehicle run included three scenarios (based on the proximity to the leading vehicle: far, near, and passing) for each low and high speed (30 mph and 60 mph) according to a prescribed schedule. Separate integrated samples were collected for background and separate periods corresponding to the driving and idle portions of each test for each fuel (i.e., Atlanta, Houston and Chicago) and emission condition (i.e., normal and malfunction mode). Data from the integrated reference methods showed observable relationships between exhaust emission rates and in-cabin exposures in a trailing vehicle.

The same two test vehicles (with and without malfunctions) were used to determine indoor exposure in a home with an attached residential garage. The vehicles were parked in a closed garage also containing a gasoline powered lawnmower and gasoline storage container filled with the test fuels, with in-garage and adjacent room monitoring conducted before, during and after the vehicle cool-down period. Time-integrated canister and cartridge samples were collected for each test (one in the garage and one in the adjacent room). A set of continuous and semi-continuous measurements by serial 10 minute average solid phase micro-extraction (SPME) sampling were made during test period of two hours.

Personal Exposures in Houston, Chicago and Atlanta

In the second approach, DRI measured personal exposures in selected MEs representing the upper end of the frequency distribution of potential population exposures. The study was conducted in Houston, TX, Chicago, IL and Atlanta, GA where MTBE-gasoline, ethanol-gasoline and conventional gasoline are used, respectively. These cities also satisfy additional requirements of the study for ongoing ambient air monitoring programs and geographic and climatologic diversity among the three cities. Sampling was performed during winter and summer and under conditions that were conducive to higher exposures within each ME (e.g., downwind, low wind speeds, rush hour traffic). Continuous measurements included both NDIR and electrochemical CO, two PIDs and in-cabin and fuel tank skin temperature. From 3 to 5 time-integrated canister and DNPH cartridge samples were collected for the following twelve microenvironments;

- ME1-cabin exposure in congested freeway during commute,
- ME2-cabin exposure in urban canyon,
- ME3-cabin exposure during refueling,
- ME4-cabin exposure in underground garage,
- ME5-cabin exposure at toll plaza,
- ME6- cabin exposure in on-road tunnel (Houston and Chicago only),
- ME7-outside exposure during refueling,
- ME8-outdoor exposure at busy street,
- ME9-outdoor exposure at bus stop,
- ME10-outdoor exposure at surface parking lot during and after event,
- ME11-outside exposure in underground garage, 12-outdoor exposure at toll plaza,
- ME13-cabin exposure following a high emitter (Atlanta only)

In addition, 5-minute integrated canister samples were collected for ME6, ME7, ME10, and ME13 during peak exposures that corresponded to collection of breath samples.

Exposure Protocol and Study Plan, and Study Schedule

The Exposure Protocol and Study Plan was developed and refined based upon results of the pilot studies and initial field measurements during summer 2002. The following chronology describes the main stages in the study and development of the Study Plan.

- First Pilot Study. Prior to the main field studies, DRI and LRRI conducted a 5-day pilot study in Reno, NV, during February 2002 to test alternative measurement approaches under field conditions similar to those that were encountered in the main study (Zielinska et al., 2002c). DRI and LRRI also evaluated the stability of the designated VOC species in breath and urine samples. Based upon the result of this pilot study, the exposure protocols and measurement methods, sampling and analytical procedures were refined and proposed in the June 13, 2002 Exposure Protocol and Study Plan (Zielinska et al., 2002a).

- Summer 2002 Field Studies. The field measurements in San Antonio, Houston, and Atlanta were completed in adherence to the June 2002 protocol during summer 2002. These data were presented in three separate reports: Interim Data Report (Zielinska et al., 2002b), Summer 2002 Atlanta Field Study Report (Zielinska et al., 2003a) and Summer 2002 San Antonio and Houston Field Study Report (Zielinska et al., 2004a). The work in Chicago in the summer of 2002 was postponed, pending further evaluation of the measurement protocol and assessment of the data collected in 2002.

- Second Pilot Study. The second pilot study in Reno was conducted to refine the exposure protocol and further evaluate the surrogate approach and SPME measurements (Zielinska et al., 2003c). Several improvements were implemented in the mobile sampling platform during this time. Additional changes were incorporated into the final version of Exposure Protocol and Study Plan (Zielinska et al., 2003d) based upon discussions between EPA and DRI on the results of these reports. The final study protocol approved by the U.S. EPA is included in the Appendix A of this Final Report.

- The final version of the protocol was applied to the summer 2003 and winter 2004/5 field study in Atlanta, Chicago and Houston and in the winter 2005 in San Antonio. A data report was previously prepared for the summer 2003 field study in Atlanta and Chicago (Zielinska et al. 2004b).

API Section 211(B) Tier-2 Exposure Database

The data have been organized into four data files (API Data_Continuous.xls, API Data_SPME.xls, API Data_Time-integrated.xls and API Data_Reconstructed.xls) containing the continuous, SPME, time-integrated and reconstructed exposure data. All files include data fields describing the sample collection conditions (e.g.; microenvironment, fuel type, test mode) as well as data flags indicating problems with the analytical or sample collection methods. Tables

explaining the meaning of each data field are also included with each file. The files are supplied in Excel workbook format for convenience, but have been formatted to be compatible with common database software (the value -99 is used for missing data points, and time is in hhmm text format)

The time-integrated data contains speciation results from canister, DNPH cartridge, and TENAX adsorbent tubes, plus time-averaged values of pollutants and environmental parameters that were measured continuously during the batch sample collection periods. Within the time-integrated data file there are 4 sub-categories that are presented separately due to the differing number of experimental variables for each type: 1) microenvironment exposure measurements from the three cities, 2) breath samples collected from subjects participating in 4 of the microenvironments, 3) residence with attached garage, and 4) trailing vehicle exposure tests.

The SPME data is assembled in essentially the same manner as the time-integrated data, but contains only the BTEX hydrocarbon compounds and uses some different sample descriptors where necessary to identify which portion of each test the sample was collected. The same sample IDs are used to facilitate comparison of the two sampling methods.

The third data file contains 1-minute averages of the pollutants and environmental parameters that were measured continuously during the microenvironment exposure tests in the 3 cities. Data were typically logged every 10 seconds during testing, but to reduce measurement noise, make the data set more manageable, and reduce the effect of minor timing discrepancies between instruments due to imperfect clock synchronization or differences in sample line residence time, the data was time averaged by minute. Each data record in this file has both a time/date stamp and an identification code that relates it to the corresponding time-integrated sample. Data flags are given to identify any missing or invalid data for each minute. Due to the large size of this file, the various sample descriptors have not been included but these can be derived from the identification code as described in the included key.

The fourth data file contains 1-min reconstructed data for benzene, 1,3-butadiane and formaldehyde based on PID and NDIR CO continuous data, as described in Chapter 1 of this report. Both full time integrated canister and DNPH-carbonyl samples and 5-min canister samples collected over a peak exposure in selected MEs, are included.

Study Findings

<u>Quantification of Personal Exposures to Motor Vehicle Emissions in High Exposure Microenvironments in Atlanta, Houston and Chicago during Summer and Winter (Chapter 1)</u>

- Since different fuels were used in each of the tree cities, only combined effect of city/fuel was examined in this study.

- Day-to-day variations in high-end (99th + percentile) benzene, 1,3-butadiene, formaldehyde, and CO concentrations in different MEs were substantial and independent of city and season, probably related to the activity and emission rates of sources in the given MEs which differ from day to day.

- With the exception of refueling, exposure levels were generally lower in outdoor MEs and higher in enclosed MEs.

- The 20-min average exposures to benzene during refueling ranged up to few hundred ppbv and showed substantial day-to-day variability.

- In-cabin exposures during on-road vehicle operation were less variable than in-cabin exposures in garages and toll plazas.

- Exposure levels of BTEX species were highest in refueling MEs, which are dominated by evaporative emissions whereas exposures to CO, formaldehyde, and 1,3-butadiene were highest in cold-start dominated MEs.

- BTEX and 1,3-butadiene measured by the time-integrated canister method correlated well with continuous PID and CO measurements, respectively, in all MEs except refueling. Correlation of formaldehyde with continuous CO was weak, probably due to photochemical production of this compound.

- Continuous PID and CO (NDIR) data can be used to reconstruct 1-minute time series for benzene and 1,3-BD, respectively, provided that the averaged continuous measurements are above the detection limits of the instruments (25 ppbv and 0.5 ppmv, respectively). CO data can also be used to reconstruct 1-minute formaldehyde data; however, less reliably so due to poorer correlation between these species.

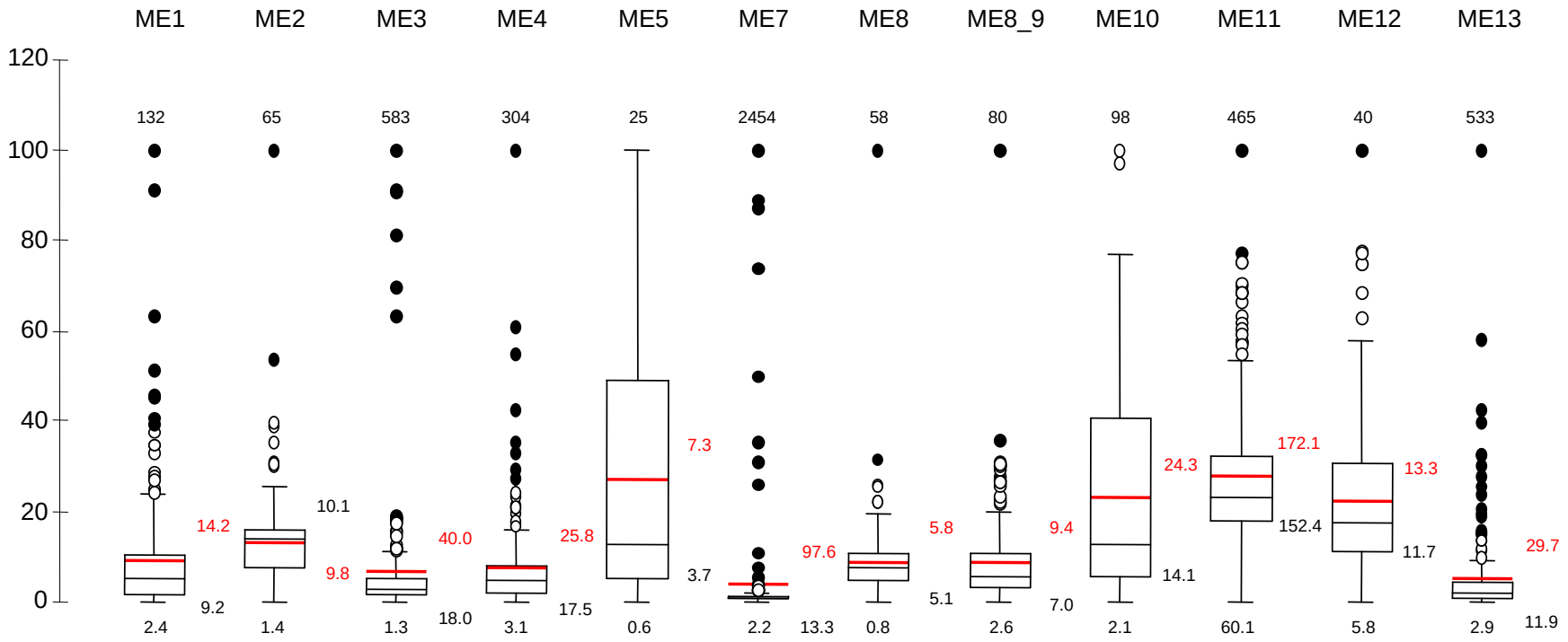
- Reconstructed 1-minute time-series data for benzene and 1,3-butadiene, averaged over five minutes, correlated well with the corresponding 5-minute canister samples after excluding the Houston refueling ME data, which were distorted by high concentrations of MTBE.

- The concentrations of benzene and 1,3-butadiene measured in post peak exposure breath samples closely tracked the corresponding microenvironmental 1-minute maximum reconstructed surrogate values.

- Increases in concentrations of measured species occur in all breath samples that were collected within a minute of a peak exposure. In Atlanta and Chicago, the highest breath concentrations of BTEX and 1,3-BD were observed in ME7 (refueling) and ME11 (underground garage), respectively. In Houston, high concentrations of MTBE were measured in ME7.

Figure E-1 shows the distribution of reconstructed 1-min BTEX concentrations in high-end MEs in Atlanta in Summer. One-min time resolution reflects the high short-time peak concentrations necessary to characterize 99th + percentile exposure. The Atlanta winter distribution as well as Houston and Chicago MEs look very similar.

Figure E-2 A and B shows the comparison of 1,3-butadiane, benzene, formaldehyde and CO averaged concentrations in three cities in Summer and Winter, respectively.



1. In-Cabin Congested Freeway	5. In-Cabin Toll Plaza	10. Outdoor Surface Parking
2. In-Cabin Urban Canyon	7. Outdoor Refueling	11. Outdoor Underground Garage
3. In-Cabin Refueling	8. Sidewalk	12. Outdoor Toll Plaza
4. In-Cabin Underground Garage	9. Sidewalk/Bus Stop	13. Following High Emitters

Figure E-1. Distribution of reconstructed 1-min BTEX exposures in high-end Atlanta MEs. Edges of the box = first and third quartiles; black line = median; red line = average. Minimum and maximum values (ppbv) are shown at the bottom and top of the plots. Whisker covers 99.3% of the data distribution. Filled circles > 3 times the box interval, empty circle are within that interval. The y-axis represents the percentage of data distribution.

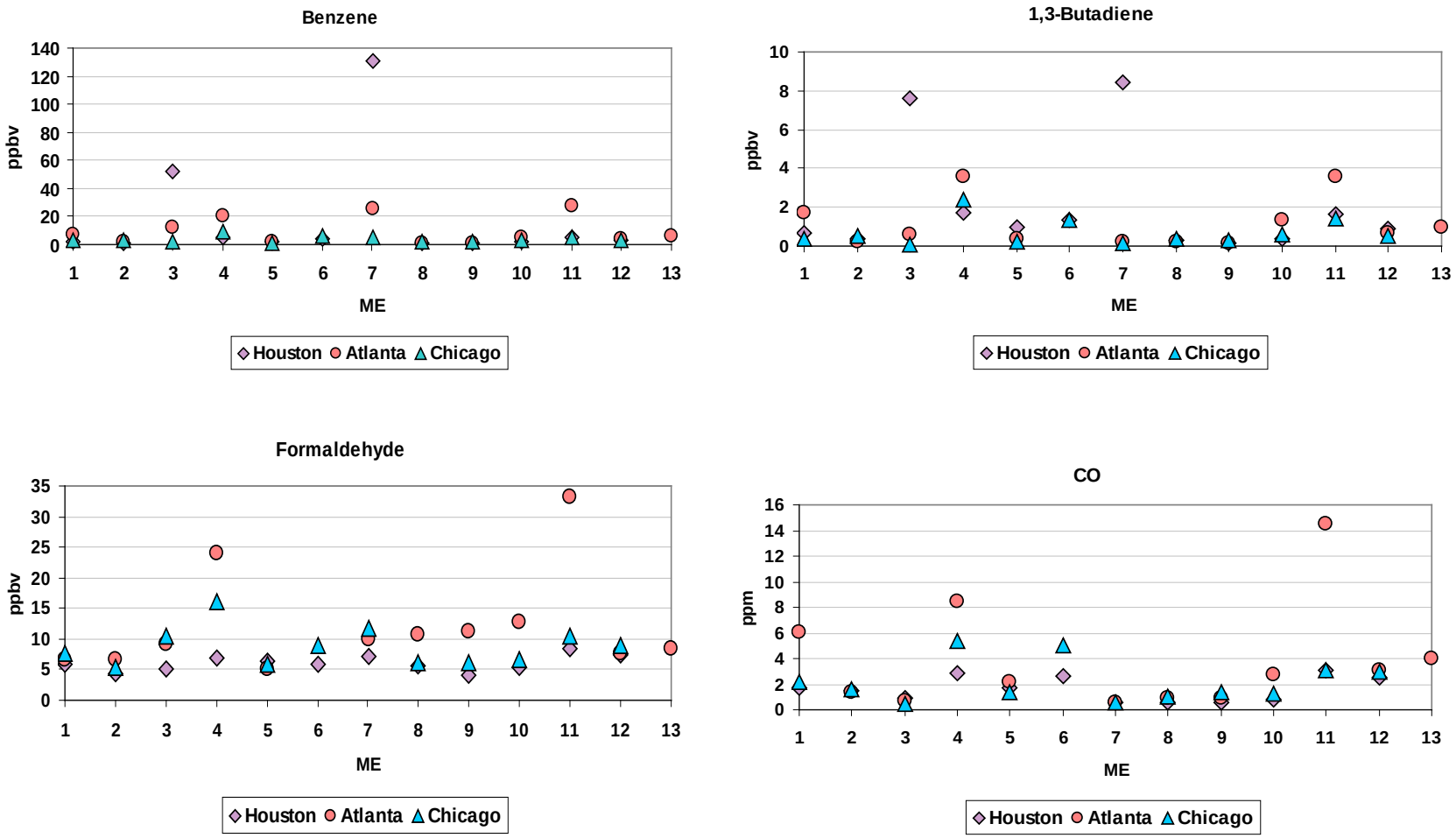


Figure E-2A. Comparison of average concentrations of benzene, 1,3-BD, HCHO and CO in three cities in Summer

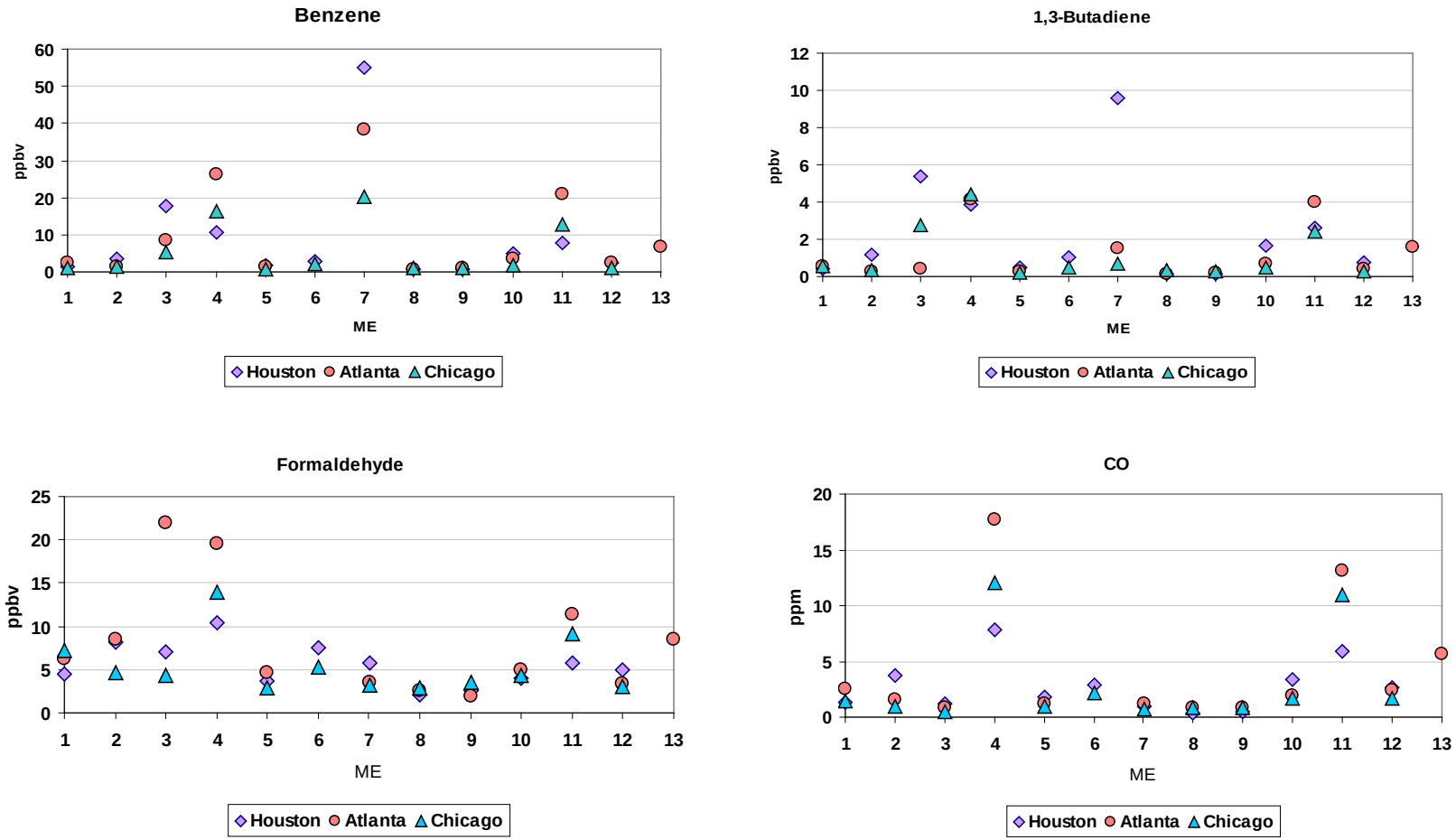


Figure E-2B. Comparison of average concentrations of benzene, 1,3-BD, HCHO and CO in three cities in Winter

Relative Contributions of Vehicle Evaporative and Exhaust Emissions to Concentrations of Volatile Air Toxics in High Exposure Microenvironments (Chapter 2)

- MTBE/benzene ratios were used to estimate the relative contributions of evaporative and exhaust emissions to MSAT. This basis for this approach is that the proportion of MTBE in exhaust is reduced during combustion relative to its proportion in the fuel while benzene is enriched in exhaust relative to its proportion in the fuel due to toluene and xylene dealkylation. Consequently, MTBE to benzene ratios are substantially lower in exhaust than in liquid fuel or headspace vapors. Exposures at the two refueling MEs (3 & 7) were dominated by evaporative emissions as expected, with MTBE/benzene ratios in Houston of 20 to 30. Ratios for all other MEs were between 1 and 4.

- The fractional contribution of evaporative and exhaust emission were estimated for each ME based on exhaust MTBE/benzene ratios from several dynamometer exhaust tests and on-road tunnel measurements and evaporative MTBE/benzene ratios for the SwRI SHED tests and composition of gasoline headspace vapor. Exposures during refueling (ME3, ME7) are 100% due to evaporative emissions within the uncertainties associated with the measurements and method. All other MEs are dominated by tailpipe emissions with fractional evaporative contributions < 10%.

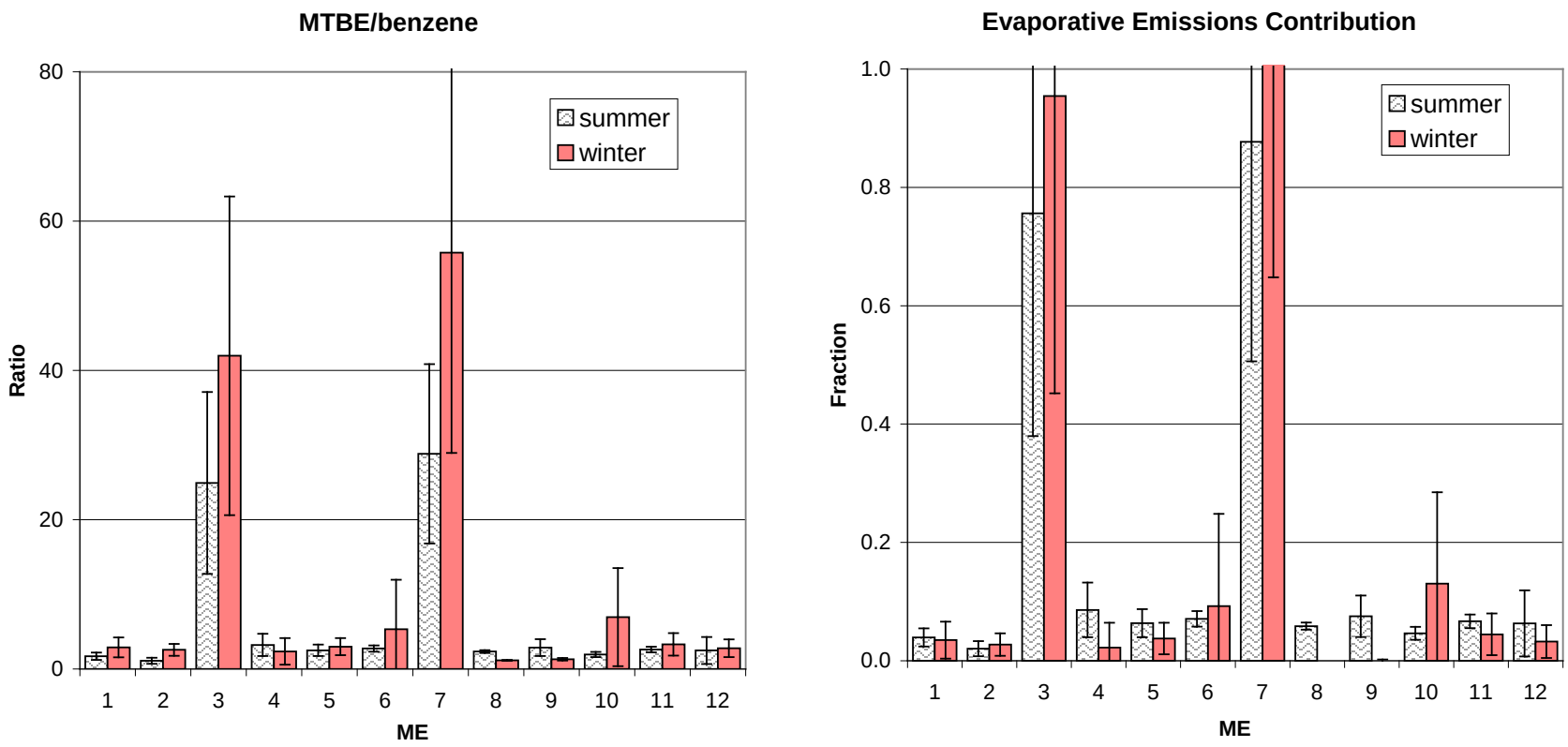
Figure E-3 shows the MTBE/benzene ratio and contribution of evaporative emissions in Houston MEs

Quantitative Relationships Between Levels of Volatile Air Toxics and Carbon Monoxide Measured in High-End Exposure Microenvironments and at Nearby Air Quality Monitoring Stations (Chapter 3)

- MEs in close proximity to running vehicle engines have enhanced CO relative to ambient levels at nearby air quality monitoring sites with enrichment ratios approaching 40 where ventilation is limited, as in underground garages. Average in-cabin CO/ambient ratios in congested freeway traffic range from 2-9. ME locations less proximate to operating vehicles, such as gas stations and urban sidewalks, have CO/ambient ratios of 0.5-2.

- The mean ratio of in-vehicle exposures on congested freeways (ME #1) to ambient levels at a monitoring station of 9.8 ± 3.8 ratio for Houston exceed the HAPEM5 median proximity factor of 4.9 (triangular distribution mode:range 1.9:0-14.3) and HAPEM4 proximity factor of 6.9 for this ME (Rosenbaum, 2005; Long & Johnson, 2004), although by less than expected.

Figure E-4 shows the mean ratios of ME concentrations to corresponding hourly measurements at the regional air monitoring station in Houston.



1. In-vehicle congested freeway	5. In-vehicle toll plaza	9. Outdoor bus stop
2. In-vehicle urban canyon	6. In-vehicle road tunnel	10. Outdoor surface parking
3. In-vehicle refueling	7. Outdoor refueling	11. Outdoor underground garage
4. In-vehicle underground garage	8. Outdoor sidewalk	12. Outdoor toll plaza

Figure E-3. MTBE/benzene ratio and contribution of evaporative emissions in Houston MEs

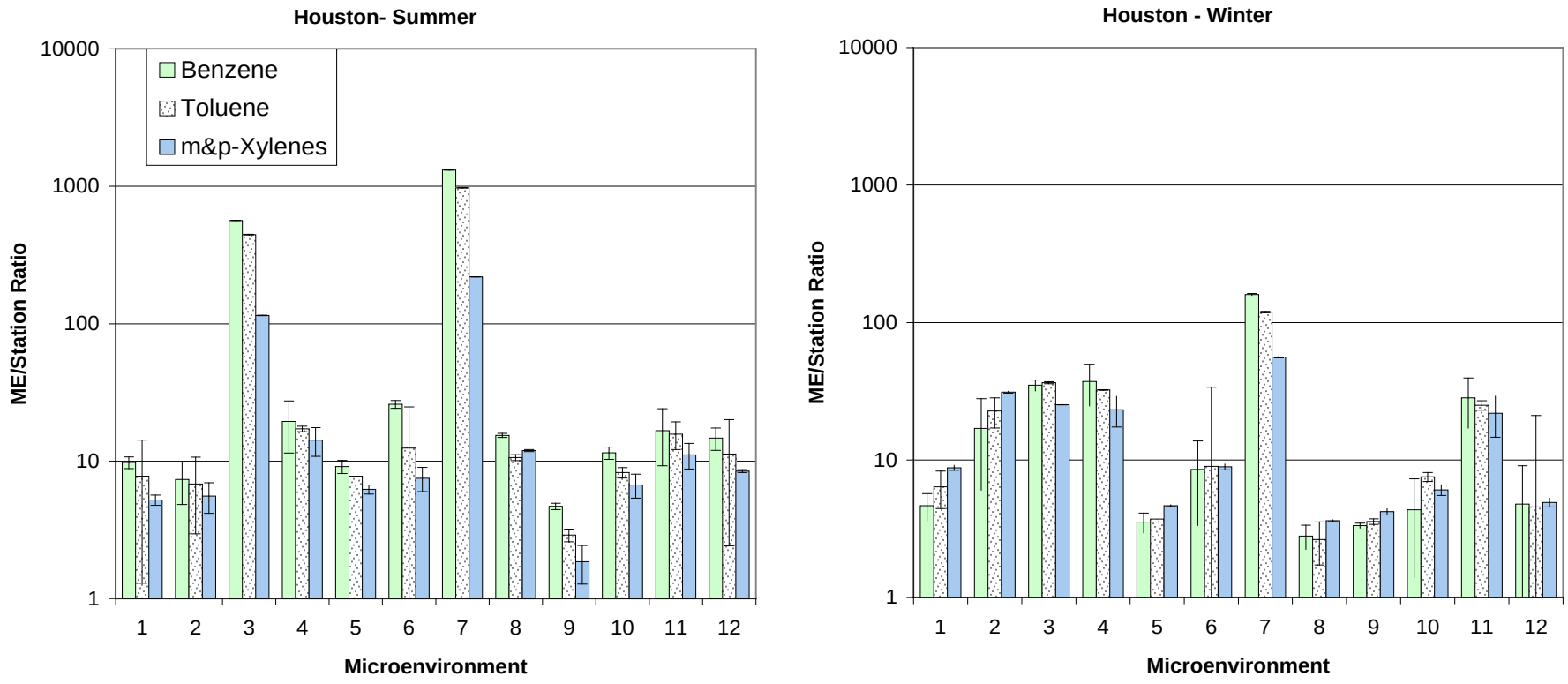


Figure E-4. Mean ratios of ME concentrations to corresponding hourly measurements at the regional air monitoring station in Houston.

Relationship of Attached Garage and Home Exposures to Fuel Type and Emission Levels of Garaged Sources (Chapter 4)

- Two target components, formaldehyde and ethanol, had high kitchen background values indicating indoor sources of these compounds. Average kitchen formaldehyde levels were higher in summer than winter, probably due to enhanced off-gassing of building materials and/or penetration of ambient photochemical formaldehyde.

- Kitchen BTEX, MTBE and CO species are higher in winter than summer. The exception is toluene which shows a minimal difference that actually averages higher in summer for normal mode vehicles. This is consistent with indoor toluene emissions from paints, adhesives, cleaning, and personal care products.

- MTBE and ethanol are highest for fuels containing those species, as anticipated.

- FTP exhaust and SHED evaporative emissions were tested for each vehicle, fuel, and emissions mode, and compared to observed levels in the garage. Neither canister nor SPME samples show strong (r^2=0.003 and 0.005, respectively) correlations with hot soak emissions, although cold-stabilized FTP Bag 2 benzene appears reasonably correlated (r^2= 0.4) to the cold-start SPME.

- Correlations of kitchen levels with garage concentrations were weak (r^2 generally below 0.1) and could not be used to predict kitchen exposures from garage levels.

Figure E-5 shows the effect of fuel and vehicle operational mode (i.e. normal or malfunction) on observed concentrations of 1,3-butadiene, BTEX, MTBE, formaldehyde, ethanol, acetaldehyde, and CO in the kitchen.

Effect of Ventilation, Proximity, and Emission Levels on In-Cabin Exposures of Trailing Vehicle (Chapter 5)

- Summer and winter in-cabin values were similar in magnitude with the exception of formaldehyde which was higher in the summer, possibly due to higher photochemical activity and higher temperatures that led to more off-gassing of formaldehyde in the vehicle cabin interior.

- Trailing vehicle cabin values were larger than background values (as measured during the first 10 min run without the test vehicle) except for formaldehyde which was actually lower than background in winter tests.

- Idle test sample values were on average twice those encountered in driving tests, suggesting that proximity and proximity duration may substantially impact in-cabin trailing vehicle concentrations.

- Average in-cabin levels were affected by both state of maintenance of the vehicle and fuel composition. Use of Atlanta fuel resulted in higher BTEX concentrations in the trailing vehicle cabin, which is consistent with higher aromatic contents of Atlanta fuel, especially in summer. Similarly BTEX concentrations were consistently higher during the summer, which is also in concert with higher aromatic contents of summer fuels, especially for Atlanta. Averaging over the fuels and vehicles, the high emitter mode resulted in 2.2 times higher in-cabin exposure levels for the trailing vehicle than the normal emitter mode except for HCHO which was relatively unchanged from background.

- Trailing vehicle ventilation status affected in-cabin values; the concentrations observed by continuous PID and CO monitors were more variable under high ventilation. This may be rationalized as the vehicle moving into and out of the exhaust plume of the leading vehicle with in-cabin values changing rapidly under high ventilation; whereas under low ventilation, in-cabin concentrations trapped as the vents were closed stayed relatively constant during the remainder of low ventilation conditions.

- Trailing vehicle tests indicated that the largest impact on in-cabin values came from the emissions mode (normal or malfunction) of the leading vehicle.

Table E-2 shows the effects of changing vehicle, fuel and operational mode (i.e. normal or malfunction) on observed concentrations of 1,3-butadiene, BTEX, MTBE, formaldehyde, acetaldehyde, and CO in the trailing vehicle cabin.

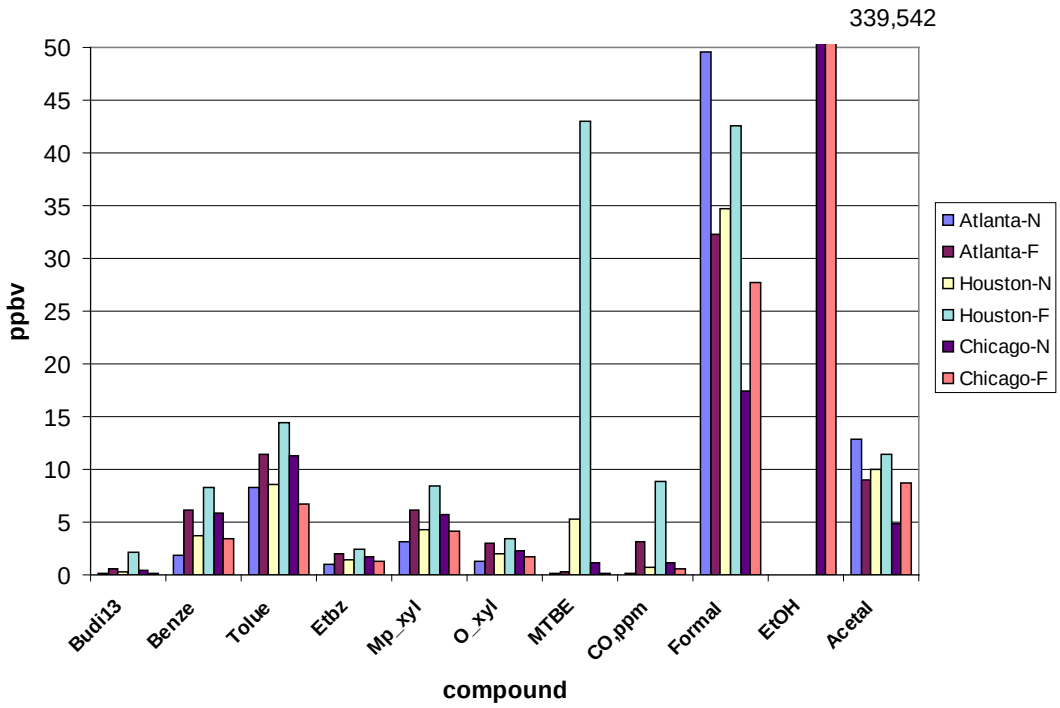


Figure E-5. The effect of fuel and vehicle operation mode (i.e. normal or malfunction) on observed concentrations in the kitchen

Table E-2. The effects of changing vehicle, fuel and operational mode (i.e. normal or malfunction) on observed concentrations in the trailing vehicle cabin.

	Budi13	Benze	Tolue	Etbz	Mp_xyl	O_xyl	MTBE	CO, ppm	Formal	Acetal
Truck only (n=12)	0.64	1.40	2.32	0.45	1.46	0.61	0.87	1.56	4.55	3.67
Car only (n=12)	0.59	1.13	1.87	0.33	1.11	0.45	0.53	1.42	5.90	3.59
Atl fuel only (n=8)	0.53	1.44	2.79	0.51	1.66	0.68	0.14	1.41	5.99	3.39
Hou fuel only (n=8)	0.89	1.52	2.20	0.48	1.58	0.66	2.17	1.91	5.61	4.37
Chi fuel only (n=8)	0.48	0.87	1.32	0.20	0.66	0.28	0.03	1.22	4.20	3.19
Normal only (n=12)	0.06	0.46	1.05	0.21	0.73	0.31	0.16	0.41	5.21	3.26
High emitter only (n=12)	1.06	1.95	2.99	0.55	1.77	0.71	1.21	2.50	5.37	3.37
St Dev high emitter only	28%	36%	38%	41%	44%	44%	177%	52%	52%	64%

Evaluation of Measurement Method's Performance

The integrated canister and DNPH sampling methods produced nearly 100 percent data capture of high quality data as confirmed by internal consistency checks. However, some challenges were encountered in applying two continuous confirmatory measurements, the Kore MS200 and formaldehyde analyzers. In most of the MEs, the MS200 had vacuum problems, most probably due to the high humidity in Houston, Chicago and Atlanta, and did not produce useful data. The instrument performed much better during first and second Pilot Study in Reno, probably because of much lower humidity. Although the formaldehyde analyzer was upgraded, it still required extensive user intervention and did not run reliably under the conditions encountered. The sensitivity of the instrument to environmental noise associated with driving limited its utility under mobile sampling. With proper operation and better characterization of instrument performance, the supplemental continuous formaldehyde analyzer may prove useful for ambient monitoring at fixed location.

The SPME also had excellent data capture, as did the continuous instruments for CO and PID. The two PIDs were compared both in controlled tests and collocated during the MEs. In both cases, they tracked each other quite well. Differences appear to be due to an offset in one unit, and a slightly different response speed between the two units. The NDIR CO and electrochemical CO (Langan T15) instruments compared favorably, usually within 1 ppm. The detailed description of data quality and QA/QC procedures are presented in Appendix H.

Conclusions

Exposure levels are directly related to the activity and emission rates of sources in the microenvironment and inversely related to the distance between sources of emissions and the measurement location and extent of dilution of emissions, which are a function of meteorological conditions and the presence of physical obstruction that inhibit dispersion. All of these factors contribute to the large temporal and spatial variations in pollutant exposures that exist within each of the microenvironments. Testing at SwRI showed that the differences in exhaust and evaporative emission rates among the three regional fuels were not statistically significant except for MTBE. With the exception of MTBE, the small differences due to fuel formulation are masked by the large variations of exposure levels within each of the microenvironments.

The information from control exposure experiments in San Antonio provided useful context for interpreting the varying exposures in the high-end microenvironments in Atlanta, Houston and Chicago. We found that the results of the trailing vehicle experiments were qualitatively consistent with our observations in the three cities. In-cabin exposure levels even in congested traffic were on the order of a factor of two higher than background. Congested stop-and-go conditions resulted in some increase in exposure levels due to shorter gaps between vehicles and highest on-road exposures were measured when following high emitters. In-cabin exposures during low ventilation conditions were relatively constant and retained the levels at the time ventilation was cut off.

Evaporative emissions were the only substantial components of high-end ME exposures during vehicle refueling operations, where they are dominant. Since refueling MEs had the highest relative levels of these components, they constituted the peak exposures, although overall the average population time spent in these high end MEs is likely the shortest. The contributions

of evaporative emissions for all other MEs were typically about 5% of the total measured exposures. Results were similar for both seasons, although evaporative contributions during refueling were marginally less during summer, possibly due to more rapid dispersion of vapors and evaporation of fuel spilled during each refueling test at higher summer temperatures. These results suggest that the contemporary Houston vehicle fleet contained relatively few carbureted or leaking vehicles given that evaporative emissions were not a substantial source in the non-refueling MEs tested. Refueling emissions released from pressurized fuel systems and spilled fuels appeared to be the primary source of peak evaporative exposures. The lack of a seasonal variability in the evaporative contribution was also consistent with this supposition. Although it was not feasible to try to distinguish further between liquid and headspace vapor contributions by the method used, the extremely low MTBE/benzene ratios observed for the roadway, sidewalk, and parking MEs strongly suggest that the impact from leaking liquid gasoline emissions were minor.

HAPEM5 proximity factors may need to be adjusted since they were based on a 1998 scoping study where measurements 'highlighted trailing behind heavy duty diesel vehicles and diesel city buses when possible'. Houston ME/ambient ratio comparisons also generally exceed the other HAPEM factors. Refueling ratios (ME3, ME7) for benzene were higher than the corresponding HAPEM factors as expected, given the refueling protocol provisions maximizing exposure discussed above and below. Concentrations of exhaust compounds such as CO and 1,3-butadiene were enhanced under reduced ventilation situations.

It must be recognized that the various microenvironments were selected with a goal to capture the 99th percentile exposure levels within each type of microenvironment, as prescribed by EPA and API. We also selected specific sampling times and locations with the greatest potential for higher exposures. These selections were based on considerations of various emission surrogates such as traffic counts, diurnal variations in average highway speeds, length of queues at toll plazas, number of cars refueling or entering and exiting parking garages. Surrogates of dispersion included wind roses and diurnal variations in temperature. Measurements in microenvironments with unrestricted dispersion were made in the early morning or evening during calm conditions and minimal vertical mixing. In moderate wind conditions, we drove parallel to the prevailing wind to reduce the impact of cross winds. Thus, the ranges of exposures determined in this study are skewed toward the higher end of the distribution of exposures for each microenvironment.

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1. Quantification of Personal Exposures to Motor Vehicle Emissions in High Exposure Microenvironments in Atlanta, Houston, and Chicago during Summer and Winter.

1.1 Introduction

Gasoline-powered vehicles emit a portion of ozone-forming volatile organic compounds (VOC) and mobile source air toxics (MSAT) in the urban areas of the country. Elevated exposures to gasoline-related MSAT have been reported in certain microenvironments (MEs), such as in vehicle cabins during commuting on congested roadways (Batterman et al., 2002; Chan et al. 1991; Rodes et al., 1998; Fedoruk and Kerger 2003; Weisel et al., 1992; Jo and Park, 1999), refueling (Vayghani and Weisel 1999; Vainitalo et al., 1999; Lindstrom and Pliel, 1996) or in urban canyons (Rodes et al., 1998; Chan et al. 1991).

Although oxygenated fuel and reformulated gasoline (RFG) programs are intended to reduce the emissions of ozone precursors and MSAT , uncertainties remain regarding the population exposures associated with oxygenated and conventional gasoline. Accordingly, in 2001 EPA issued testing requirements under Alternative Tier 2 provisions of the fuel and fuel additive (F/FA) health effects testing regulations, required pursuant to Section 211(b) of the Clean Air Act.

The population exposure study reported here targets conventional gasoline and two oxygenated blends containing methyl tertiary butyl ether (MTBE) and ethanol (EtOH) and conducts studies in prospective high-end microenvironments (MEs) likely associated with the most-exposed populations. Personal exposures are quantified in selected MEs representing the upper end of the frequency distribution of potential population exposures. The studies take place in cities that have ongoing ambient air monitoring programs, located in hot and cold parts of the country, using one of the three target fuels. Sampling was performed during winter and summer seasons and under conditions (e.g., downwind, low wind speeds, rush hour traffic, fuel spillage, trailing high emission vehicles) thought to maximize exposure within each ME. The same sampling protocols (e.g., location, duration, cabin ventilation) were used in both seasons whenever possible. A number of fuel emission and exhaust components [carbon monoxide (CO), carbon dioxide (CO_2), benzene, toluene, ethylbenzene, xylenes (BTEX), MTBE, 1,3-butadiene (1,3-BD), EtOH, formaldehyde (HCHO), and acetaldehyde (CH_3CHO)] were measured within thirteen MEs in personal breathing zones, and in breath immediately after measured peak exposures. The results of these microenvironmental studies were intended to include the upper-end (99+th percentile) of the frequency of annual average inhalation exposures to evaporative and combustion emissions from the three targeted gasolines. The study also estimates the relative proportion of evaporative and combustion emissions by ME in breathing zone air.

The specific objectives of the study are to provide information allowing EPA to:

- Quantify personal exposures to motor vehicle gasoline evaporative and combustion emissions in MEs representing the upper end of the population exposure frequency distribution (99+th centile) of such exposures;

- Determine quantitative relationships between personal exposures in selected MEs and fixed site measurements in these MEs and at nearby air monitoring stations;

- Determine how personal exposures differ across seasons and cities using the three target fuels (conventional-, MTBE-, and EtOH-gasoline);

- Extrapolate study data to other cities and other oxygenated fuels; and

- Apportion the relative contributions of vehicle fuel combustion vs. evaporative emissions to personal exposures in high-end MEs.

1.2 Experimental

1.2.1 Selection of Microenvironments

Houston (TX), Chicago (IL) and Atlanta (GA) were selected as the study sites. These cities have ongoing ambient monitoring programs and dispense MTBE-RFG, EtOH-RFG, and conventional gasoline formulations, respectively. One of the goals of the project was to sample high-end MEs, plausibly characterized in the upper 99+th percentile of exposures to exhaust/evaporative emissions from gasoline-fueled vehicles. Selection of high-end MEs[1] was made in consultation with EPA and independent peer reviewers according to the selection criteria described in the Exposure Protocol and Study Plan (Zielinska et al, 2003a) included in Appendix A. Table 1.2.1-1 lists the MEs chosen along with the number of replicate measurements taken in each ME, whether biomarker (breath) measurements were taken for that ME, and the sampling time spent in each ME.

[1] **ME1**: In-cabin congested freeway; **ME2**: In-cabin urban canyon; **ME3**: In-cabin refueling; **ME4**: In-cabin underground garage; **ME5**: In-cabin toll plaza; **ME6**: In-cabin roadway tunnel; **ME7**: Out-of-cabin refueling; **ME8**:Out-of-cabin sidewalk; **ME9**: Out-of-cabin sidewalk/bus stop; **ME10**: Out-of-cabin surface parking; **ME11**: Out-of-cabin underground garage; **ME12**: Outside toll plaza; **ME13**: In-cabin trailing high-emitter vehicle

Table 1.2.1-1. Microenvironmental Sampling.

ME #	ME Description	Replicates	Biomarker	SamplingTime (min)**
1	In-Cabin Congested Freeway	5		40 (20 H and 20 L)
2	In-Cabin Urban Canyon	3		40(20 H and 20 L)
3	In-Cabin Refueling	5		20 (10 H and 10 L)
4	In-Cabin Underground Garage	5		40 (20 H and 20 L)
5	In-Cabin Toll Plaza	3		40 (20 H and 20 L)
6*	In-Cabin Roadway Tunnel	5	yes	40 (20 H and 20 L)
7	Out-of-Cabin Refueling	5	yes	20
8	Out-of-Cabin Sidewalk	3		40
8/9	Out-of-Cabin Sidewalk/Bus Stop	3		40
10	Out-of-Cabin Surface Parking	3		40
11	Out-of-Cabin Underground Garage	5	yes	40
12	Outdoor Toll Plaza	3		40
13*	In-Cabin Trailing High-Emitting Vehicles	5	yes	40 (20 H and 20 L)

*ME6 was sampled in Houston & Chicago and ME13 in Atlanta
** H refers to high ventilation and L to low ventilation conditions (see Monitoring Methods below)

The ME number refers to the same type of ME in each city studied. Since ME6 refers to a roadway tunnel and a suitable tunnel was not found in Atlanta, ME13 (following a high emitting vehicle) was substituted.

Prior to selecting specific ME locations, Desert Research Institute (DRI) personnel surveyed potential high-end MEs in each city. The objectives of these surveys with portable gas analyzers were to determine the suitability of candidate sampling locations with respect to access, maximal exposure levels, and the variability of these exposures. The sampling period in each ME was selected to coincide with maximum activity level (i.e., emissions and exposure) as described in the Protocol (Appendix A). In the absence of data on the range of actual emission component exposures in various MEs in each city, we considered available surrogate parameters for emission and dispersion to select locations and sampling periods with the greatest potential for maximal exposures. These emission surrogates included diurnal traffic counts, variations in highway speeds, length of queues at toll plazas, concurrent numbers of cars refueling, and count rates entering and exiting parking garages. Surrogates for dispersion included diurnal wind roses and variations in temperature. Where possible we drove parallel to the prevailing wind direction to reduce the impact of cross winds and sampled downwind of the nearest emission sources. Our sampling strategy also recognized that vehicle exhaust emissions are significantly higher for identified high emitting vehicles and all vehicles during cold starts (e.g., at parking lots, underground garages, and service stations) and accelerations (e.g., at toll plazas, roadway intersections). All of these factors are important in understanding the high-end perspective of sampling and the temporal and spatial variations that exist within these high-end MEs.

1.2.2 Monitoring Methods

Instrumented Van. All in-cabin and out-of-cabin exposure measurements were performed with the mobile sampling van, a 1996 Chrysler Minivan, DRI-modified for on-road and stationary sampling. The power system included two banks of rechargeable AGM gel batteries with minimal H_2 out-gassing during either charge or discharge. Each bank had a 1750 watt inverter for 110v AC power and direct connections for 12v DC, giving maximum flexibility. The suspension of the vehicle was upgraded to support the additional battery and instrument weight. Seats were removed and replaced with an adjustable equipment racks. For refueling experiments, a second fuel pump was installed to facilitate prompt removal of fuel. In-cabin and exterior temperature and relative humidity sensors were installed along with an additional sensor measuring fuel tank temperature. The data acquisition system has eight analog-to-digital inputs to record instrument outputs, which include a global positioning satellite (GPS) sensor, and compiles spatially-located data into a single database. All in-cabin equipment was manifolded to sample from a point in the driver's breathing zone. This manifold inlet could also be extended outside for stationary sampling purposes (e.g., into the subject breathing zone during refueling tests). Infiltration of outside air was adjusted by opening or closing windows in the front and rear of the cabin and switching the heating/AC system from vent to recirculate. In this manner two ventilation modes, high (all open) and low (all closed), were included in all in-cabin tests.

Equipment Cart. For sidewalk, bus stop and outdoor toll plaza tests, sampling equipment was placed on a cart that was pushed along the sidewalk of a busy street in an urban canyon (ME8), patrolled a bus stop sidewalk at a high traffic density intersection (ME9) or was stationed next to a toll booth during rush hour traffic (ME12). Sampling inlets were positioned in the subject breathing zone. Detailed protocols for sampling in each ME are described in the Exposure Protocol and Study Plan (Zielinska et al, 2003a), included in Appendix A. Measurements in each ME were repeated three to five times for each city-season as noted in Table 1.2.1-1.

Sampling and Analysis Methods. Three approaches were used to measure targeted compounds in the high-end MEs: (1) reference method time-integrated samplers to quantify concentrations over 20-40 minute sampling periods; (2) continuous surrogate method monitors to determine short-term concentration variations over 10-60 second sampling periods; and (3) supplemental methods to provide additional short-term surrogate concentration estimates over intermediate time frames of several minutes. Supplemental methods included newer methods that have not been fully adapted or ruggedized for field use. The supplemental methods provide independent checks and periodic corroboration of the surrogate approach used to estimate time-series values for species not directly measured by the surrogate methods.

1. The reference methods include passive and pressurized whole-air canister samplers used to collect ambient and breath CO, CO_2, BTEX, MTBE, and 1,3-BD; acidified 2,4-dinitrophenylhydrazine (DNPH) cartridges to collect HCHO and CH_3CHO; and a multi-bed (TenaxTA-Carbotrap-Carbosieve) solid adsorbent tube for ambient EtOH (Chicago only). After collection, these samples are sent to the DRI Organic Analytical Laboratory for analysis. Canister CO and CO_2 are chromatographed and converted to methane for analysis by flame ionization detection (GC/FID); BTEX, MTBE, and 1,3-BD are quantified by capillary GC/FID [GC/mass spectrometry (MS) for breath samples] using a separate system (Zielinska et al, 1998). The DNPH cartridges are eluted with acetonitrile

and aldehydes analyzed by high performance liquid chromatography (LC) with photodiode array ultraviolet (UV) detection of their hydrazone derivatives. The multi-bed sorption tubes are thermally desorbed into a GC and quantified by MS. These methods are basically standard TO-15, -11A, and -17 EPA procedures with some improvements incorporated by DRI as described in Appendix B.

2. The surrogate methods include both active non-dispersive infrared (NDIR) and passive T-15 Langan electrochemical cell devices for CO, and an active photo-ionization detector (PID) for volatile organic compounds (VOCs) with ionization potentials below 10.6 eV (principally olefins and aromatic species). These continuous instruments respond to concentration changes within a few seconds and provide sensitive proportionate measures of the short-term variability of exhaust and evaporative species quantified by the time-integrated reference methods. Surrogate methods are used to generate normalized continuous time-series of concentrations for BTEX, MTBE, EtOH, 1,3-BD, and the aldehydes quantified by the reference methods.

3. The supplemental methods include both active continuous BTEX and HCHO instruments with several minute response times and a passive microextraction fiber sampling a flowing analyte stream for BTEX over a 10-minute period. The continuous BTEX monitor, a Kore MS200, quantifies species diffusing through its semi-permeable membrane inlet by 70eV electron impact ionization and time-of-flight MS. The HCHO instrument bubbles ambient air into a flowing aqueous 2,4-pentanedione and ammonia reagent to produce a HCHO-specific product, 3,5-diacetyl-1,4-dihydrolutidene, that is quantified by UV fluorescence. The 75 um film solid phase microextraction carboxen/polydimethylsiloxane (SPME-CAR/PDMS) fiber is passively exposed in a flowing air stream for 10 minutes, retracted into its syringe holder, and promptly injected into a GC with PID/FID detection optimized for BTEX quantification.

All sampling and analysis methods are described in detail in Appendix B. In addition, the validation of the SPME method is described in detail in Appendix C. Quality Assurance procedures are described in Appendix H.

1.2.3 Exposure Biomarkers

Breath measurements were used as exposure biomarkers in four high-end MEs: out-of-vehicle cabin refueling (ME7); parking in an underground garage (ME11); driving through a roadway tunnel (ME6); and trailing a high emitting vehicle (ME13). The test subject took three breath samples. One sample was taken before initiating ME sampling; the second, ten seconds immediately after completing the active refueling task or within a minute of experiencing a measured peak exposure in the other three MEs, and a third, immediately following the second. The 3rd sample was analyzed if there was a problem with the second sample. The subject used a 1-liter evacuated canister, placing its inlet tube into his mouth and breathing smoothly and regularly through the mouth around the tube until a resting tidal breathing pattern was established. At the end of a normal tidal exhalation, the subject closed his mouth around the tube, opened the canister valve expelling his expiratory reserve and filled the canister, collecting one liter of the expiratory reserve. When the canister was filled, the technician closed the canister valve to capture the sample (Pleil and Lindstrom, 2002; Lindstrom and Pleil, 1996). All breath samples were analyzed by GC/MS for BTEX, MTBE, 1,3-BD, and EtOH as described by Pleil

and Lindstrom (2002); CO_2 was methanized and quantified by GC/FID. Four subjects, labeled as 1, 2, 3, and 4 in the time- integrated database, were utilized for breath sample measurements.

1.3 Results and Discussion

This section summarizes the distributions of high-end exposure levels observed for each ME by city and season. These exposure levels are examined as 20 to 40 minute averages from the integrated reference measurements, 5-10 minute averages from the surrogate data as corroborated by the supplemental measures, and as peak exposures using the one minute reconstructed surrogate time series.

1.3.1 Variation of day-to-day exposures by ME in each city

Table 1.3.1-1 and 1.3.1-2 summarize the three city, summer-winter, 20-40 minute average, maximum, and minimum ME canister levels of CO, benzene, and sum of BTEX and the HCHO and CH_3CHO values from DNPH cartridges. Average, maximum, and minimum in/out-cabin temperature and relative humidity (T/ RH) values are also listed. In-cabin T/RH values are in parentheses. Figures 1.3.1-1 through 1.3.1-6 show the day-to-day variations in benzene, 1,3-BD, HCHO, and CO concentrations.

In general, exposure levels should be proportionate to the number of sources and their emission rates in the ME and inverse to increasing distance to the emission source and the extent of emissions dilution. Dilution is a function of meteorology and the presence of physical obstructions that may inhibit emissions dispersion. With the exception of refueling activities, we generally find that exposure levels are lower in outdoor environments and higher in enclosed environments. However, substantial variations exist among outdoor environments with respect to proximity to emission sources and the magnitude of their emissions. For example, the 40-minute average exposures for most urban canyon sidewalk/bus stop samples are on the order of a 1-2 ppbv for benzene, whereas benzene exposures on outdoor surface parking lots or toll plaza aprons are usually higher. Refueling samples range up to few hundred ppbv benzene over 20 minute sampling times and show substantial day-to-day variability. In-cabin exposures during vehicle roadway operation show more consistency sample to sample and more temporal uniformity than the other MEs.

As it could be expected, MTBE and the BTEX species show the highest concentrations in refueling MEs dominated by evaporative emissions whereas CO, HCHO and 1,3-BD are highest in cold-start dominated MEs (underground garage, roadway tunnel, toll plaza, surface parking). Several Houston refueling 1,3-BD values had to be invalidated due to the interferences stemming from elevated MTBE concentrations in these MEs. MTBE decomposes slightly (on the order of 1 – 5%) at GC injector temperatures forming isobutene (2-methylpropene), a decomposition product that elutes just prior to 1,3-BD on the DB-1 (or equivalent) chromatographic column. When concentrations of isobutene are much higher than 1,3-BD, they tail into the butadiene peak biasing its apparent concentration upward. This interference was confirmed by GC/MS. As noted in Tables 1.3.1-1 and 1.3.1-2, one value for ME3 and two for ME7 were invalidated in summer samples and one value for ME3 and four for ME7 in winter samples.

Table 1.3.1-1. Summer average, maximum, and minimum ME concentrations (ppbv) of BTEX, 1,3-BD, HCHO, CH3CHO, EtOH, MTBE, and CO (ppmv)

Atlanta (Conventional Fuel)

ME		ME1	ME2	ME3	ME4	ME5	ME7	ME8	ME9	ME10	ME11	ME12	ME13
Replicates		5	3	5	5	3	5	3	3	3	5	3	5
1,3-butadiene	Ave.	1.7	0.3	0.6	3.6	0.3	0.3	0.2	0.1	1.3	3.6	0.7	1.0
	Min.	1.2	0.1	0.1	1.2	0.0	0.1	0.1	0.0	0.4	1.2	0.5	0.7
	Max.	2.2	0.4	2.1	7.3	0.7	0.6	0.2	0.4	2.2	6.2	0.8	1.1
Benzene	Ave.	6.8	2.0	12.3	20.4	2.4	25.9	1.0	1.6	4.6	28.1	3.6	6.0
	Min.	4.2	1.4	5.8	6.0	1.7	6.2	0.9	1.4	1.6	17.7	3.0	3.7
	Max.	9.3	2.4	22.9	40.3	3.7	74.2	1.1	1.8	9.0	35.3	3.9	9.3
Toluene	Ave.	13.6	4.2	30.6	63.2	4.2	43.7	2.5	4.1	9.8	76.5	5.3	18.0
	Min.	8.4	2.4	15.7	19.7	3.1	10.5	2.4	3.6	3.3	49.2	4.9	9.1
	Max.	21.2	5.4	43.0	122.6	6.2	104.1	2.8	4.7	19.4	93.6	5.6	37.6
Ethylbenzene	Ave.	2.2	0.7	4.1	9.9	0.7	4.6	0.4	0.7	2.0	12.8	0.8	2.6
	Min.	1.5	0.4	1.8	3.4	0.5	1.1	0.4	0.6	0.6	8.2	0.8	1.6
	Max.	3.5	0.9	5.1	18.7	1.0	8.7	0.5	0.9	4.0	17.2	0.9	4.8
Xylene	Ave.	8.7	2.9	15.2	37.0	2.6	17.1	1.8	3.0	8.0	48.8	3.6	10.3
	Min.	5.5	1.6	6.6	12.5	1.5	4.4	1.8	2.6	2.9	30.9	3.4	6.1
	Max.	13.7	3.7	18.5	69.2	3.9	29.2	1.9	3.8	15.5	63.4	3.9	19.1
Formaldehyde	Ave.	6.6	6.7	9.3	25.7	5.1	10.0	10.7	11.2	12.8	33.2	7.6	8.6
	Min.	3.9	5.0	5.5	15.4	4.4	7.2	9.6	10.5	8.8	22.2	7.0	7.3
	Max.	8.4	8.5	11.1	32.3	6.2	11.5	11.3	12.5	19.7	50.6	8.3	11.1
Acetaldehyde	Ave.	6.6	4.6	4.3	10.8	2.8	3.4	2.7	3.0	4.0	12.2	2.4	5.2
	Min.	2.0	3.5	1.2	7.3	2.1	1.1	2.5	2.1	2.5	7.4	1.5	4.4
	Max.	18.6	6.5	5.9	15.1	3.4	5.1	3.1	4.0	6.8	20.9	3.5	6.7
CO canister	Ave.	6.1	1.4	0.7	8.5	2.1	0.6	0.8	1.1	2.7	14.5	3.1	4.0
	Min.	3.7	0.7	0.4	1.7	2.0	0.2	0.7	1.0	0.8	9.8	2.8	2.3
	Max.	11.7	2.1	1.4	16.2	2.4	1.2	1.0	1.1	5.6	20.0	3.5	6.2
Temp ˚C	Ave.	(22.3)		(27.2)	(31.7)		27.8				32.3		(24.6)
(in-cabin)	Min.	(21.2)		(19.6)	(30.5)		22.1				31.0		(23.6)
	Max.	(23.9)		(33.6)	(33.8)		30.4				33.8		(25.6)
RH, %	Ave.	(57.8)		(60.0)	(51.8)		65.3				47.4		(48.8)
(in-cabin)	Min.	(56.0)		(43.0)	(46.0)		56.0				41.0		(46.0)
	Max.	(59.0)		(73.0)	(60.0)		86.0				51.0		(54.0)

Note: Urban canyon loop for Atlanta: Peachtree Street NW, Forsyth-Carnegie, Spring Street NW, and Harris Street

ME1: In-cabin congested freeway; **ME2**: In-cabin urban canyon loop; **ME3**: In-cabin refueling; **ME4**: In-cabin underground garage; **ME5**: In-cabin toll plaza; **ME6**: In-cabin roadway tunnel; **ME7**: Out-of-cabin refueling; **ME8**:Out-of-cabin sidewalk; **ME9**: Out-of-cabin sidewalk/bus stop; **ME10**: Out-of-cabin surface parking; **ME11**: Out-of-cabin underground garage; **ME12**: Outside toll plaza; **ME13**: In-cabin trailing high-emitter vehicle

Chicago (Oxygenated Fuel - Ethanol)

ME		ME1	ME2	ME3	ME4	ME5	ME6	ME7	ME8	ME9	ME10	ME11	ME12
1,3-butadiene	Ave.	0.4	0.5	0.1	2.4	0.3	1.3	0.1	0.3	0.3	0.6	1.4	0.5
	Min.	0.2	0.3	0.0	1.5	0.2	1.2	0.0	0.3	0.1	0.4	0.2	0.3
	Max.	0.5	1.0	0.1	4.0	0.3	1.6	0.3	0.4	0.4	0.9	2.6	0.8
Benzene	Ave.	2.7	2.9	2.1	8.9	1.5	5.8	4.9	2.5	1.7	3.3	5.1	3.1
	Min.	1.7	1.6	0.5	5.6	1.4	4.2	0.6	1.8	1.3	1.8	1.2	2.6
	Max.	4.9	5.2	4.6	12.2	1.5	8.7	11.4	3.6	2.2	5.7	8.2	3.4
Toluene	Ave.	4.8	4.7	6.6	23.3	2.8	15.0	11.2	3.4	2.4	7.5	11.8	3.6
	Min.	2.4	2.6	1.4	13.6	2.3	6.7	0.7	2.0	1.5	3.5	3.4	2.6
	Max.	9.3	7.5	18.6	37.8	3.3	25.5	27.3	6.1	3.5	13.6	18.4	4.3
Ethylbenzene	Ave.	0.8	0.7	1.7	3.3	0.4	1.9	1.4	0.6	0.5	0.8	2.0	0.6
	Min.	0.4	0.3	0.2	1.8	0.3	1.4	0.1	0.4	0.3	0.7	0.6	0.4
	Max.	1.3	1.2	7.2	4.5	0.5	2.8	2.6	0.9	0.8	1.1	3.0	0.7
Xylene	Ave.	3.1	2.7	7.2	13.4	1.7	6.6	5.9	2.1	1.8	3.2	7.8	2.3
	Min.	1.6	1.2	0.9	6.9	1.4	5.1	0.5	1.4	1.1	2.7	2.2	1.9
	Max.	5.1	4.5	29.8	17.1	2.0	9.4	10.2	3.4	3.0	4.0	12.1	2.8
Formaldehyde	Ave.	7.7	5.5	10.5	16.1	5.9	8.9	11.7	6.2	6.1	6.7	10.5	8.8
	Min.	5.4	4.6	8.4	10.7	5.3	8.0	3.4	3.8	3.7	5.9	5.8	6.2
	Max.	9.4	7.3	13.7	26.7	6.5	10.1	24.6	7.6	7.8	8.1	14.1	11.6
Acetaldehyde	Ave.	6.3	7.7	6.3	10.9	5.1	8.4	4.5	3.8	3.7	3.4	6.5	5.4
	Min.	3.6	4.1	2.8	8.1	4.5	7.4	2.5	3.7	2.2	2.5	3.4	3.8
	Max.	8.6	14.7	9.4	15.0	5.8	8.8	6.1	4.0	4.5	4.4	8.3	7.8
CO canister	Ave.	2.2	1.7	0.4	5.3	1.4	5.1	0.6	1.0	1.4	1.2	3.1	3.0
	Min.	1.5	1.3	0.3	4.0	1.1	4.0	0.3	0.8	0.9	1.0	0.6	2.5
	Max.	3.0	2.4	0.6	8.2	1.6	7.1	0.7	1.2	1.7	1.8	5.1	3.7
EtOH	Ave.	6.7	10.5	13.0	15.4	5.7	20.6	28.3	0.0	0.8	1.3	12.2	3.1
	Min.	0.0	4.9	0.0	0.0	0.7	12.5	0.0	0.0	0.0	0.0	0.0	0.0
	Max.	12.1	20.0	36.7	30.4	10.4	29.4	115.4	0.0	2.4	3.8	42.1	4.9
Temp ˚C	Ave.	(23.3)	(22.3)	(28.3)	(26.8)	(21.0)	(21.7)	26.7	25.0	26.0	22.6	27.3	31.5
(in-cabin)	Min.	(21.2)	(21.9)	(25.6)	(25.9)	(20.3)	(20.2)	23.5	23.4	24.5	20.7	22.7	30.2
	Max.	(25.8)	(23.2)	(30.2)	(28.4)	(21.4)	(25.0)	28.8	26.5	27.8	24.6	29.7	33.5
RH, %	Ave.	(51.6)	(44.7)	(51.5)	(60.2)	(56.0)	(53.0)	58.2	54.3	52.7	69.7	56.0	42.3
(in-cabin)	Min.	(46.0)	(41.0)	(45.0)	(55.0)	(53.0)	(50.0)	49.0	53.0	50.0	66.0	45.0	30.0
	Max.	(55.0)	(48.0)	(63.0)	(65.0)	(60.0)	(57.0)	67.0	56.0	55.0	73.0	66.0	56.0

Note: Urban canyon loop for Chicago: Lake Street, Wabash Avenue, Van Buren Street, and State Street

ME1: In-cabin congested freeway; **ME2**: In-cabin urban canyon loop; **ME3**: In-cabin refueling; **ME4**: In-cabin underground garage; **ME5**: In-cabin toll plaza; **ME6**: In-cabin roadway tunnel; **ME7**: Out-of-cabin refueling; **ME8**:Out-of-cabin sidewalk; **ME9**: Out-of-cabin sidewalk/bus stop; **ME10**: Out-of-cabin surface parking; **ME11**: Out-of-cabin underground garage; **ME12**: Outside toll plaza; **ME13**: In-cabin trailing high-emitter vehicle

Houston (Oxygenated Fuel – MTBE)

ME		ME1	ME2	ME3	ME4	ME5	ME6	ME7	ME8	ME9	ME10	ME11	ME12
1,3-butadiene	Ave.	0.7	0.4	0.6*	1.7	0.9	1.4	1.2*	0.3	0.1	0.4	1.6	0.9
	Min.	0.3	0.3	0.3	0.2	0.6	0.8	0.5	0.2	0.1	0.3	0.5	0.4
	Max.	1.0	0.5	0.7*	4.5	1.2	2.8	2.1*	0.5	0.2	0.5	2.9	1.4
Benzene	Ave.	1.9	1.4	52.6	5.1	2.5	3.7	130.7	1.4	0.6	1.6	5.4	3.2
	Min.	1.3	1.2	5.6	1.0	1.9	2.5	13.3	0.7	0.3	1.0	2.3	1.3
	Max.	2.7	1.9	175.1	11.1	3.1	7.1	281.9	2.6	0.7	1.9	9.8	5.0
Toluene	Ave.	3.4	2.7	80.3	11.5	4.6	6.6	183.0	3.3	1.0	2.7	12.0	5.8
	Min.	2.1	2.2	15.9	2.5	3.0	4.1	27.4	1.7	0.7	1.9	5.6	1.7
	Max.	4.2	3.3	277.5	22.7	5.5	13.7	425.6	4.4	1.3	3.1	19.4	12.2
Ethylbenzene	Ave.	0.6	0.5	10.6	2.4	0.9	1.3	21.0	0.7	0.2	0.7	2.6	1.3
	Min.	0.4	0.5	2.6	0.6	0.6	0.9	3.5	0.3	0.1	0.5	1.1	0.3
	Max.	0.7	0.7	35.0	5.2	1.1	2.5	50.8	1.3	0.2	0.8	4.5	2.9
Xylene	Ave.	2.6	2.3	35.7	9.3	3.8	5.4	71.5	2.7	0.9	2.6	10.1	5.6
	Min.	1.7	2.0	10.2	2.5	2.6	3.8	10.2	1.1	0.6	1.8	4.5	1.3
	Max.	3.4	2.8	110.2	18.5	4.4	10.3	143.0	5.1	1.0	3.2	16.8	12.2
Formaldehyde	Ave.	5.9	4.3	5.2	6.8	6.5	5.8	7.3	5.5	4.1	5.3	8.4	7.3
	Min.	3.4	2.9	4.1	4.9	4.4	5.2	4.5	4.9	2.7	4.5	6.0	5.1
	Max.	10.9	5.1	7.7	8.1	8.9	6.2	10.2	6.4	6.4	5.8	10.1	10.0
Acetaldehyde	Ave.	0.7	0.6	0.8	0.8	0.8	0.7	1.0	0.7	0.5	0.7	1.0	0.8
	Min.	0.5	0.4	0.7	0.6	0.6	0.6	0.7	0.6	0.4	0.6	0.7	0.6
	Max.	1.2	0.6	1.1	0.9	1.0	0.7	1.3	0.8	0.8	0.7	1.1	1.1
CO canister	Ave.	1.7	1.5	1.0	2.9	1.7	2.7	0.6	0.6	0.5	0.8	3.1	2.5
	Min.	1.2	0.9	0.7	0.5	1.7	1.8	0.3	0.5	0.4	0.5	1.1	1.8
	Max.	2.1	2.6	1.6	7.0	1.8	4.5	0.8	0.6	0.7	1.1	6.2	3.2
MTBE	Ave.	2.8	1.3	1325.5	11.2	5.6	8.8	3129	2.9	1.3	2.6	12.2	8.7
	Min.	2.1	0.8	79.8	4.8	3.7	5.1	414.3	1.3	1.2	2.1	6.3	1.5
	Max.	3.8	1.7	4284.1	18.8	7.9	16.5	5767	5.4	1.4	2.9	23.7	20.1
Temp ˚C	Ave.	(23.7)	(24.5)	(28.2)	(28.3)	(22.5)	(24.5)	33.1	31.1	31.4	31.7	28.1	30.0
(in-cabin)	Min.	(22.9)	(23.5)	(26.0)	(24.0)	(21.3)	(23.3)	28.4	28.5	27.9	28.5	21.8	29.5
	Max.	(25.2)	(25.7)	30.9	(33.6)	(24.7)	(25.6)	35.0	33.4	33.6	36.5	37.1	30.4
RH, %	Ave.	(54.8)	(47.0)	(47.6)	(47.0)	(55.3)	(50.2)	53.6	58.3	58.7	58.0	48.8	67.5
(in-cabin)	Min.	(50.0)	(42.0)	(41.0)	(36.0)	(53.0)	(47.0)	47.0	41.0	48.0	40.0	41.0	65.0
	Max.	(62.0)	(51.0)	(58.0)	(57.0)	(57.0)	(57.0)	70.0	75.0	77.0	69.0	58.0	70.0

Note: Urban canyon for Houston: Louisiana , Clay, Walker, and Smith Streets *For 1,3-BD in Houston, one extreme value for ME3 and two for ME7 were invalidated.

ME1: In-cabin congested freeway; **ME2**: In-cabin urban canyon loop; **ME3**: In-cabin refueling; **ME4**: In-cabin underground garage; **ME5**: In-cabin toll plaza; **ME6**: In-cabin roadway tunnel; **ME7**: Out-of-cabin refueling; **ME8**:Out-of-cabin sidewalk; **ME9**: Out-of-cabin sidewalk/bus stop; **ME10**: Out-of-cabin surface parking; **ME11**: Out-of-cabin underground garage; **ME12**: Outside toll plaza; **ME13**: In-cabin trailing high-emitter vehicle

Table 1.3.1-2. Winter average, maximum, and minimum ME concentrations (ppbv) of BTEX, 1,3-BD, HCHO, CH3CHO, EtOH, MTBE, and CO (ppmv)

Atlanta (Conventional Fuel)

ME		ME1	ME2	ME3	ME4	ME5	ME7	ME8	ME9	ME10	ME11	ME12	ME13
Replicates		5	3	5	5	3	6	3	3	3	5	3	5
1,3-BD	Ave.	0.6	0.3	0.4	4.1	0.3	1.5	0.2	0.2	0.7	4.0	0.4	1.6
	Min.	0.3	0.0	0.1	1.7	0.2	0.2	0.1	0.1	0.3	1.0	0.3	0.9
	Max.	0.8	0.4	0.7	7.9	0.5	3.6	0.3	0.3	1.5	6.3	0.5	2.8
Benzene	Ave.	2.6	1.4	8.4	26.4	1.4	38.5	0.9	1.0	3.5	21.0	2.4	6.7
	Min.	1.9	0.3	1.6	6.1	1.1	10.0	0.7	0.6	1.3	3.2	1.6	3.5
	Max.	3.5	2.3	17.6	49.9	1.7	99.4	1.2	1.3	6.4	28.6	3.2	11.1
Toluene	Ave.	5.3	4.0	14.5	60.5	3.5	58.8	1.5	1.8	8.7	53.0	3.7	17.7
	Min.	3.7	0.8	4.0	14.5	2.2	23.3	1.0	1.2	2.8	7.1	2.2	9.1
	Max.	7.3	6.5	26.4	112.7	4.5	125.1	2.5	2.7	15.4	87.4	6.0	33.5
Ethylbenzene	Ave.	1.0	0.8	1.7	11.5	0.6	4.8	0.3	0.3	1.5	9.7	0.6	2.8
	Min.	0.7	0.1	0.5	2.5	0.5	2.7	0.2	0.2	0.5	1.4	0.4	1.5
	Max.	1.5	1.4	2.6	22.1	0.9	7.4	0.4	0.5	2.7	15.0	1.0	5.4
Xylene	Ave.	4.4	3.2	6.4	42.6	2.6	17.2	1.1	1.3	5.7	37.2	2.4	11.4
	Min.	3.0	0.4	2.2	9.7	2.0	10.2	0.8	0.9	2.0	5.4	1.5	6.0
	Max.	6.2	5.7	9.3	79.7	3.7	26.4	1.6	1.8	10.5	58.5	3.8	22.1
Formaldehyde	Ave.	6.2	8.6	21.9	19.6	4.6	3.4	2.6	2.0	5.0	11.4	3.4	8.4
	Min.	2.6	5.1	4.1	5.6	3.3	2.3	1.4	1.1	3.4	4.0	3.0	5.7
	Max.	8.0	12.4	89.1	28.1	6.0	5.0	4.1	3.1	6.2	15.7	3.7	10.4
Acetaldehyde	Ave.	2.8	2.9	5.4	8.2	2.0	2.0	1.7	1.5	2.3	6.8	2.5	4.3
	Min.	0.9	2.5	1.5	4.2	1.1	1.1	1.5	0.9	1.3	2.8	1.7	3.6
	Max.	5.6	3.5	17.4	12.0	3.1	2.6	2.1	1.9	2.9	9.8	3.0	5.2
CO canister	Ave.	2.6	1.5	0.8	17.7	1.2	1.2	0.8	0.9	1.9	13.2	2.4	5.7
	Min.	2.0	1.3	0.5	4.3	0.9	0.4	0.7	0.6	0.9	2.9	1.5	2.7
	Max.	3.2	1.8	1.4	36.1	1.5	2.2	1.0	1.1	3.9	21.9	2.8	9.0
Temp ˚C	Ave.	(21.3)	(24.6)	(17.9)	(21.1)	(22.8)	10.1	4.8	3.8	10.6	14.5	9.4	(22.2)
(in-cabin)	Min.	(15.2)	(23.1)	(15.0)	(14.0)	(20.6)	5.9	4.1	1.2	5.1	5.5	6.0	(17.9)
	Max.	(28.4)	(25.8)	(20.2)	(24.6)	(24.0)	16.7	5.5	5.7	14.2	19.4	15.3	(26.4)
RH, %	Ave.	(35.0)	(32.3)	(40.4)	(41.8)	(31.0)	54.8	58.0	63.0	52.0	47.4	55.7	(37.2)
(in-cabin)	Min.	(21.0)	(28.0)	(28.0)	(30.0)	(27.0)	41.0	45.0	45.0	38.0	26.0	22.0	(23.0)
	Max.	(48.0)	(36.0)	(56.0)	(47.0)	(34.0)	81.0	71.0	73.0	63.0	65.0	77.0	(50.0)

ME1: In-cabin congested freeway; **ME2**: In-cabin urban canyon loop; **ME3**: In-cabin refueling; **ME4**: In-cabin underground garage; **ME5**: In-cabin toll plaza; **ME6**: In-cabin roadway tunnel; **ME7**: Out-of-cabin refueling; **ME8**:Out-of-cabin sidewalk; **ME9**: Out-of-cabin sidewalk/bus stop; **ME10**: Out-of-cabin surface parking; **ME11**: Out-of-cabin underground garage; **ME12**: Outside toll plaza; **ME13**: In-cabin trailing high-emitter vehicle

Chicago (Oxygenated Fuel - Ethanol)

		ME1	ME2	ME3	ME4	ME5	ME6	ME7	ME8	ME9	ME10	ME11	ME12
1,3-BD	Ave.	0.6	0.4	2.8	4.4	0.2	0.5	0.7	0.3	0.3	0.5	2.4	0.3
	Min.	0.2	0.2	0.0	1.6	0.1	0.4	0.2	0.2	0.2	0.1	1.3	0.2
	Max.	1.2	0.6	13.2	7.7	0.2	0.9	1.2	0.5	0.3	0.8	3.2	0.4
Benzene	Ave.	1.2	1.3	5.2	16.4	0.7	2.3	20.4	1.0	1.0	1.8	12.9	1.2
	Min.	0.5	1.0	0.2	5.7	0.7	1.4	1.4	0.9	0.9	0.6	5.6	0.9
	Max.	2.2	1.6	12.9	24.2	0.8	4.8	39.1	1.2	1.1	2.9	20.7	1.9
Toluene	Ave.	1.8	2.5	4.6	29.0	1.1	3.1	13.8	1.4	1.2	2.9	22.7	1.3
	Min.	0.5	2.0	1.2	10.8	1.0	1.8	2.1	1.2	1.1	0.9	12.3	0.9
	Max.	3.1	2.9	8.9	39.1	1.3	6.5	26.6	1.8	1.4	4.9	36.4	2.0
Ethylbenzene	Ave.	0.5	0.4	0.6	5.5	0.2	0.6	1.4	0.3	0.3	0.6	4.4	0.3
	Min.	0.2	0.3	0.0	1.9	0.1	0.4	0.5	0.2	0.2	0.2	2.3	0.2
	Max.	0.8	0.5	1.4	7.6	0.2	1.4	3.0	0.4	0.3	1.0	7.4	0.4
Xylene	Ave.	1.9	1.5	2.8	22.7	0.8	2.5	6.9	1.1	0.9	2.3	18.3	1.1
	Min.	0.9	1.2	0.2	7.5	0.7	1.4	1.9	0.8	0.9	0.7	10.3	0.8
	Max.	3.6	1.8	6.0	31.2	0.9	5.2	15.7	1.4	1.0	3.8	29.5	1.8
Formaldehyde	Ave.	7.2	4.6	4.3	13.9	2.8	5.3	3.2	2.9	3.5	4.4	9.1	3.0
	Min.	2.1	3.2	2.3	7.2	1.8	2.9	1.8	2.5	2.8	3.3	2.9	2.5
	Max.	21.5	6.0	7.7	18.2	3.5	7.8	4.3	3.2	4.2	5.9	15.3	3.6
Acetaldehyde	Ave.	5.0	3.1	3.6	12.7	2.3	3.8	2.8	2.1	2.5	2.5	7.6	2.2
	Min.	1.1	2.4	2.4	5.9	1.4	1.5	2.0	1.6	2.1	1.4	1.6	2.0
	Max.	16.8	4.5	7.4	17.7	2.9	6.9	3.8	2.7	3.1	3.8	12.8	2.6
CO canister	Ave.	1.5	1.0	0.4	12.0	0.9	2.2	0.7	0.9	0.9	1.7	11.0	1.7
	Min.	1.1	0.4	0.4	4.5	0.8	1.7	0.2	0.7	0.8	0.6	3.8	1.3
	Max.	2.1	1.4	0.5	18.4	1.0	3.4	1.8	1.1	1.0	2.7	16.8	2.0
EtOH	Ave.	6.8	2.1	5.1	1.4	4.3	1.6	2.2	1.8	4.0	3.3	3.7	0.9
	Min.	1.6	0.0	2.8	0.1	1.4	0.0	0.0	0.0	0.0	1.3	1.9	0.0
	Max.	12.3	3.1	9.8	2.6	7.9	2.7	4.8	3.9	8.0	5.9	6.0	2.3
Temp ˚C	Ave.	(21.5)	(22.8)	(17.3)	(21.6)	(22.6)	(20.9)	1.6	4.9	6.5	6.4	(17.0)	1.9
(in-cabin)	Min.	(18.1)	(21.3)	(11.2)	(15.9)	(21.6)	(16.3)	-3.3	1.3	2.1	4.1	(13.6)	0.0
	Max.	(30.6)	(24.8)	(19.8)	(24.7)	(23.5)	(24.7)	6.6	9.5	12.3	8.7	(22.1)	4.6
RH, %	Ave.	(19.2)	(23.7)	(22.0)	(37.5)	(17.7)	(24.8)	44.7	46.3	42.7	37.0	(41.4)	53.0
(in-cabin)	Min.	(9.0)	(21.0)	(13.0)	(25.0)	(13.0)	(14.0)	32.0	32.0	27.0	32.0	(29.0)	25.0
	Max.	(25.0)	(25.0)	(32.0)	(60.0)	(21.0)	(41.0)	62.0	62.0	60.0	42.0	(61.0)	77.0

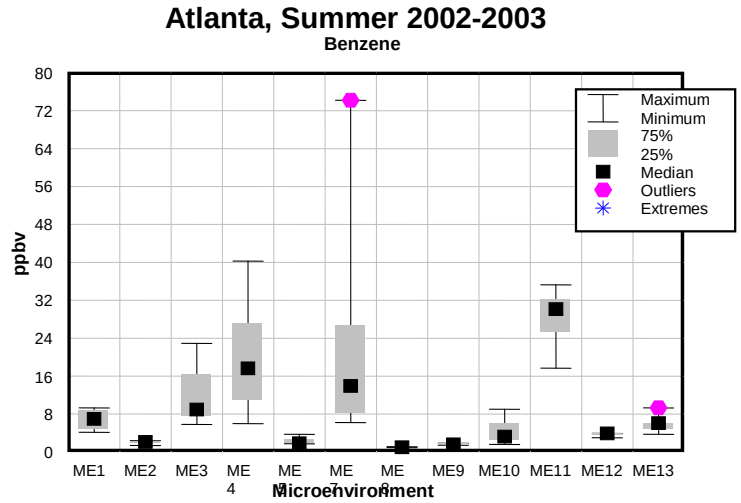
ME1: In-cabin congested freeway; **ME2**: In-cabin urban canyon loop; **ME3**: In-cabin refueling; **ME4**: In-cabin underground garage; **ME5**: In-cabin toll plaza; **ME6**: In-cabin roadway tunnel; **ME7**: Out-of-cabin refueling; **ME8**:Out-of-cabin sidewalk; **ME9**: Out-of-cabin sidewalk/bus stop; **ME10**: Out-of-cabin surface parking; **ME11**: Out-of-cabin underground garage; **ME12**: Outside toll plaza; **ME13**: In-cabin trailing high-emitter vehicle

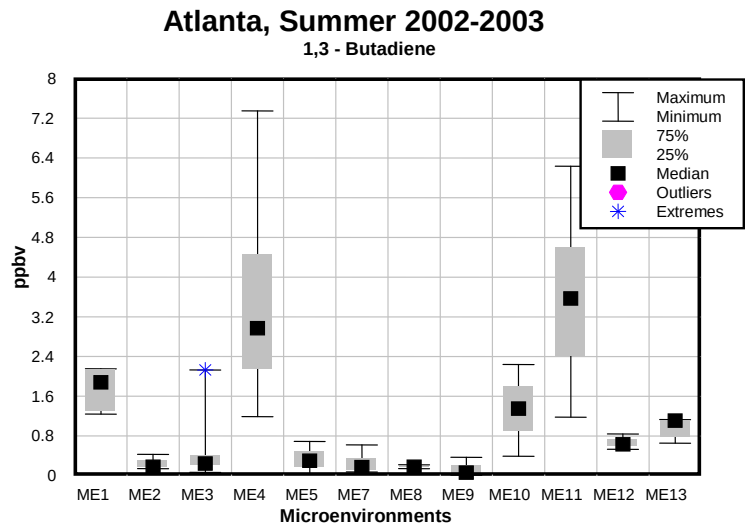
Houston (Oxygenated Fuel - MTBE)

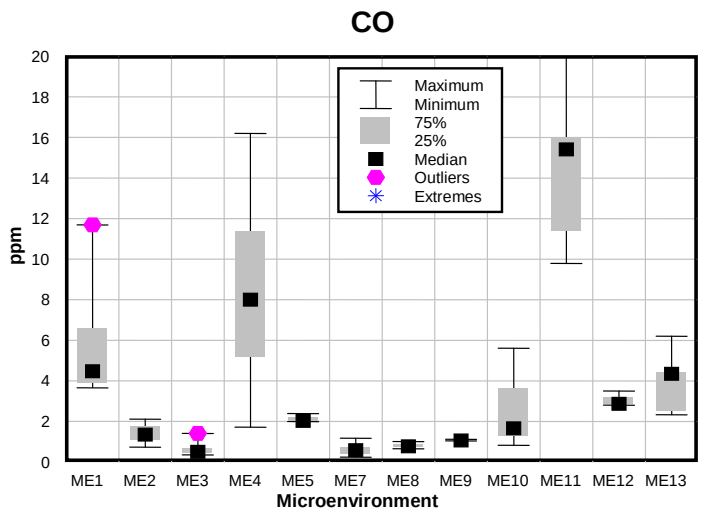
		ME1	ME2	ME3	ME4	ME5	ME6	ME7	ME8	ME9	ME10	ME11	ME12
1,3-BD	Ave.	0.4	1.2	1.8*	3.8	0.5	1.1	1.9*	0.1	0.2	1.7	2.7	0.8
	Min.	0.3	0.4	0.4	0.4	0.4	0.1	1.9*	0.1	0.1	0.2	0.4	0.5
	Max.	0.6	2.7	3.6	5.7	0.6	2.3	1.9*	0.2	0.2	4.3	4.3	1.3
Benzene	Ave.	1.4	3.7	17.7	10.6	1.7	2.7	55.0	0.5	0.6	5.0	7.8	2.5
	Min.	1.1	1.4	2.3	1.6	1.4	0.7	7.7	0.5	0.4	1.5	1.4	1.8
	Max.	2.0	8.2	56.6	14.5	2.1	4.2	97.7	0.7	0.8	11.9	13.7	3.8
Toluene	Ave.	3.0	6.5	25.6	21.8	3.6	4.6	64.3	0.8	1.1	10.5	17.3	4.2
	Min.	2.3	2.9	4.2	4.2	3.2	1.6	10.9	0.7	0.8	3.5	3.1	2.7
	Max.	5.2	13.4	69.7	30.9	3.8	6.7	106.0	1.0	1.4	21.7	31.4	6.3
Ethylbenzene	Ave.	0.7	1.4	2.4	4.3	0.8	0.9	4.5	0.2	0.3	1.9	3.3	0.8
	Min.	0.5	0.7	0.7	1.1	0.7	0.4	1.8	0.2	0.2	0.7	0.7	0.5
	Max.	1.1	2.6	4.4	5.9	0.8	1.4	8.0	0.2	0.3	4.3	5.8	1.2
Xylene	Ave.	3.4	6.3	10.9	17.6	3.5	4.4	18.7	0.8	1.1	8.1	13.9	3.6
	Min.	2.5	3.3	3.6	5.5	3.5	1.5	4.4	0.7	0.7	3.4	3.7	2.1
	Max.	5.9	11.5	18.4	24.7	3.6	6.9	35.2	1.0	1.4	17.5	25.0	6.3
Formaldehyde	Ave.	4.5	8.2	7.1	10.5	3.8	7.6	5.7	2.1	2.5	4.0	5.7	5.0
	Min.	3.0	4.7	4.6	7.9	2.7	5.4	3.5	1.9	2.0	1.2	2.9	4.0
	Max.	5.1	12.6	8.4	12.1	4.5	8.8	10.6	2.3	3.1	7.6	8.6	6.1
Acetaldehyde	Ave.	1.9	4.3	6.5	5.3	1.9	4.4	5.3	1.7	1.7	4.5	3.4	2.0
	Min.	1.2	2.5	3.5	4.7	1.5	2.6	3.2	1.4	1.2	3.4	1.0	1.8
	Max.	2.4	7.0	9.2	5.9	2.2	6.1	10.0	1.9	1.9	5.7	4.9	2.4
CO canister	Ave.	1.4	3.7	1.2	7.8	1.8	2.9	1.0	0.4	0.5	3.4	6.0	2.7
	Min.	0.9	1.4	0.5	1.1	1.6	0.8	0.3	0.3	0.4	0.7	1.1	1.7
	Max.	1.6	6.9	2.7	12.5	2.1	5.5	2.6	0.5	0.7	8.4	9.8	4.5
MTBE	Ave.	3.9	10.2	890.6	25.4	4.2	7.3	2568.9	0.5	0.7	15.1	26.0	6.7
	Min.	1.4	2.6	23.3	1.8	3.2	3.3	347.8	0.5	0.6	6.5	2.7	2.6
	Max.	8.1	25.3	3135.3	68.1	4.8	10.4	5629.9	0.6	0.8	20.9	63.6	13.2
Temp ˚C	Ave.	(22.3)	(22.9)	(21.6)	(22.6)	(21.0)	(22.4)	15.7	9.8	11.4	17.1	15.5	14.9
(in-cabin)	Min.	(18.0)	(20.4)	(19.3)	(19.9)	(19.1)	(19.9)	10.9	7.2	7.9	13.4	10.3	7.9
	Max.	(26.5)	(24.3)	(23.4)	(25.2)	(22.2)	(24.8)	20.9	12.2	14.7	21.0	18.6	20.2
RH, %	Ave.	(41.2)	(36.7)	(52.0)	(54.2)	(49.3)	(46.0)	67.0	61.0	55.3	63.0	69.6	77.7
(in-cabin)	Min.	(29.0)	(33.0)	(37.0)	(36.0)	(43.0)	(34.0)	55.0	53.0	46.0	48.0	43.0	70.0
	Max.	(58.0)	(42.0)	(61.0)	(69.0)	(56.0)	(54.0)	77.0	71.0	67.0	76.0	87.0	83.0

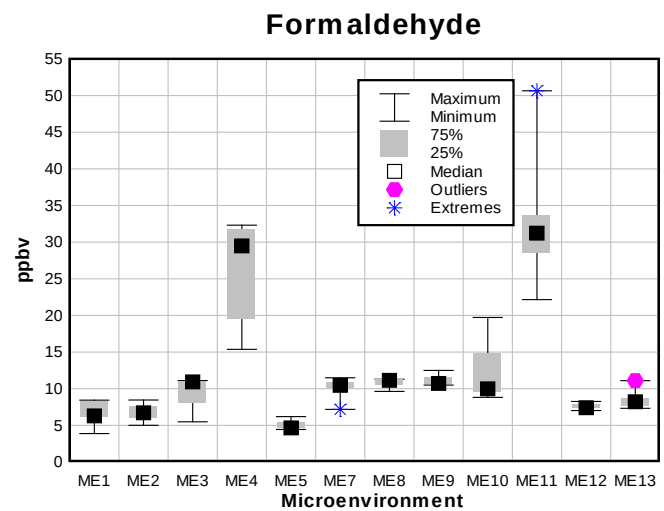
*Note: For 1,3-BD in Houston, one extreme value for ME3 and four for ME7 were invalidated

ME1: In-cabin congested freeway; **ME2**: In-cabin urban canyon loop; **ME3**: In-cabin refueling; **ME4**: In-cabin underground garage; **ME5**: In-cabin toll plaza; **ME6**: In-cabin roadway tunnel; **ME7**: Out-of-cabin refueling; **ME8**:Out-of-cabin sidewalk; **ME9**: Out-of-cabin sidewalk/bus stop; **ME10**: Out-of-cabin surface parking; **ME11**: Out-of-cabin underground garage; **ME12**: Outside toll plaza; **ME13**: In-cabin trailing high-emitter vehicle









ME1: In-cabin congested freeway; **ME2**: In-cabin urban canyon; **ME3**: In-cabin refueling; **ME4**: In-cabin underground garage; **ME5**: In-cabin toll plaza; **ME6**: In-cabin roadway tunnel; **ME7**: Out-of-cabin refueling; **ME8**:Out-of-cabin sidewalk; **ME9**: Out-of-cabin sidewalk/bus stop; **ME10**: Out-of-cabin surface parking; **ME11**: Out-of-cabin underground garage; **ME12**: Outside toll plaza; **ME13**: In-cabin trailing high-emitter vehicle

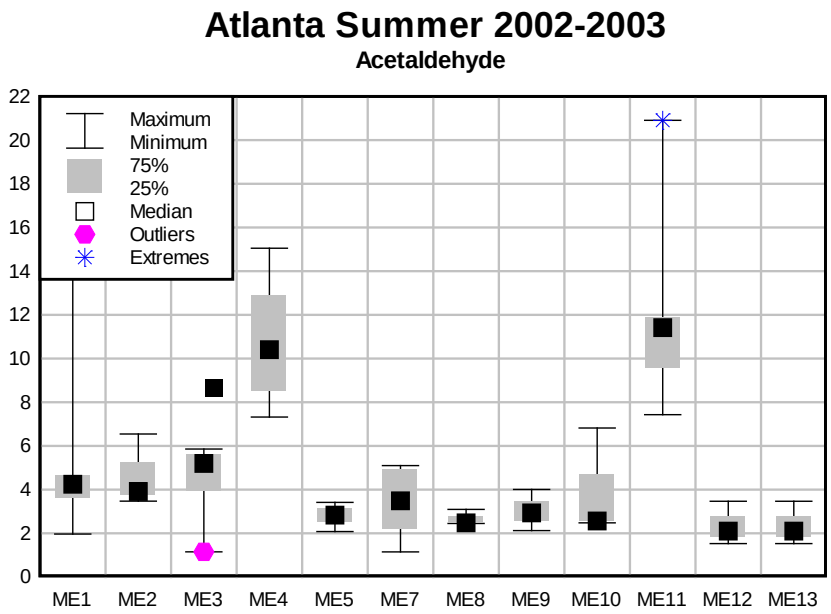
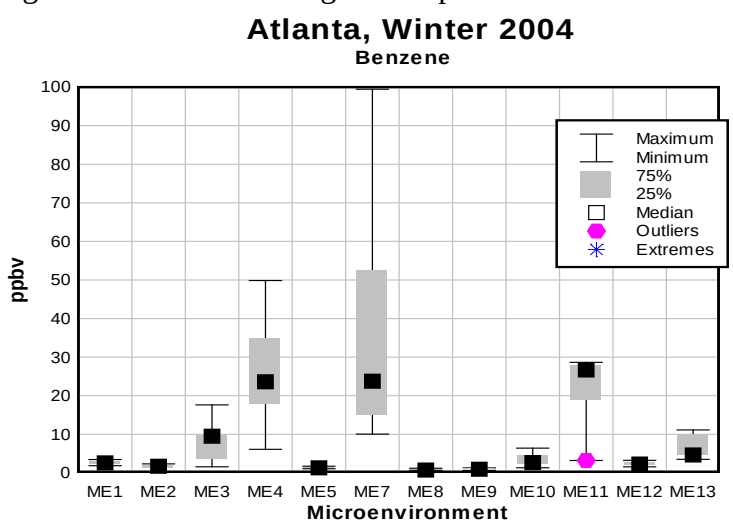
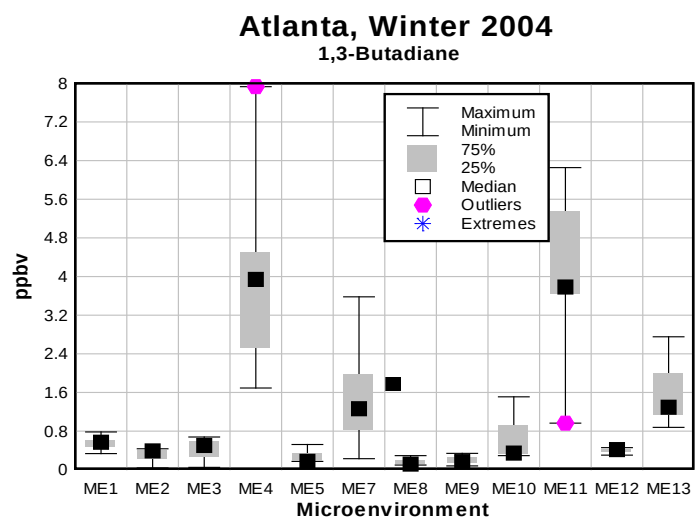
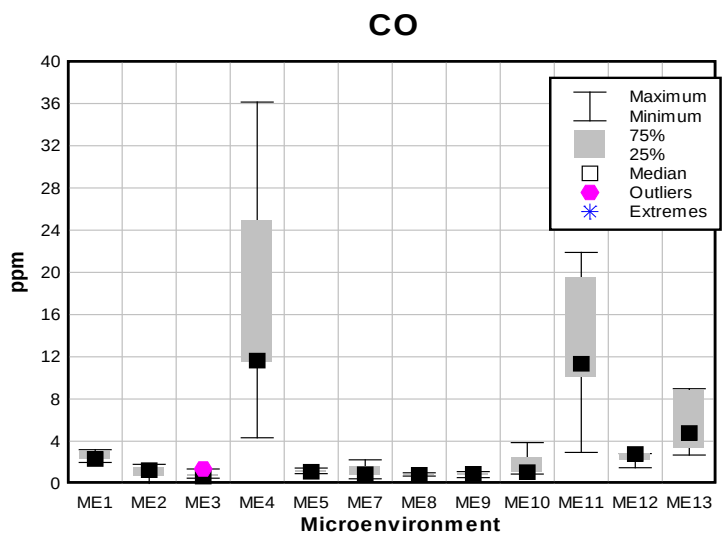


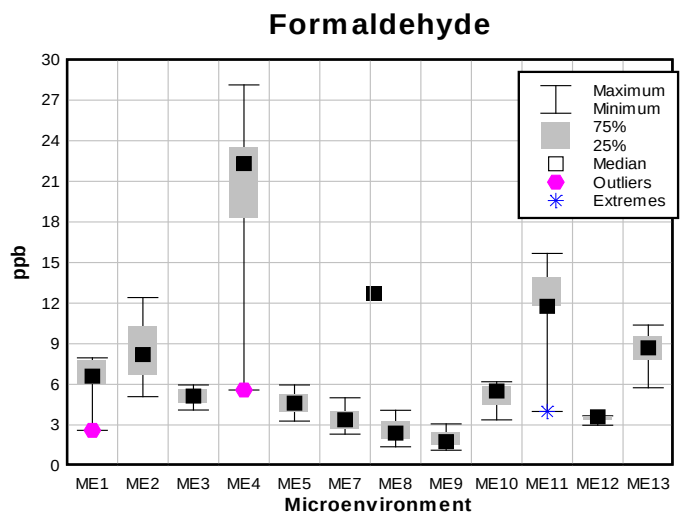
Figure 1.3.1-1. Time-integrated exposure levels in different MEs in Atlanta, Summer 2002 and 2003

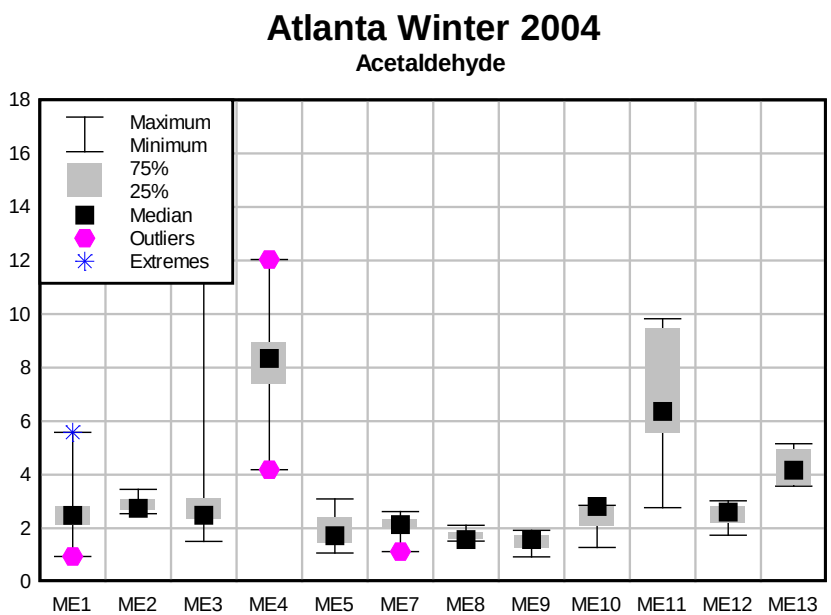




ME1: In-cabin congested freeway; **ME2**: In-cabin urban canyon; **ME3**: In-cabin refueling; **ME4**: In-cabin underground garage; **ME5**: In-cabin toll plaza; **ME6**: In-cabin roadway tunnel; **ME7**: Out-of-cabin refueling; **ME8**:Out-of-cabin sidewalk; **ME9**: Out-of-cabin sidewalk/bus stop; **ME10**: Out-of-cabin surface parking; **ME11**: Out-of-cabin underground garage; **ME12**: Outside toll plaza; **ME13**: In-cabin trailing high-emitter vehicle

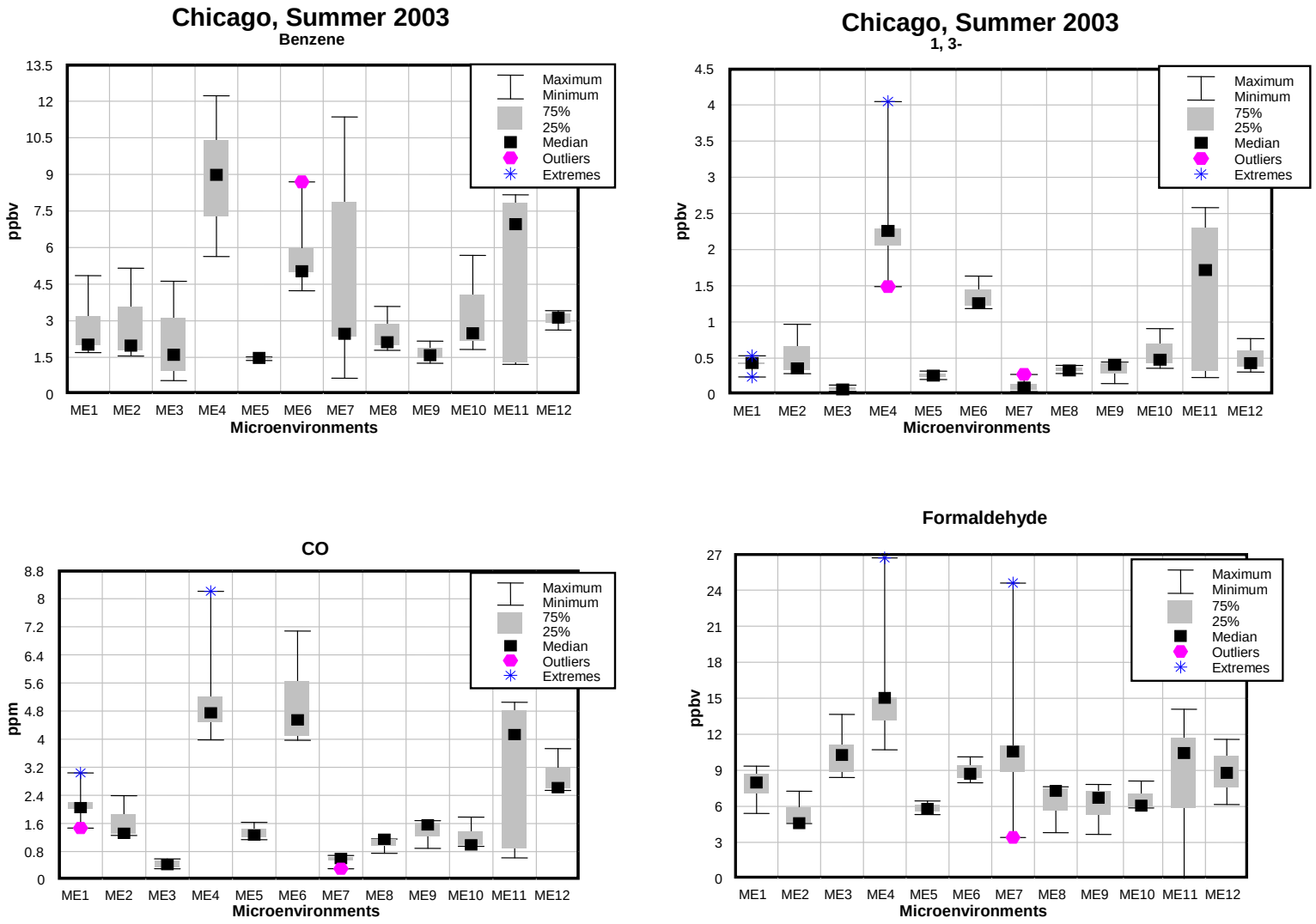






ME1: In-cabin congested freeway; **ME2**: In-cabin urban canyon; **ME3**: In-cabin refueling; **ME4**: In-cabin underground garage; **ME5**: In-cabin toll plaza; **ME6**: In-cabin roadway tunnel; **ME7**: Out-of-cabin refueling; **ME8**:Out-of-cabin sidewalk; **ME9**: Out-of-cabin sidewalk/bus stop; **ME10**: Out-of-cabin surface parking; **ME11**: Out-of-cabin underground garage; **ME12**: Outside toll plaza; **ME13**: In-cabin trailing high-emitter vehicle

Figure 1.3.1-2. Time-integrated exposure levels in different MEs in Atlanta, Winter 2004



ME1: In-cabin congested freeway; **ME2**: In-cabin urban canyon; **ME3**: In-cabin refueling; **ME4**: In-cabin underground garage; **ME5**: In-cabin toll plaza; **ME6**: In-cabin roadway tunnel; **ME7**: Out-of-cabin refueling; **ME8**:Out-of-cabin sidewalk; **ME9**: Out-of-cabin sidewalk/bus stop; **ME10**: Out-of-cabin surface parking; **ME11**: Out-of-cabin underground garage; **ME12**: Outside toll plaza; **ME13**: In-cabin trailing high-emitter vehicle

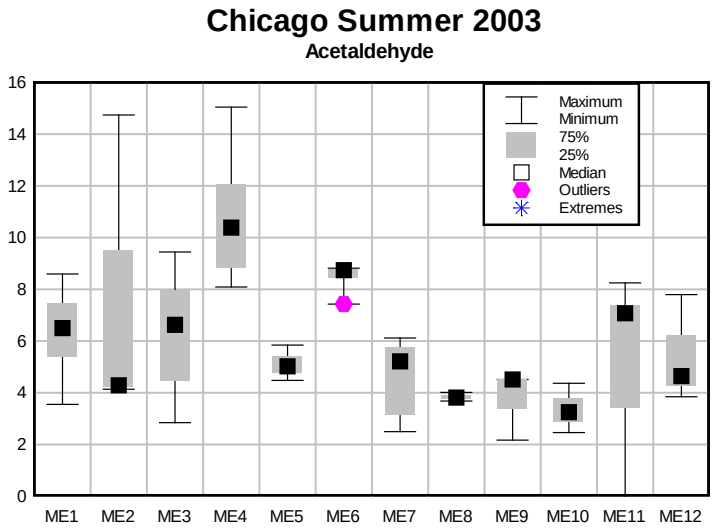
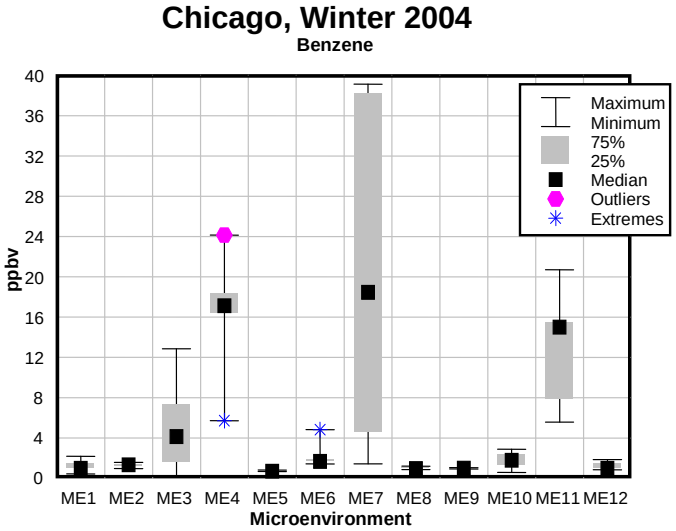
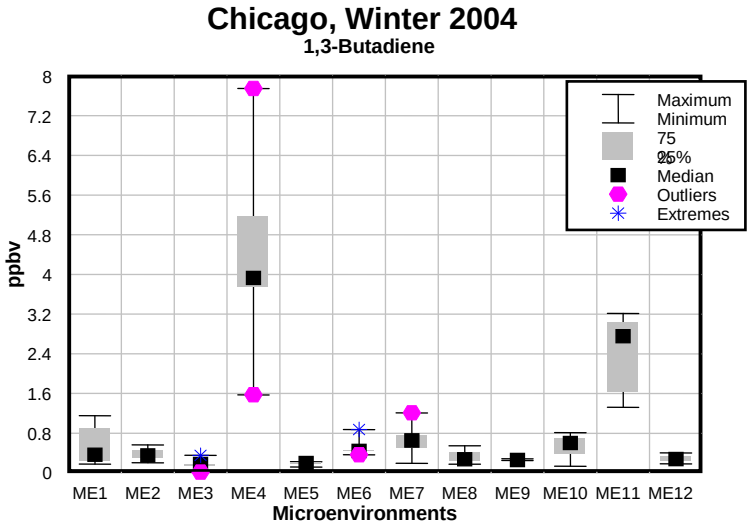


Figure 1.3.1-3. Time-integrated exposure levels in different MEs in Chicago, Summer 2003





ME1: In-cabin congested freeway; **ME2**: In-cabin urban canyon; **ME3**: In-cabin refueling; **ME4**: In-cabin underground garage; **ME5**: In-cabin toll plaza; **ME6**: In-cabin roadway tunnel; **ME7**: Out-of-cabin refueling; **ME8**:Out-of-cabin sidewalk; **ME9**: Out-of-cabin sidewalk/bus stop; **ME10**: Out-of-cabin surface parking; **ME11**: Out-of-cabin underground garage; **ME12**: Outside toll plaza; **ME13**: In-cabin trailing high-emitter vehicle

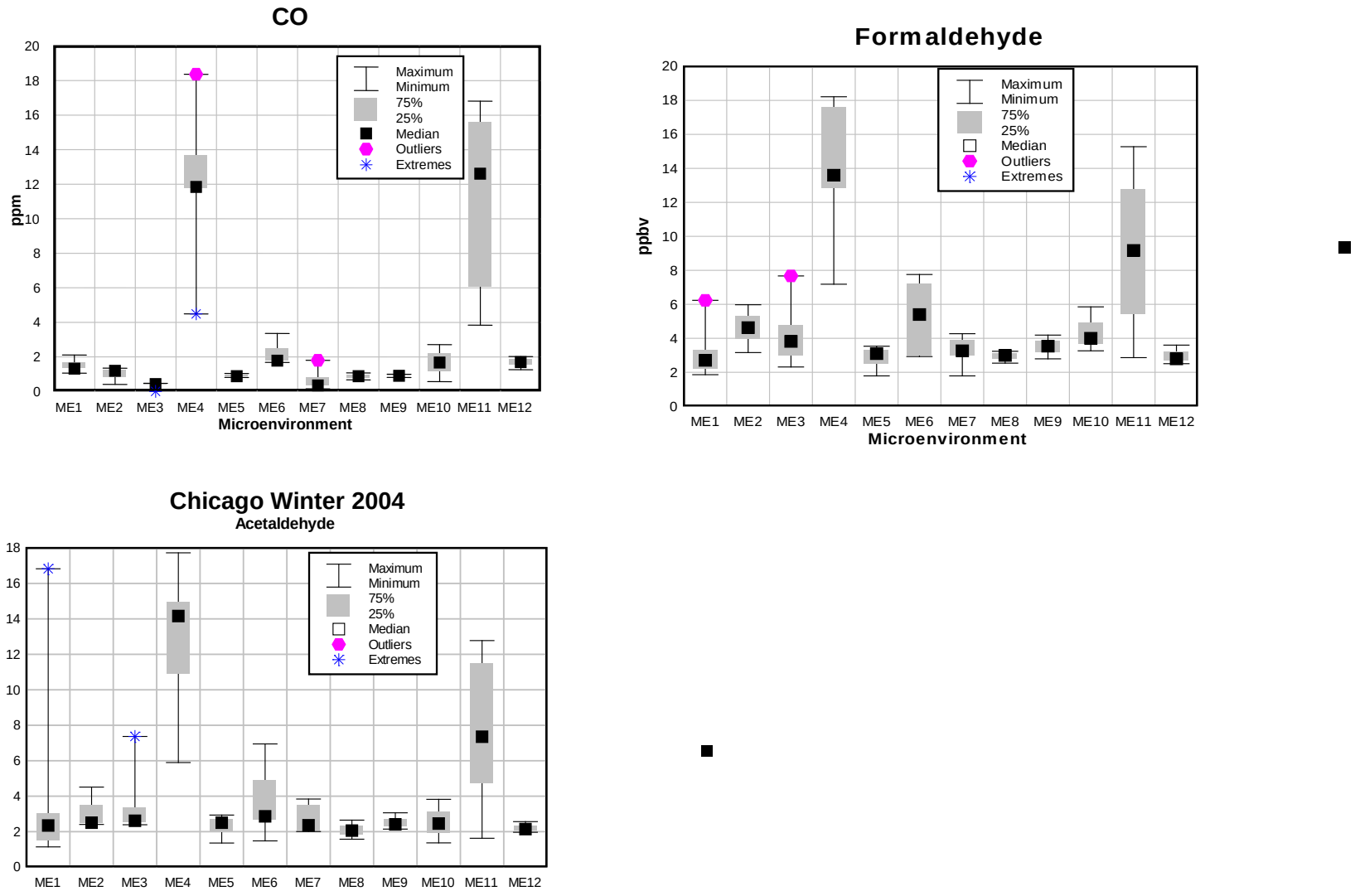
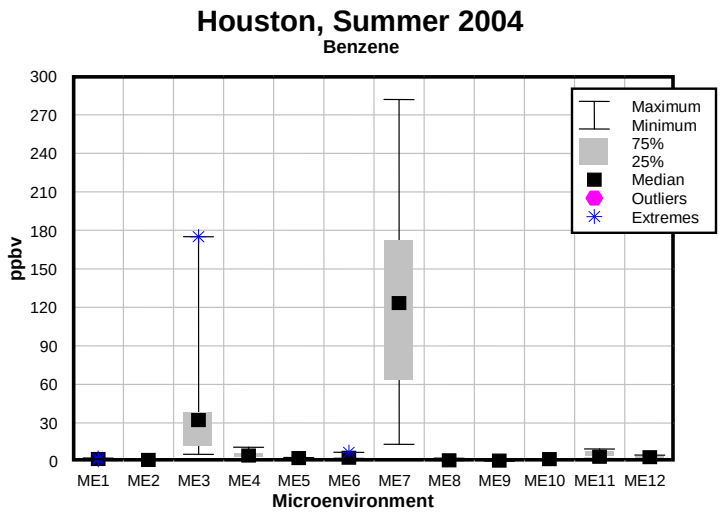
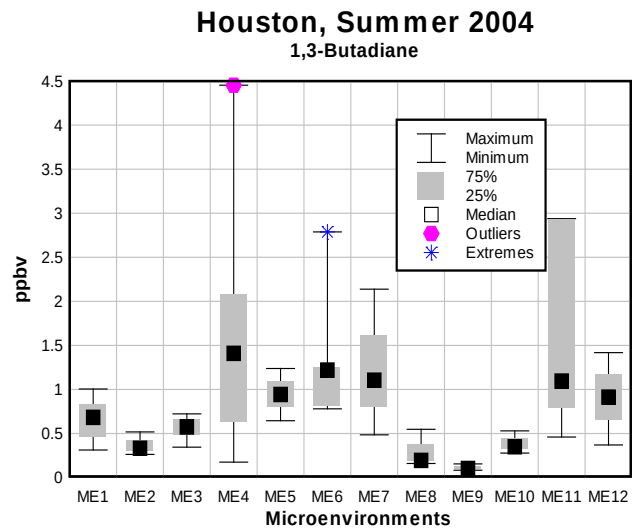
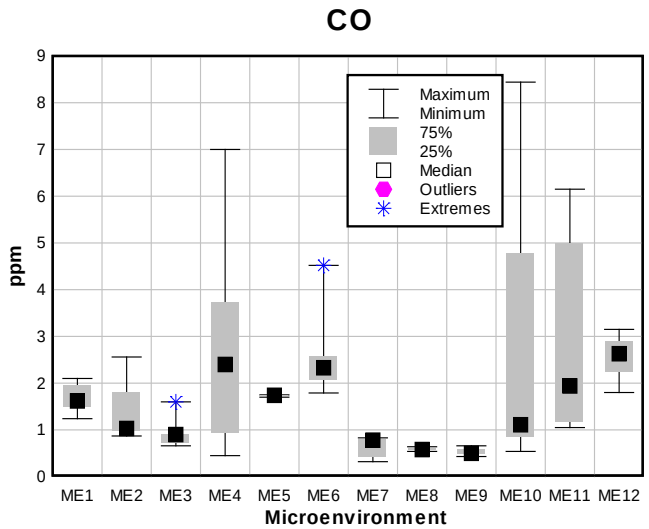


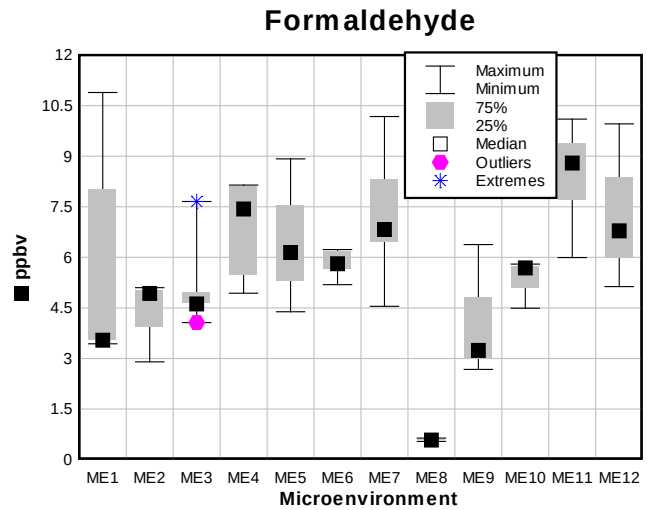
Figure 1.3.1-4. Time-integrated exposure levels in different MEs in Chicago, Winter 2004

ME1: In-cabin congested freeway; **ME2**: In-cabin urban canyon; **ME3**: In-cabin refueling; **ME4**: In-cabin underground garage; **ME5**: In-cabin toll plaza; **ME6**: In-cabin roadway tunnel; **ME7**: Out-of-cabin refueling; **ME8**:Out-of-cabin sidewalk; **ME9**: Out-of-cabin sidewalk/bus stop; **ME10**: Out-of-cabin surface parking; **ME11**: Out-of-cabin underground garage; **ME12**: Outside toll plaza; **ME13**: In-cabin trailing high-emitter vehicle









ME1: In-cabin congested freeway; **ME2**: In-cabin urban canyon; **ME3**: In-cabin refueling; **ME4**: In-cabin underground garage; **ME5**: In-cabin toll plaza; **ME6**: In-cabin roadway tunnel; **ME7**: Out-of-cabin refueling; **ME8**:Out-of-cabin sidewalk; **ME9**: Out-of-cabin sidewalk/bus stop; **ME10**: Out-of-cabin surface parking; **ME11**: Out-of-cabin underground garage; **ME12**: Outside toll plaza; **ME13**: In-cabin trailing high-emitter vehicle

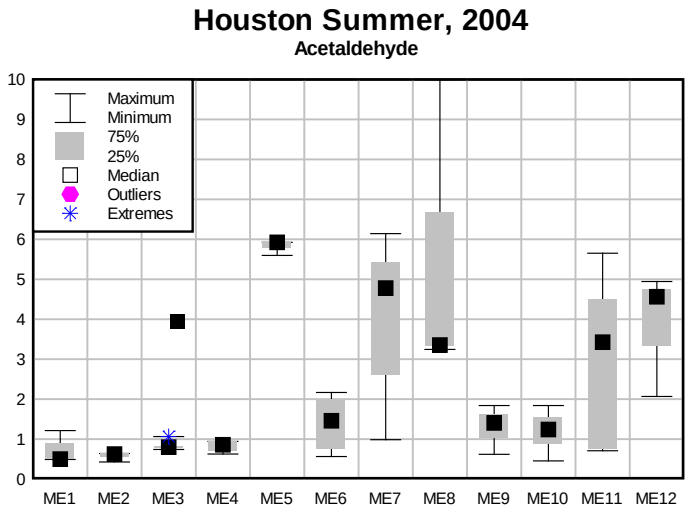
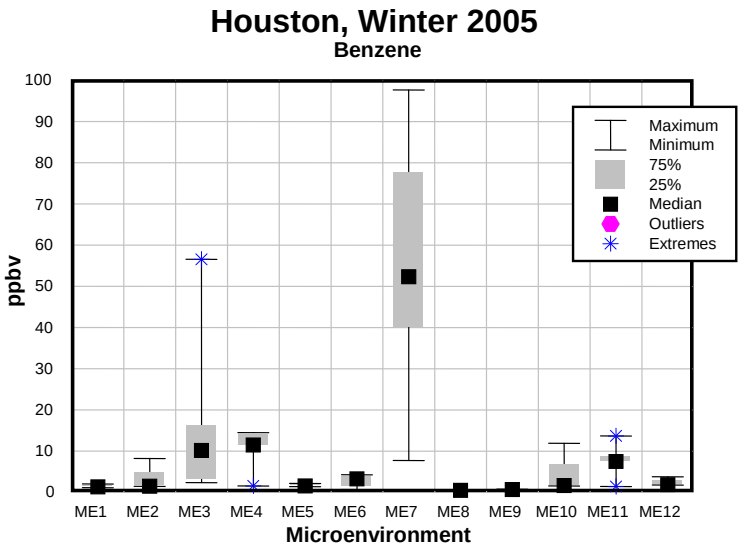
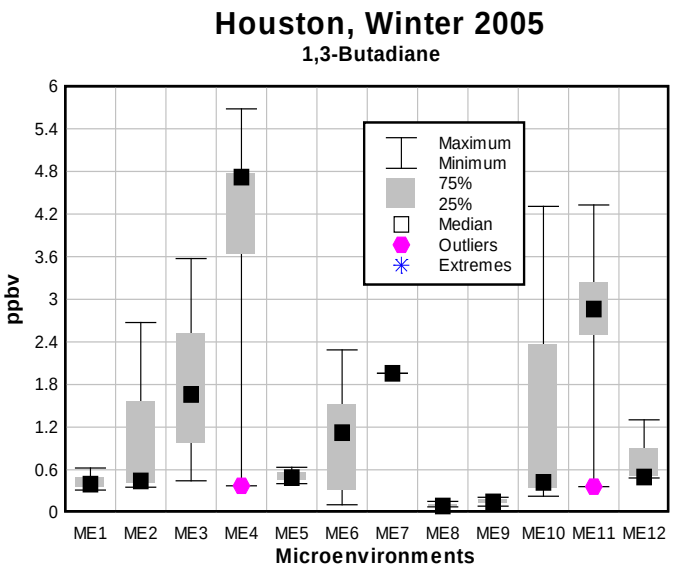


Figure 1.3.1-5. Time-integrated exposure levels in different MEs in Houston, Summer 2004





ME1: In-cabin congested freeway; **ME2**: In-cabin urban canyon; **ME3**: In-cabin refueling; **ME4**: In-cabin underground garage; **ME5**: In-cabin toll plaza; **ME6**: In-cabin roadway tunnel; **ME7**: Out-of-cabin refueling; **ME8**:Out-of-cabin sidewalk; **ME9**: Out-of-cabin sidewalk/bus stop; **ME10**: Out-of-cabin surface parking; **ME11**: Out-of-cabin underground garage; **ME12**: Outside toll plaza; **ME13**: In-cabin trailing high-emitter vehicle

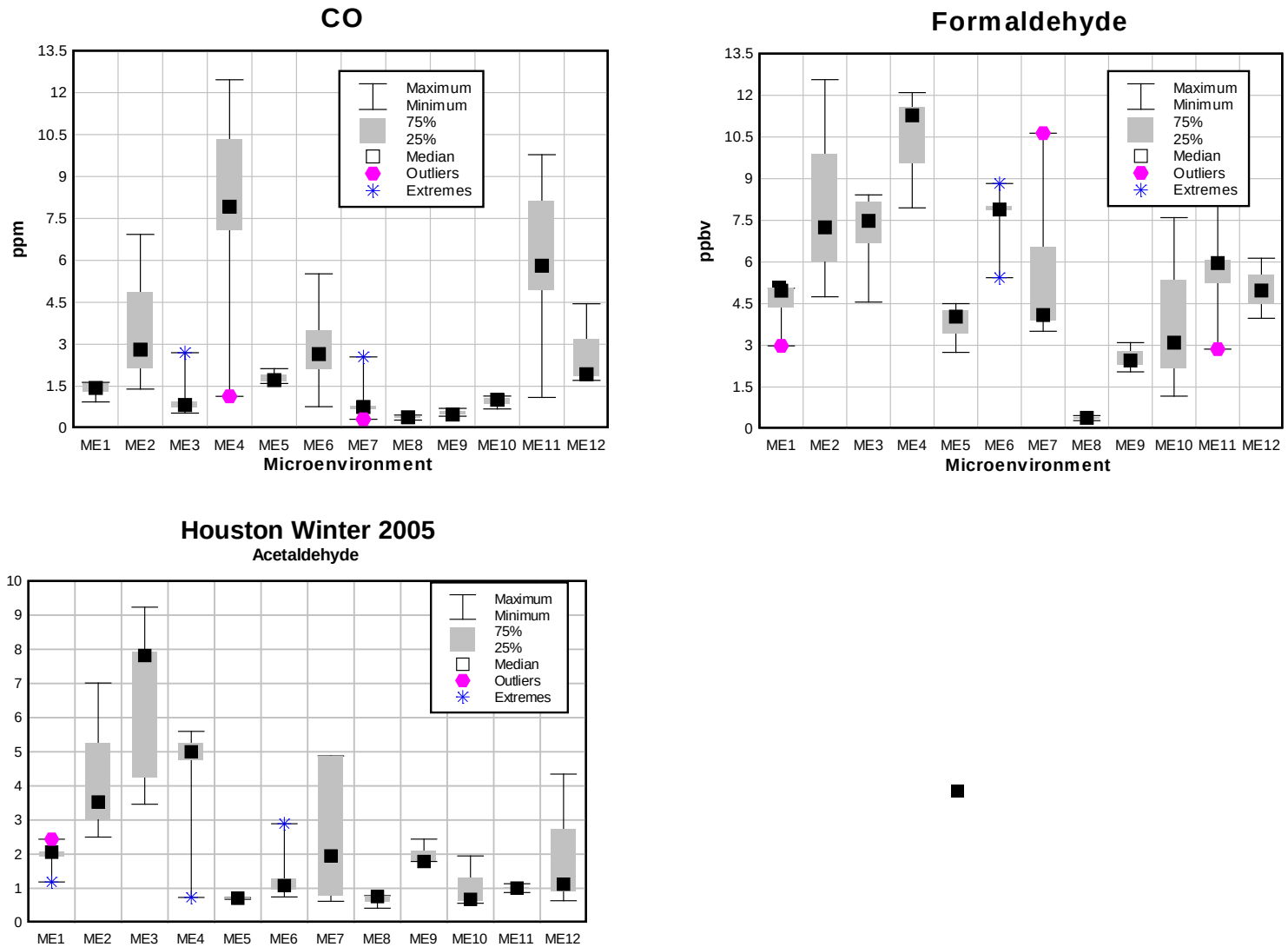


Figure 1.3.1-6. Time-integrated exposure levels in different MEs in Houston, Winter 2005

ME1: In-cabin congested freeway; **ME2**: In-cabin urban canyon; **ME3**: In-cabin refueling; **ME4**: In-cabin underground garage; **ME5**: In-cabin toll plaza; **ME6**: In-cabin roadway tunnel; **ME7**: Out-of-cabin refueling; **ME8**:Out-of-cabin sidewalk; **ME9**: Out-of-cabin sidewalk/bus stop; **ME10**: Out-of-cabin surface parking; **ME11**: Out-of-cabin underground garage; **ME12**: Outside toll plaza; **ME13**: In-cabin trailing high-emitter vehicle

1.3.2 Distribution of exposures within MEs in each city (1-minute time series)

The study protocol (Appendix A) specifies a sampling period of 20 (ME3/ME7) to 40 minutes beginning at the top of the hour to correlate with the local air quality monitoring network sampling periods. Because large variations are expected within these time frames in exposures for most MEs, the protocol includes continuous measurements of target species with time resolutions of about a minute. The supplemental Kore MS200 MS (deployed for BTEX) and Alpha Omega HCHO analyzer used to measure these species at 1-minute resolutions directly had not been earlier proven under such field conditions and only worked well intermittently. Furthermore, there were no acceptable continuous methods for 1,3-BD, MTBE, EtOH, CH_3CHO, or non-methane VOCs (NMVOC) that could be used in portable modes of operation with the necessary sensitivity. Accordingly, our sampling strategy consisted of a three-tiered approach classified as reference, surrogate, and confirmatory measurements. The base set or reference (R) measurements consist of three well-established time-integrated methods (canisters, DNPH, and solid adsorbent cartridges) as described in Section 1.2.2. These three methods together measure all species of interest over the 20-40 minute sampling periods within each ME and had excellent data capture rates. Although the integrated methods do not characterize short-term peak exposures in MEs with highly varying exposure levels, they provide a basis for quantifying and deriving correlations between the integrated values and continuous surrogate (S) measures, such as the CO and PID NMVOC monitors, in order to reconstruct short-term time series. For example, data for BTEX, and 1, 3-BD from the canister measurements can be used to normalize continuous CO and NMVOC traces taken over the same periods to construct component time series in exhaust-dominated environments. In a similar manner, the time series of HCHO values can be reconstructed from the correlation of the integrated DNPH samples with continuous CO measures.

Tables 1.3.2-1A and 1.3.2-1B list correlation coefficients (R^2), slopes, P-values and performance statistic for correlations of benzene, 1,3-BD, HCHO, and CO measured from canisters with NMVOC PID and continuous CO, measured by NDIR, for all ME with exception of ME3 and ME7, and for ME3 and ME7 only, respectively. It can be seen from Table 1.3.2-1A that 1,3-BD correlates with CO somewhat better than with NMVOC so continuous CO values were used for reconstructing 1-minute time series for 1,3-BD for all MEs with exception of refueling experiments (ME3 and ME7). However, for refueling MEs (Table1.3.2-1B), the correlations are worse, although the correlations of benzene with NMVOC are still statistically significant for all three cities. The correlations of 1,3-BD with NMVOC PID and CO_NDIR are not statistically significant, since neither 1,3-BD, nor CO is abundant in evaporative emissions. Thus, the calculation of 1-min time series for 1,3-BD in ME3 and ME7 is not valid for evaporative gasoline exposure. However, these species are often measured at some gas stations, since they originate from exhaust emissions of higher-emitting vehicles. In addition, HCHO does not correlate very well with CO probably due to the photochemical production of this compound in outdoor MEs.

The reconstructed 1-minute peak exposures were calculated based on the method used in the Atlanta Summer 2002 and Atlanta and Chicago Summer 2003 (Zielinska et al, 2003b, 2004b) reports. The NMVOC PID time series was used to reconstruct benzene values (the remaining TEX species follow the benzene time series) and the CO time series was used to reconstruct HCHO and 1,3-BD values. No CO and NMVOC data were used where the average CO or

NMVOC was below the approximate detection limit of the instruments (0.5 ppmv and 25 ppbv, respectively). In each case the approach was the same. The mean value of the compound to be reconstructed was multiplied by the ratio of the surrogate mean to the instantaneous reading. For example, to produce the 1st minute value for benzene, the mean benzene canister value was multiplied by the 1st minute NMVOC reading divided by the mean NMVOC reading. For HCHO and 1,3-BD, the NDIR CO value was used for all cases where it was available and valid.

A summary of the reconstructed data is presented in Tables 1.3.2-2 and 1.3.2-3 for benzene, 1,3-BD and HCHO (the complete data set is submitted in electronic form) for summer and winter, respectively. The average maximum and minimum values for each ME in each city and season are shown. The reconstructed time series are graphically presented in Figure 1.3.2-1 through 1.3.2-3 for selected MEs to illustrate the variability of exposure.

For in-cabin exposures in Figure 1.3.2-1 and upper part of Figure 1.3.2-2, the first 20 minutes of measurement was carried out under high ventilation conditions (i.e. window open, air recirculation off), whereas for the remaining 20 minutes at low ventilation (i.e. window closed, air conditioning or heating on, air recirculation on). As can be seen, the second 20 minutes of measurement are less variable. In addition, the concentration of benzene is rising steadily for this latter sampling period, reflecting the rising NMVOC signal, probably due to accumulation of outgasing emissions from vehicle cabin material and the breath of people present in the vehicle cabin.

For refueling experiments (in-cabin ME3 and active out-of-cabin refueling ME7) the highest exposures occurred during the active refueling performed during the second 10 minutes of the sampling period. The highest concentrations are observed for BTEX species as expected from evaporative and spillage emissions during active refueling. HCHO and 1,3-BD present in exhaust emissions are lower and usually not correlated with benzene, as can be seen for ME3 in Fig. 1.3.2-2.

As shown in Figure 1.3.2-3, outdoor exposures (ME8, ME9 and ME12) are usually low and less variable. HCHO seems higher than benzene and 1,3-BD as is also evident from Figures 1.3.1-1 to 1.3.1-6 and Tables 1.3.1-1 and -2. On the other hand, outdoor surface parking (ME10) and out-of-cabin underground garage (ME11) MEs show much higher variability corresponding to vehicles exiting the parking lots after the game (ME10) or at the end of a work day (ME11).

We collected 5-minute canister samples at peak of exposures for ME7, ME11, and ME6 in Houston and Chicago and ME13 in Atlanta. Table 1.3.2-4 shows the average concentrations of BTEX, 1,3-BD and MTBE for these selected samples (full data set provided in electronic form). Figures 1.3.2-4 show the correlations for benzene and 1,3-BD, respectively, quantified from these 5-minute canisters and averaged over corresponding 5-minute surrogate 1-minute measurements. ME7 values for Houston were removed from these correlations since high MTBE levels distort NMVOC PID signal correlation to benzene. An obvious outlier from Atlanta (ME7, summer) was also removed. As seen from these figures, correlations are reasonable, especially for benzene ($R^2 = 0.87$).

Table 1.3.2-1A. Correlation coefficients (R^2) and associated statistic for relationships of time-integrated measurements with continuous methods (NMVOC and CO) for 3 cities, without ME3 and ME7

	PID							**CO_NDIR**						
	r2	Slope	Intercept	df	F-stat	Fcrit	P-value	r2	Slope	Intercept	df	F-stat	Fcrit	P-value
Atlanta														
Benzene	0.88	7.36	2.38	88	675	3.9	0.00%							
1,3-BD	0.55	31.05	20.29	88	107	3.9	0.00%	0.68	2.43	1.25	41	88	4.1	0.00%
Formaldehyde								0.39	0.35	1.79	41	27	4.1	0.00%
CO_can								0.93	0.90	-0.01	41	514	4.1	0.00%
Chicago														
Benzene	0.82	7.86	-0.85	87	406	4.0	0.00%							
1,3-BD	0.61	25.55	6.33	87	136	4.0	0.00%	0.70	2.35	0.82	46	106	4.052	0.00%
Formaldehyde								0.20	0.38	0.65	46	11	4.052	0.15%
CO_can								0.94	0.95	-0.07	46	687	4.052	0.00%
Houston														
Benzene	0.70	9.02	26.16	71	162	4.0	0.00%							
1,3-BD	0.70	24.86	28.75	71	169	4.0	0.00%	0.81	2.00	0.11	43	181	4.1	0.00%
Formaldehyde								0.29	0.70	-1.37	43	18	4.1	0.01%
CO_can								0.88	1.08	-0.38	43	309	4.1	0.00%

Notes: F-stat = performance statistic for regression slope of 2-tailed paired data: Critical F-value for 95% confidence is shown.
P-value = probability that correlation is not significant
df = degrees of freedom (number of data pairs - 2)

Table 1.3.2-1B. Correlation coefficients (R^2) and associated statistic for relationships of time-integrated measurements with continuous methods (NMVOC and CO) for ME3 and ME7 in 3 cities

	PID							**CO_NDIR**						
	r2	Slope	Intercept	df	F-stat	Fcrit	P-value	r2	Slope	Intercept	df	F-stat	Fcrit	P-value
Atlanta														
Benzene	0.57	12.15	1274.84	53	70	4.0	0.00%							
1,3-BD	0.34	159.97	729.81	47	5	4.0	2.47%	0.06	-0.03	0.55	12	1	4.7	41.71%
Formaldehyde								0.01	0.02	1.09	2	1	18.5	38.31%
CO_can								0.41	0.58	0.59	2	2	18.5	28.05%
Chicago														
Benzene	0.96	15.76	-4.47	25	590	4.2	0.00%							
1,3-BD	0.04	43.11	238.60	25	1	4.2	30.37%	insufficient data available						
Formaldehyde								insufficient data available						
CO_can								insufficient data available						
Houston														
Benzene	0.52	10.94	2896.65	27	30	4.2	0.00%							
1,3-BD	0.22	116.19	1878.18	19	5	4.4	3.36%	0.01	0.01	0.92	5	1	6.6	34.28%
Formaldehyde								0.42	-0.22	2.72	3	2	10.1	22.15%
CO_can								0.75	0.78	-0.08	3	11	10.1	4.49%

Notes: F-stat = performance statistic for regression slope of 2-tailed paired data: Critical F-value for 95% confidence is shown.
P-value = probability that correlation is not significant
df = degrees of freedom (number of data pairs - 2)

Table 1.3.2-2. Summary of the reconstructed 1-minute data (ppbv), Summer

City	**ME**	**Benzene**		**1,3-BD**		**HCHO**	
		min	max	min	max	min	max
A	01	0.00	47.38	0.00	16.59	0.00	34.25
A	02						
A	03	0.00	103.60	0.00	0.67	0.00	29.42
A	04	0.00	49.48	0.00	8.20	0.00	92.53
A	05						
A	07	0.00	976.35				
A	08						
A	09						
A	10	0.95	18.57	0.00	8.55	0.00	75.30
A	11	7.68	51.30	0.90	9.19	12.82	70.80
A	12	1.62	11.57	0.31	3.40	3.79	29.95
A	13	0.00	253.74	0.00	19.14	0.00	141.72
C	01	0.00	31.98	0.01	0.85	0.00	13.56
C	02	0.00	11.42	0.01	1.75	0.11	13.09
C	03	0.00	30.18				
C	04	0.50	15.39	0.74	4.61	3.64	35.66
C	05				0.80	0.00	17.55
C	06	0.10	65.31	0.20	11.65	1.13	64.03
C	07	0.00	111.01				
C	08			0.29	0.40	3.81	7.65
C	09			0.15	0.45	3.66	7.85
C	10			0.01	2.14	0.04	14.25
C	11	0.20	20.73	0.09	4.11	0.00	25.99
C	12			0.31	0.77	6.15	11.60
H	01	0.95	6.89	0.06	9.25	0.50	47.92
H	02	0.82	2.02	0.03	7.95	0.27	78.24
H	03	0.00	1346.97	0.23	3.66	1.67	26.55
H	04	2.09	13.44	0.48	6.00	1.86	23.44
H	05	1.19	4.04	0.14	2.80	0.63	26.49
H	06	1.31	16.95	0.12	6.23	0.89	25.61
H	07	0.00	1948.10			2.85	45.79
H	08	0.27	2.80	0.00	0.68	0.00	17.17
H	09	0.18	0.87	0.04	0.43	1.20	17.69
H	10	0.90	5.71	0.11	3.93	1.47	50.49
H	11	1.88	15.71	0.14	6.08	1.13	53.69
H	12	0.85	17.54	0.08	2.74	0.95	13.09

Table 1.3.2-3. Summary of the reconstructed 1-min data (ppbv), Winter

City	**ME**	**Benzene**		**13-BD**		**Formaldehyde**	
		min	max	min	max	min	max
A	01			0.02	1.28	0.25	15.70
A	02	1.60	3.87	0.07	1.34	0.82	15.71
A	03	0.59	107.31				
A	04	2.71	67.30	0.07	13.32	0.22	43.93
A	05			0.02	1.98	0.24	17.49
A	07	0.00	1080.63		3.44		19.02
A	08	0.74	2.17	0.23	0.41	3.15	5.69
A	09	1.06	1.81	0.27	0.53	2.48	4.79
A	10	3.11	13.55	0.08	3.07	1.35	41.48
A	11	1.66	49.76	0.05	17.32	0.21	50.86
A	12	0.81	6.53	0.17	1.33	1.11	11.75
A	13	0.53	33.96	0.05	6.36	0.20	42.78
C	01	0.17	1.20	0.07	7.40	0.26	64.35
C	02						
C	03	0.00	98.94				
C	04	3.72	31.25	0.97	8.97	4.45	25.70
C	05			0.04	0.72	0.65	11.37
C	06	0.13	8.53	0.06	1.63	0.45	14.92
C	07	0.00	511.90	0.58	4.57	0.86	6.75
C	08			0.10	1.71	0.94	10.07
C	09			0.00	0.53	0.00	8.02
C	10			0.07	2.54	0.47	18.27
C	11	3.01	33.48	0.11	5.63	0.45	26.76
C	12			0.00	0.65	0.00	8.87
H	01	0.60	6.34	0.06	3.13	0.58	23.47
H	02	0.82	13.93				
H	03	0.47	335.71	0.11	1.86	0.74	12.11
H	04	1.22	17.85	0.11	6.57	2.40	33.89
H	05	0.67	3.25	0.07	1.68	0.69	16.77
H	06	0.46	7.77	0.01	4.72	0.15	23.07
H	07	0.15	1203.84			0.25	20.29
H	08	0.35	0.62				
H	09	0.28	1.06				
H	10	1.16	32.64	0.08	12.89	0.13	22.73
H	11	3.71	18.66	1.23	12.10	2.41	16.98
H	12	1.43	3.76				

Table 1.3.2-4. Summary of the 5-minute canister data (ppbv)

City		**Atlanta, Summer**			**Atlanta, Winter**		
ME		7	11	13	7	11	13
Replicates		5	5	4	6	5	5
1,3-BD	Ave.	1.53	5.39	1.20	6.48	7.23	1.79
	Min.	0.04	3.97	0.79	0.78	0.51	0.48
	Max.	4.09	7.50	1.90	15.47	10.13	2.72
Benzene	Ave.	163.98	33.26	6.30	89.52	27.95	8.11
	Min.	3.06	24.80	4.36	13.52	1.51	1.90
	Max.	475.82	45.07	10.34	256.31	42.40	16.02
Toluene	Ave.	253.17	94.52	15.30	139.88	70.84	29.44
	Min.	8.90	68.88	10.97	48.39	3.94	4.62
	Max.	649.81	126.79	20.41	360.24	113.45	67.34
Ethylbenzene	Ave.	23.15	16.06	2.42	8.82	11.89	3.91
	Min.	1.45	11.89	1.89	3.86	0.64	0.69
	Max.	57.14	22.88	2.93	20.24	19.79	8.50
Xylene	Ave.	79.33	62.04	9.60	29.86	48.27	17.52
	Min.	6.21	44.84	7.39	15.90	2.69	3.01
	Max.	202.27	87.73	12.72	64.24	77.88	38.85

City		**Chicago, Summer**			**Chicago, Winter**		
ME		6	7	11	6	7	11
Replicates		5	5	5	5	4	4
1,3-BD	Ave.	1.51	0.21	2.33	0.73	2.19	4.00
	Min.	0.94	0.03	0.80	0.51	1.44	1.79
	Max.	2.66	0.39	3.01	1.45	2.74	5.75
Benzene	Ave.	8.87	13.56	7.75	2.22	84.25	12.00
	Min.	4.11	0.56	2.50	1.59	24.98	6.15
	Max.	24.00	37.23	10.00	3.94	160.53	17.32
Toluene	Ave.	25.53	22.74	19.40	3.56	56.51	23.92
	Min.	5.87	0.57	5.57	2.14	32.96	12.82
	Max.	78.10	61.34	25.73	6.48	100.48	36.75
Ethylbenzene	Ave.	2.69	2.77	3.31	0.59	6.11	4.03
	Min.	1.23	0.11	1.17	0.36	2.12	2.01
	Max.	6.80	6.78	4.63	1.04	11.90	6.00
Xylene	Ave.	9.43	11.19	12.74	2.89	25.92	18.75
	Min.	4.83	0.38	4.35	1.67	9.31	9.43
	Max.	23.42	26.91	18.57	5.33	51.91	27.41

City		**Houston, Summer**			**Houston, Winter**		
ME		6	7	11	6	7	11
Replicates		4	5	5	5	5	5
1,3-BD	Ave.	4.55	4.04	4.22	1.79	76.11	3.18
	Min.	1.24	1.36	0.55	0.81	13.03	0.39
	Max.	10.07	6.72	12.85	3.18	174.21	5.15
Benzene	Ave.	12.51	918.86	11.05	4.32	379.48	9.47
	Min.	4.17	181.85	1.99	2.53	49.61	1.91
	Max.	27.86	2429.61	26.71	7.91	607.22	16.60
Toluene	Ave.	21.28	815.73	27.31	7.30	420.64	19.84
	Min.	6.59	360.54	4.79	4.98	64.85	2.98
	Max.	50.32	1142.43	62.52	13.52	835.98	38.04
Ethylbenzene	Ave.	4.25	94.58	5.34	1.32	23.92	3.85
	Min.	1.47	44.53	1.12	0.85	4.22	0.50
	Max.	10.08	135.65	13.00	2.70	51.83	7.59
Xylene	Ave.	5.31	368.47	6.40	5.78	100.90	16.07
	Min.	6.74	132.36	4.38	4.13	16.87	2.14
	Max.	11.78	553.69	15.03	10.98	205.55	32.78
MTBE	Ave.	36.50	26977.95	30.06	15.28	9705.27	32.96
	Min.	13.65	3319.53	5.71	5.47	2019.60	14.29
	Max.	67.35	61643.39	48.23	39.34	15484.50	65.53

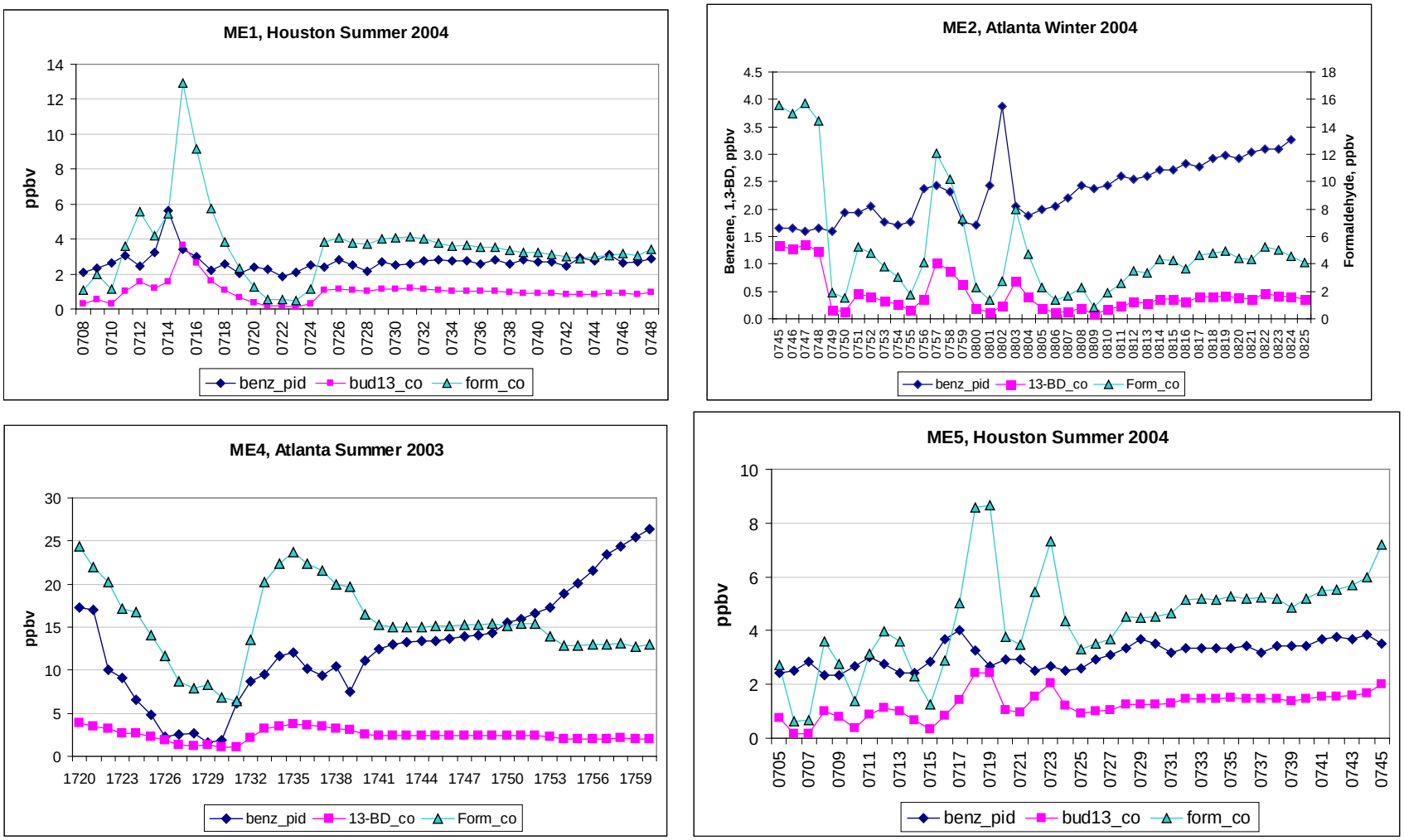


Figure 1.3.2-1. 1-Minute time series for in-cabin exposures: ME1 (congested freeway), ME2 (urban canyon); ME4 (underground garage) and ME5 (toll plaza)

ME1: In-cabin congested freeway; **ME2**: In-cabin urban canyon; **ME3**: In-cabin refueling; **ME4**: In-cabin underground garage; **ME5**: In-cabin toll plaza; **ME6**: In-cabin roadway tunnel; **ME7**: Out-of-cabin refueling; **ME8**:Out-of-cabin sidewalk; **ME9**: Out-of-cabin sidewalk/bus stop; **ME10**: Out-of-cabin surface parking; **ME11**: Out-of-cabin underground garage; **ME12**: Outside toll plaza; **ME13**: In-cabin trailing high-emitter vehicle

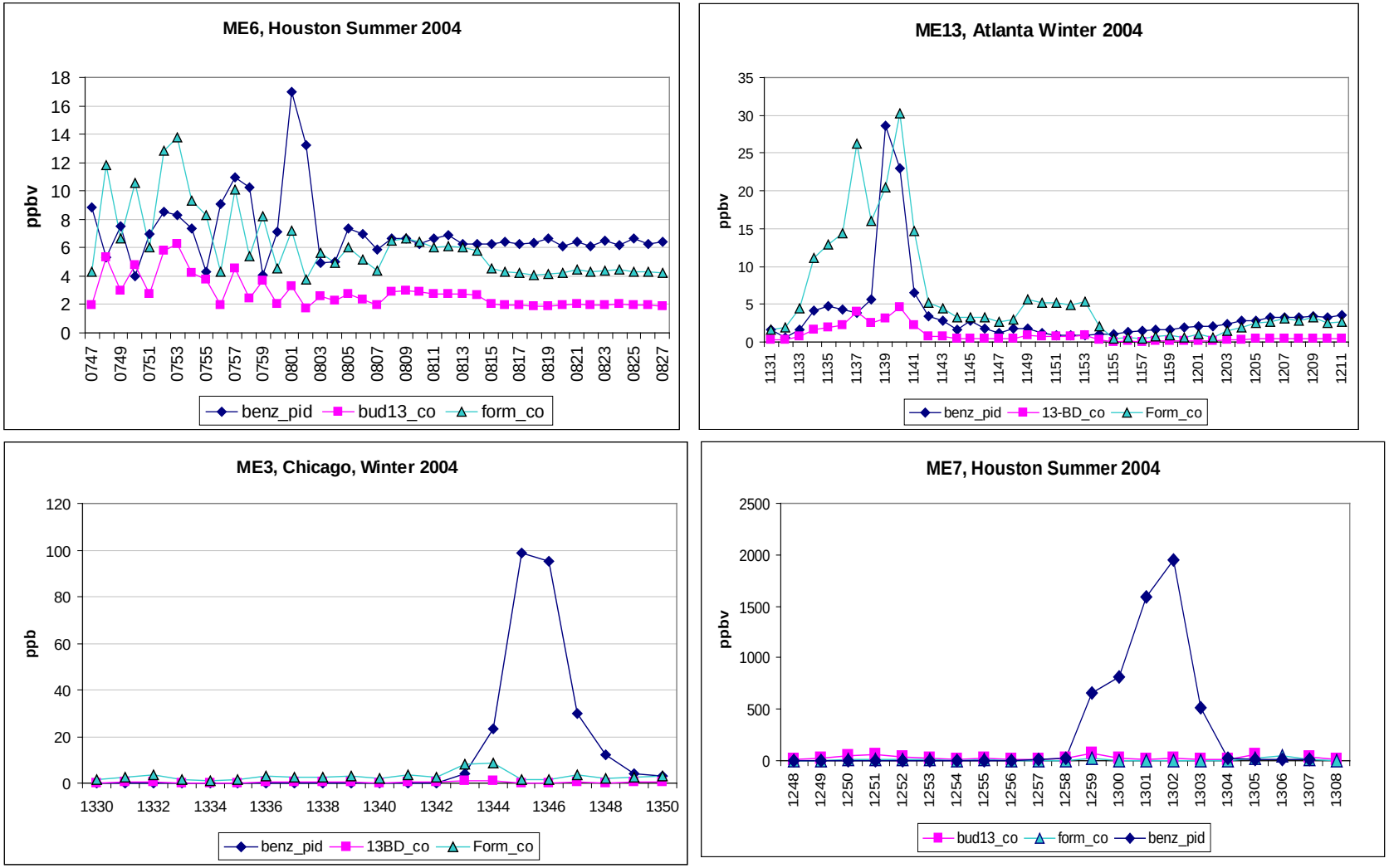


Figure 1.3.2-2. 1-Minute time series for in-cabin exposures: ME6 (tunnel); ME13 (following high-emitting vehicle); ME3 (in-cabin refueling) and out-of-cabin refueling, ME7

ME1: In-cabin congested freeway; **ME2**: In-cabin urban canyon; **ME3**: In-cabin refueling; **ME4**: In-cabin underground garage; **ME5**: In-cabin toll plaza; **ME6**: In-cabin roadway tunnel; **ME7**: Out-of-cabin refueling; **ME8**:Out-of-cabin sidewalk; **ME9**: Out-of-cabin sidewalk/bus stop; **ME10**: Out-of-cabin surface parking; **ME11**: Out-of-cabin underground garage; **ME12**: Outside toll plaza; **ME13**: In-cabin trailing high-emitter vehicle

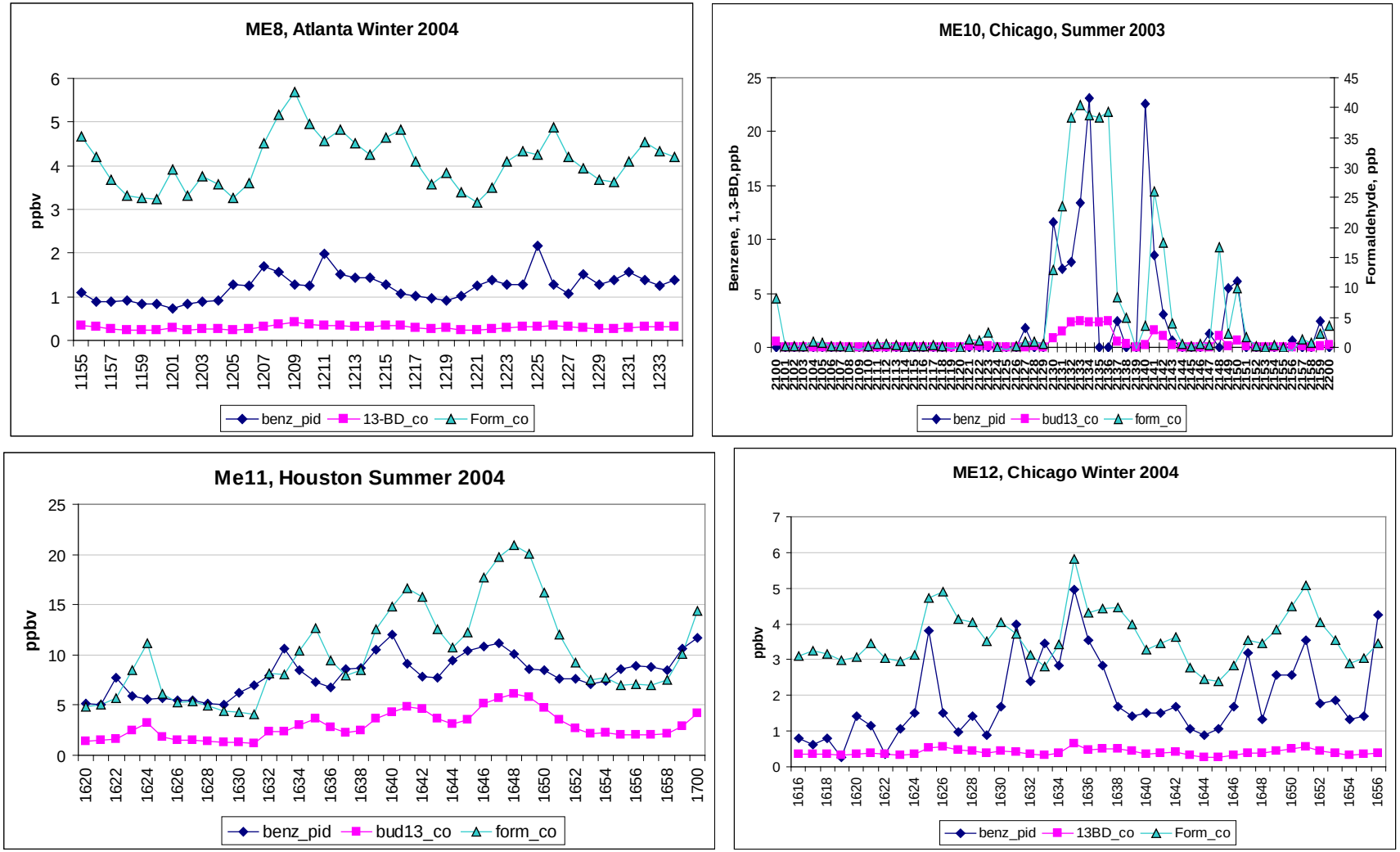
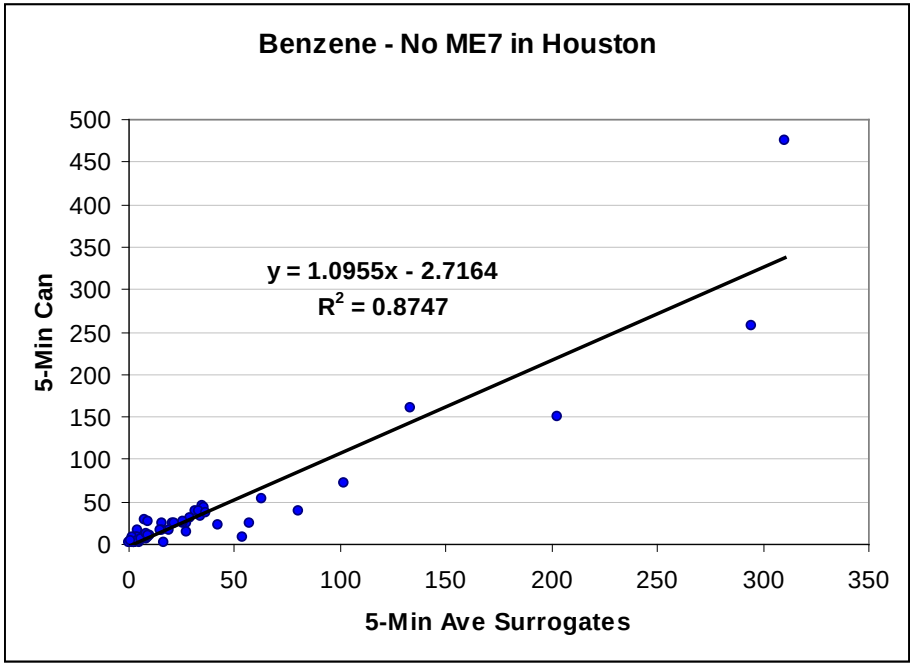


Figure 1.3.2-3. 1-Minute time series for out-of cabin outdoor exposures:ME8 (sidewalk); ME10 (surface parking); ME11 (underground garage) and ME12 (toll plaza)

ME1: In-cabin congested freeway; **ME2**: In-cabin urban canyon; **ME3**: In-cabin refueling; **ME4**: In-cabin underground garage; **ME5**: In-cabin toll plaza; **ME6**: In-cabin roadway tunnel; **ME7**: Out-of-cabin refueling; **ME8**:Out-of-cabin sidewalk; **ME9**: Out-of-cabin sidewalk/bus stop; **ME10**: Out-of-cabin surface parking; **ME11**: Out-of-cabin underground garage; **ME12**: Outside toll plaza; **ME13**: In-cabin trailing high-emitter vehicle



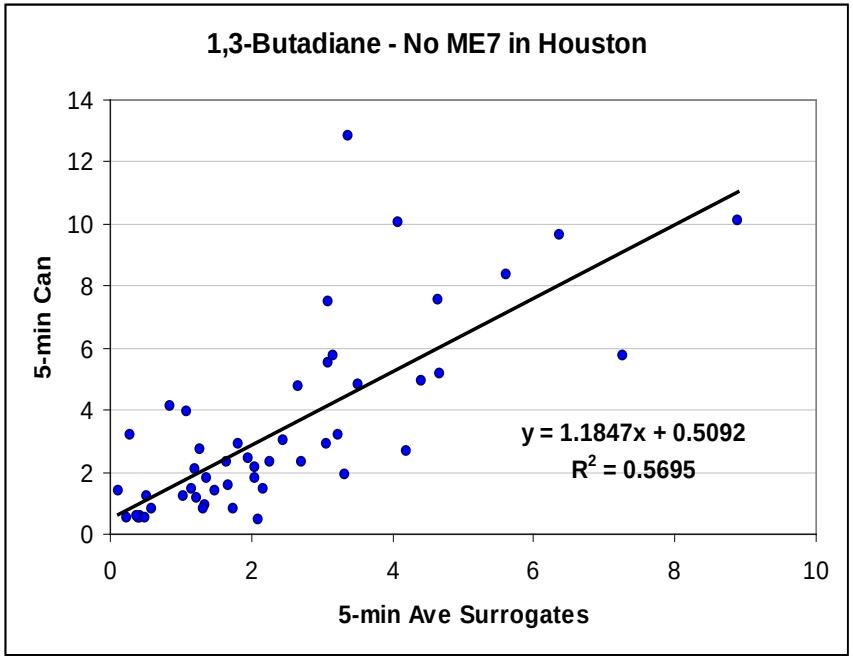


Figure 1.3.2-4. Correlations between 5-minute canister samples and surrogate 1-minute values, averaged over corresponding 5 minutes.

ME1: In-cabin congested freeway; **ME2**: In-cabin urban canyon; **ME3**: In-cabin refueling; **ME4**: In-cabin underground garage; **ME5**: In-cabin toll plaza; **ME6**: In-cabin roadway tunnel; **ME7**: Out-of-cabin refueling; **ME8**:Out-of-cabin sidewalk; **ME9**: Out-of-cabin sidewalk/bus stop; **ME10**: Out-of-cabin surface parking; **ME11**: Out-of-cabin underground garage; **ME12**: Outside toll plaza; **ME13**: In-cabin trailing high-emitter vehicle

1.3.3 Oxygenated and conventional gasoline (difference between cities)

The MTBE and EtOH concentration variability by ME in Houston and Chicago is shown in Figure 1.3.3-1. The complete data are provided in electronic form. Although MTBE is measured in all Houston MEs, the concentrations recorded during refueling are relatively high, in the range of a few ppmv. In contrast, Chicago ethanol concentrations are lower, especially during winter time. We generally use the same gas station in each city (absent problems with the gas station manager) and we select a station with high traffic close to a major freeway. For example, the gas station in Houston was situated next to Tollway 8 and was always very busy.

The high concentrations of MTBE during refueling in Houston caused occasional problems with 1,3-BD quantification in canister samples as discussed at Section 1.3.1. In addition, MTBE PID response changed the slope of canister benzene and NMVOC PID regressions in Houston MEs from those observed in Chicago and Atlanta, as shown in Table 1.3.2-1. However, when ME3 and ME7 data are removed from correlations, the slopes are more consistent among the three cities.

Figures 1.3.3-2 and -3 show comparisons of average benzene, 1,3-BD, HCHO, and CO concentrations by ME in the three cities by season. Tables 1.3.1-1 and 1.3.1-2 provide the data for all species measured with the time-integrated methods. For refueling MEs, the highest benzene concentrations are observed in Houston, in both seasons. However, for underground garage MEs, Atlanta shows the highest concentrations of benzene, HCHO, and CO. It is however not clear whether these findings result from the different fuels, choice of specific ME locations, or the greater variability of high-end ME exposures in general.

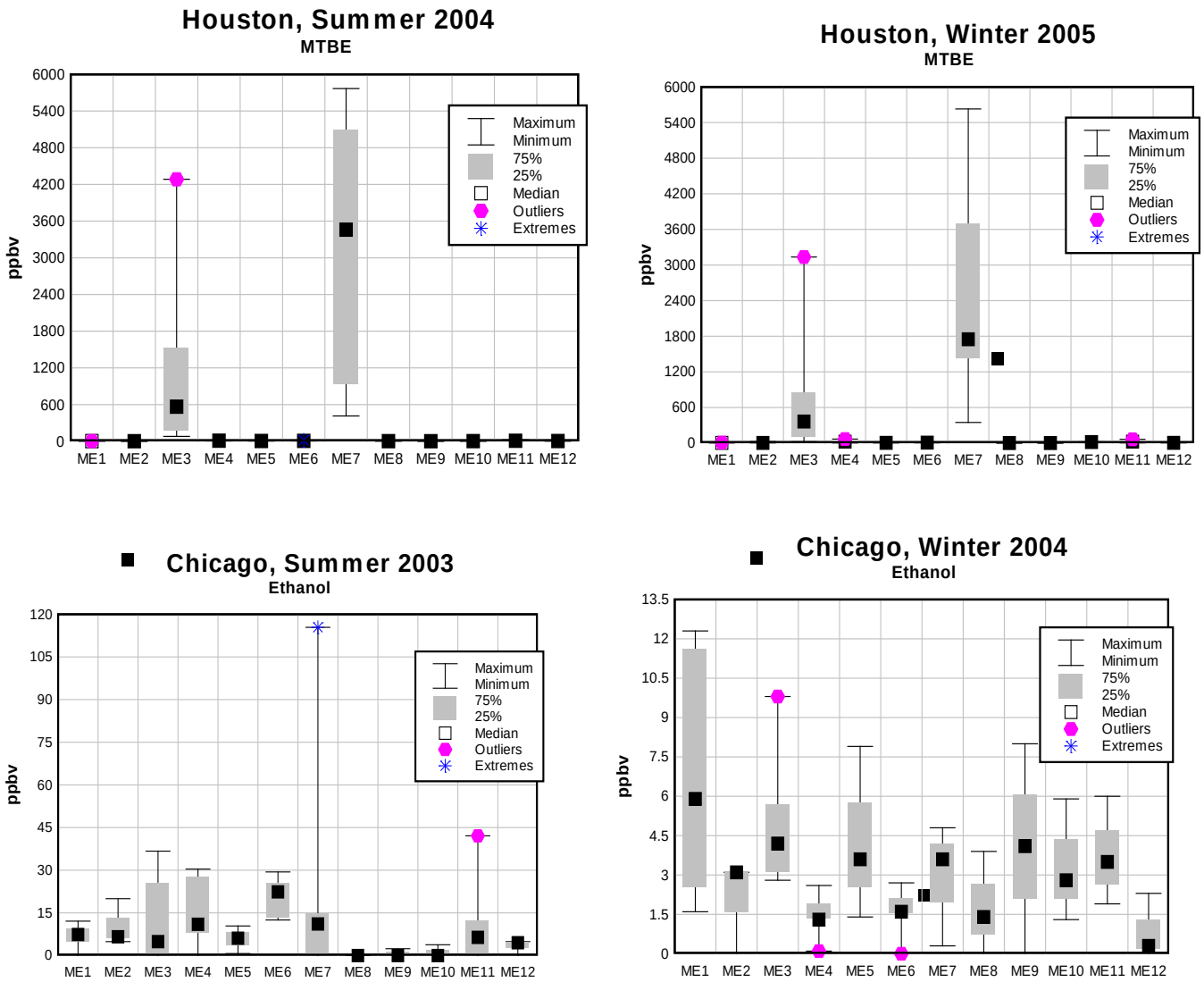


Figure 1.3.3-1. MTBE and EtOH concentrations in Houston and Chicago, respectively..Note different y-axis scales for Chicago Sumer and Winter

ME1: In-cabin congested freeway; **ME2**: In-cabin urban canyon; **ME3**: In-cabin refueling; **ME4**: In-cabin underground garage; **ME5**: In-cabin toll plaza; **ME6**: In-cabin roadway tunnel; **ME7**: Out-of-cabin refueling; **ME8**:Out-of-cabin sidewalk; **ME9**: Out-of-cabin sidewalk/bus stop; **ME10**: Out-of-cabin surface parking; **ME11**: Out-of-cabin underground garage; **ME12**: Outside toll plaza; **ME13**: In-cabin trailing high-emitter vehicle

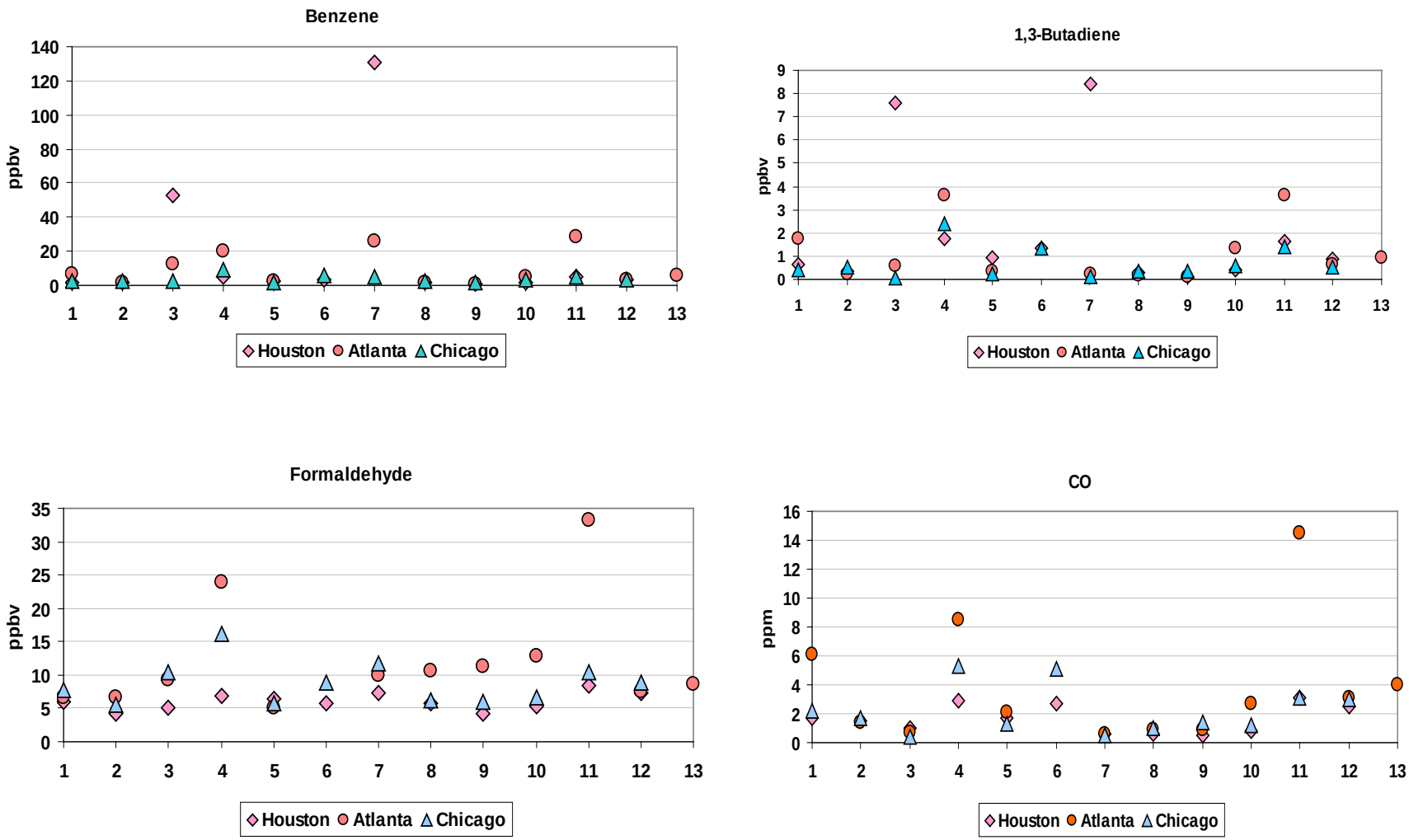


Figure 1.3.3-2. Comparison of benzene, 1,3-BD, HCHO, and CO average concentrations in three cities in Summer

ME1: In-cabin congested freeway; **ME2**: In-cabin urban canyon; **ME3**: In-cabin refueling; **ME4**: In-cabin underground garage; **ME5**: In-cabin toll plaza; **ME6**: In-cabin roadway tunnel; **ME7**: Out-of-cabin refueling; **ME8**:Out-of-cabin sidewalk; **ME9**: Out-of-cabin sidewalk/bus stop; **ME10**: Out-of-cabin surface parking; **ME11**: Out-of-cabin underground garage; **ME12**: Outside toll plaza; **ME13**: In-cabin trailing high-emitter vehicle

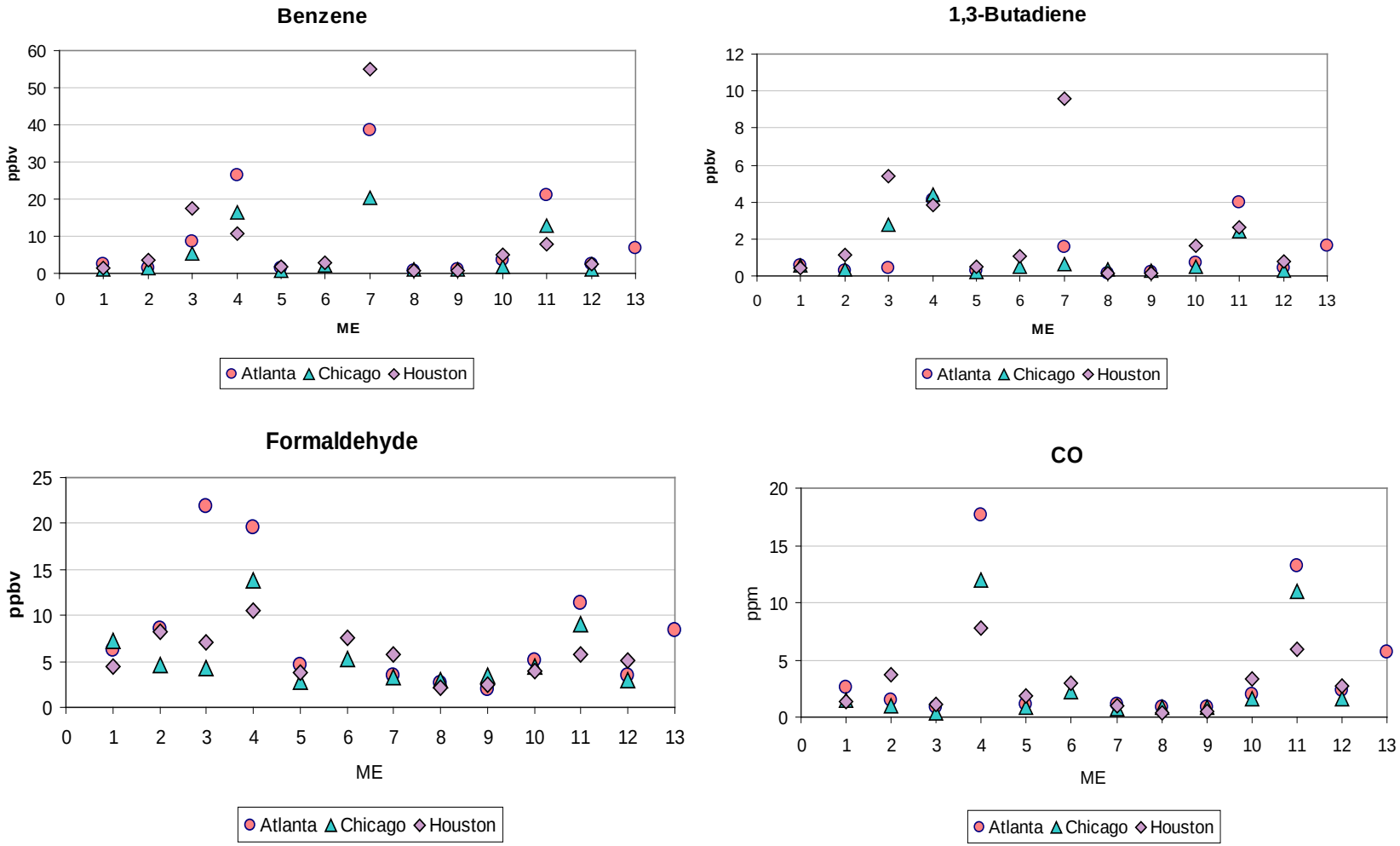


Figure 1.3.3-3. Comparison of benzene, 1,3-BD, HCHO, and CO average concentrations in three cities in Winter

ME1: In-cabin congested freeway; **ME2**: In-cabin urban canyon; **ME3**: In-cabin refueling; **ME4**: In-cabin underground garage; **ME5**: In-cabin toll plaza; **ME6**: In-cabin roadway tunnel; **ME7**: Out-of-cabin refueling; **ME8**:Out-of-cabin sidewalk; **ME9**: Out-of-cabin sidewalk/bus stop; **ME10**: Out-of-cabin surface parking; **ME11**: Out-of-cabin underground garage; **ME12**: Outside toll plaza; **ME13**: In-cabin trailing high-emitter vehicle

1.3.4 Effect of meteorology on exposure

As shown in Figures 1.3.3-1 through 1.3.3-6 the highest day-to-day variations in in-cabin or out-of-cabin exposures occur during refueling, in ME3 and ME7. ME4 and ME11 relate to exposures in an underground garage so these MEs are not subject to different meteorological conditions. However, wind speed and direction play an important role in refueling MEs. As a general rule, we performed refueling experiments under calm conditions (wind speeds ≤ 4 mph). Also, it was usually possible to find a pump location that was relatively sheltered from the direct influences of the wind. Subjects generally stood downwind during refueling tests. As a result, correlations of wind speed and concentrations in the refueling MEs were weak. For example, summer ME7 BTEX levels were highest in Chicago with a steady wind speed of 2-3 mph and lowest at variable wind speeds of 1-3 mph.

Table 1.3.4-1 lists average outdoor ambient temperatures and relative humidity by ME, city, and season. The detailed data recorded during each test are provided in electronic form.

Table 1.3.4-1. Average, minimum, and maximum ambient temperatures and RH

City	Season	ME	Replicate	Temperature (ºC)			RH (%)		
				ave	min	max	ave	min	max
A	S	1	5	27.6	27	29	58.4	56	60
A	S	2	3	24.3	22	27	42.6	33	63
A	S	3	5	32.0	26	37	61.8	44	74
A	S	4	5	32.2	31	33	52.2	46	61
A	S	5	3	24.2	22	26	49.9	36	72
A	S	7	5	29.5	22	34	63.0	57	86
A	S	8	3	33.7	29	39	41.0	29	65
A	S	9	3	33.7	29	39	41.0	29	65
A	S	10	3	31.9	22	41	42.6	20	69
A	S	11	5	33.2	32	35	47.8	42	51
A	S	12	3	27.1	24	32	58.8	42	77
A	S	13	5	41.2	37	46	49.4	47	54
C	S	1	5	27.0	26	28	52.2	46	55
C	S	2	3	25.0	24	26	45.7	42	49
C	S	3	6	30.5	24	35	51.8	45	63
C	S	4	5	26.4	23	28	60.8	56	66
C	S	5	3	29.7	26	33	56.7	54	61
C	S	6	5	30.0	29	31	53.4	50	57
C	S	7	5	28.6	24	31	59.0	50	68
C	S	8	3	25.0	23	27	55.0	54	56
C	S	9	3	26.3	25	28	53.3	51	55
C	S	10	3	21.0	20	23	70.3	67	73
C	S	11	5	28.4	22	33	56.6	46	67
C	S	12	3	31.7	30	34	43.0	31	57
H	S	1	5	33.8	30	37	55.6	51	63

City	Season	ME	Replicate	Temperature (ºC)			RH (%)		
				ave	min	max	ave	min	max
H	S	3	5	36.8	30	41	48.6	42	59
H	S	4	5	31.0	30	33	43.0	37	53
H	S	5	3	29.3	29	30	56.0	54	58
H	S	6	5	37.8	32	42	51.0	48	57
H	S	7	5	36.6	29	40	54.0	48	70
H	S	8	3	31.0	28	33	59.3	42	76
H	S	9	3	31.7	28	34	59.3	49	78
H	S	10	3	36.0	27	53	58.0	40	69
H	S	11	5	31.8	27	35	49.6	41	59
H	S	12	3	30.0	30	30	68.0	66	70
A	W	1	5	12.2	4	27	35.4	21	49
A	W	2	3	10.0	7	13	33.0	29	37
A	W	3	5	11.8	7	18	40.8	29	56
A	W	4	5	15.2	9	19	42.0	30	47
A	W	5	3	13.3	7	17	31.0	27	34
A	W	7	6	10.7	7	17	55.8	42	82
A	W	8	3	3.7	1	6	64.3	45	76
A	W	9	3	3.7	1	6	63.3	45	73
A	W	10	3	10.3	7	15	52.7	38	64
A	W	11	5	15.4	8	21	47.8	27	64
A	W	12	3	9.3	6	15	55.7	22	77
A	W	13	5	14.2	4	26	37.2	23	50
C	W	1	5	7.0	0	12	19.8	10	26
C	W	2	3	6.7	4	9	24.0	21	26
C	W	3	5	6.3	4	11	22.0	14	32
C	W	4	5	11.4	13	16	30.2	26	60
C	W	5	3	7.0	3	10	18.0	13	22
C	W	6	5	6.8	3	10	25.0	14	42
C	W	7	5	6.9	2	9	27.0	32	63
C	W	8	3	4.7	1	9	46.7	32	63
C	W	9	3	6.3	2	12	43.3	28	61
C	W	10	3	6.0	1	9	37.3	32	42
C	W	11	5	13.6	11	15	42.0	30	62
C	W	12	3	2.0	0	5	53.7	25	78
H	W	1	5	14.8	9	24	41.6	30	59
H	W	2	3	14.7	9	21	37.3	34	43
H	W	3	5	16.2	10	23	52.8	38	62
H	W	4	5	15.6	10	19	54.4	36	69
H	W	5	3	15.0	8	20	49.7	44	56
H	W	6	5	22.4	14	25	46.6	34	55
H	W	7	5	15.8	10	22	67.6	56	77
H	W	8	3	9.7	7	12	61.0	53	71
H	W	9	3	11.7	8	15	56.0	47	67
H	W	10	3	16.3	14	21	63.3	48	76
H	W	11	5	15.4	9	19	69.8	43	87
H	W	12	3	15.0	8	20	78.0	70	83

1.3.5 Comparison of summer and winter exposures

Figures 1.3.5-1 through 1.3.5-3 shows the differences between exposures in each city during the summer and winter seasons. For Chicago, the concentrations of benzene, 1,3-BD, and CO are higher in the underground garage (ME4 and ME11) during winter season. The same is true for ME3 and ME7, although CO concentrations are low and comparable for these refueling MEs, as expected. However, HCHO is clearly higher during the summer season in all MEs, perhaps a result of photochemical formation of this compound. In Houston, benzene is clearly much higher in refueling MEs in summer. However, for ME4 and ME11, winter concentrations are also marginally higher for benzene, 1,3-BD and CO. HCHO is less consistent, but clearly higher in summer in outdoor MEs (8, 9, 10, and 12). For Atlanta, the differences are not very large between winter and summer seasons, and not very consistent between different species and MEs. However, HCHO is clearly higher in summer in outdoor MEs (7, 8, 9, 10, and 12).

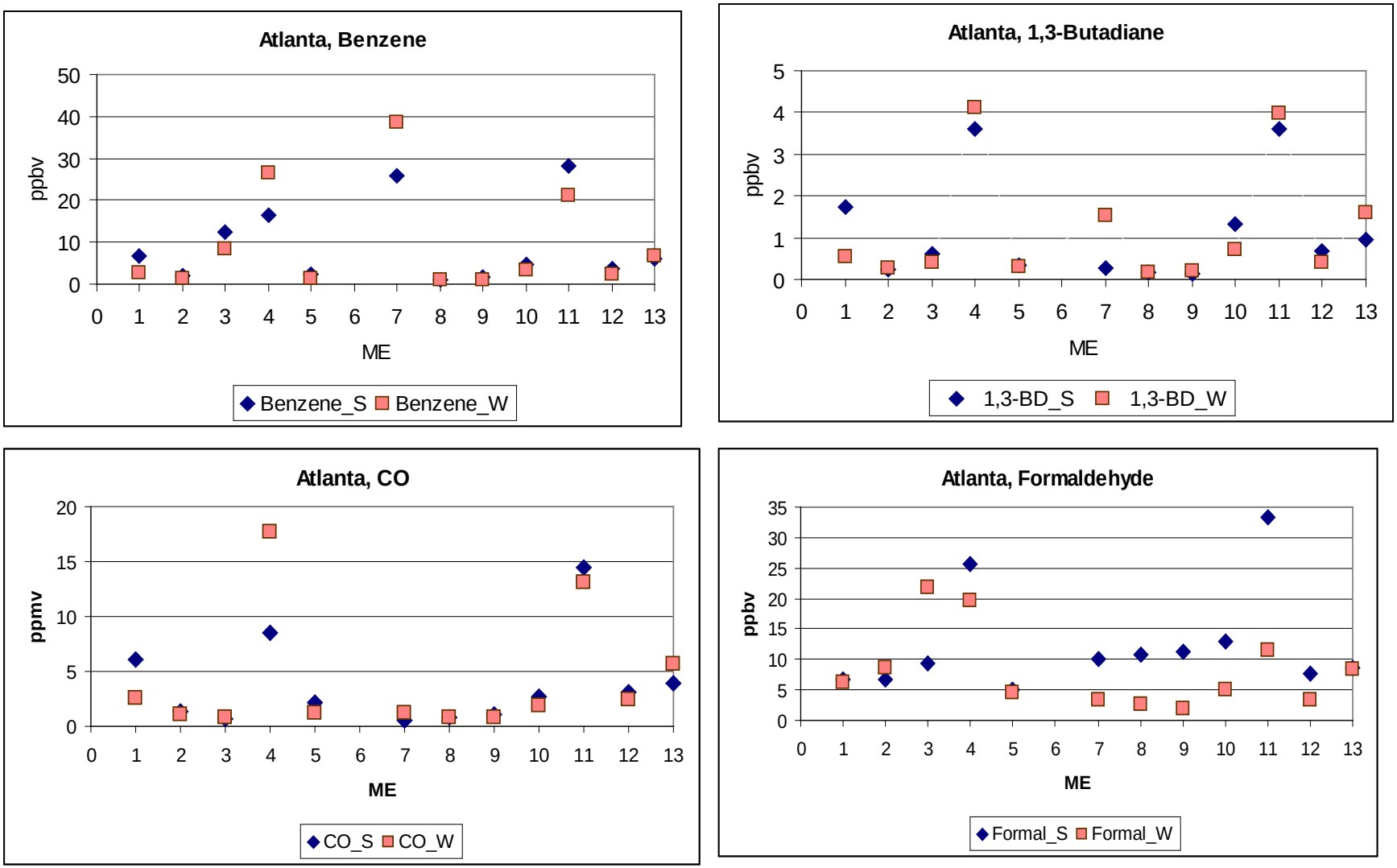


Figure 1.3.5-1. Time integrated average exposure levels in different MEs in Atlanta in Summer and Winter season.

ME1: In-cabin congested freeway; **ME2**: In-cabin urban canyon; **ME3**: In-cabin refueling; **ME4**: In-cabin underground garage; **ME5**: In-cabin toll plaza; **ME6**: In-cabin roadway tunnel; **ME7**: Out-of-cabin refueling; **ME8**:Out-of-cabin sidewalk; **ME9**: Out-of-cabin sidewalk/bus stop; **ME10**: Out-of-cabin surface parking; **ME11**: Out-of-cabin underground garage; **ME12**: Outside toll plaza; **ME13**: In-cabin trailing high-emitter vehicle

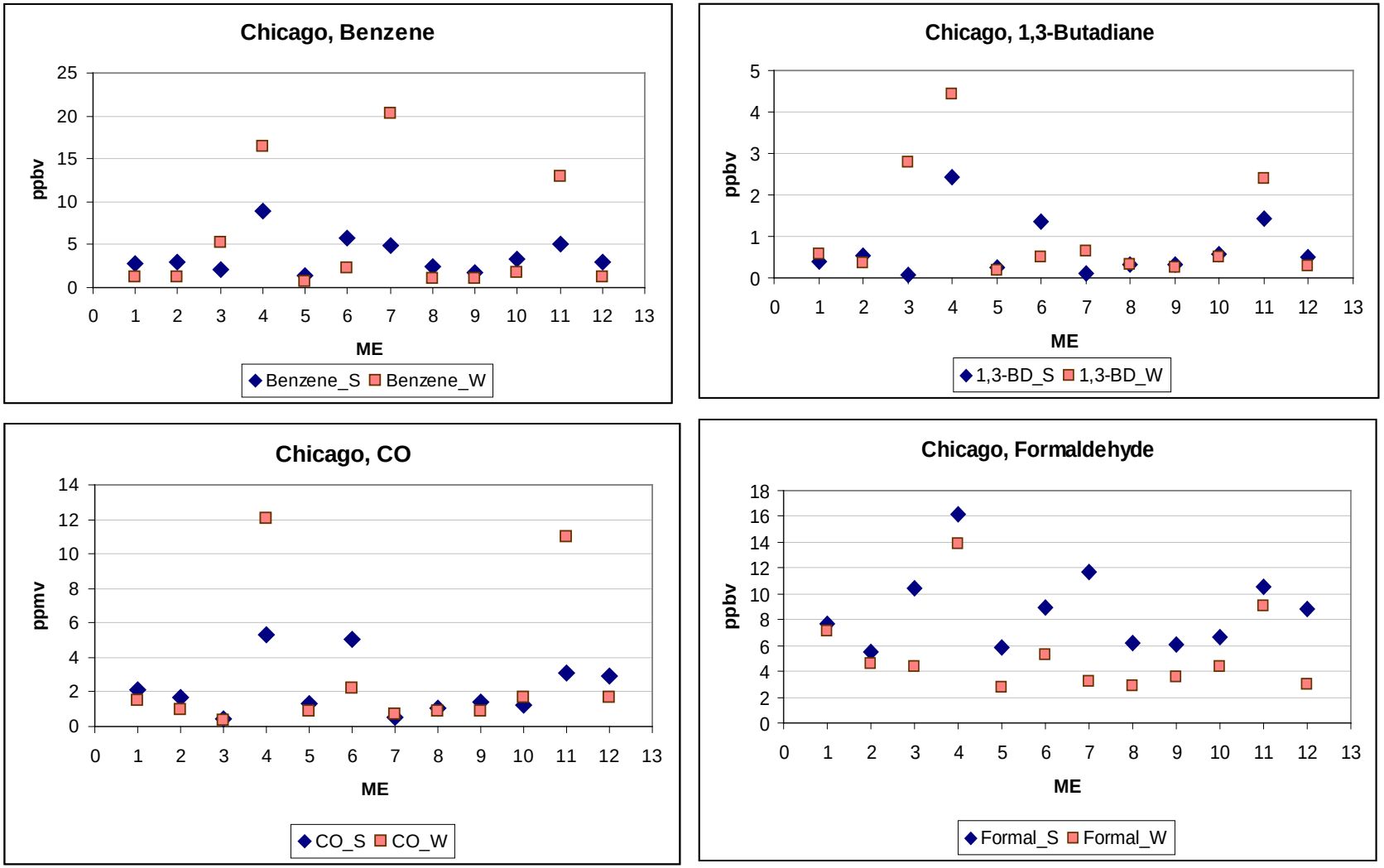


Figure 1.3.5-2. Time integrated average exposure levels in different MEs in Chicago in Summer and Winter season

ME1: In-cabin congested freeway; **ME2**: In-cabin urban canyon; **ME3**: In-cabin refueling; **ME4**: In-cabin underground garage; **ME5**: In-cabin toll plaza; **ME6**: In-cabin roadway tunnel; **ME7**: Out-of-cabin refueling; **ME8**:Out-of-cabin sidewalk; **ME9**: Out-of-cabin sidewalk/bus stop; **ME10**: Out-of-cabin surface parking; **ME11**: Out-of-cabin underground garage; **ME12**: Outside toll plaza; **ME13**: In-cabin trailing high-emitter vehicle

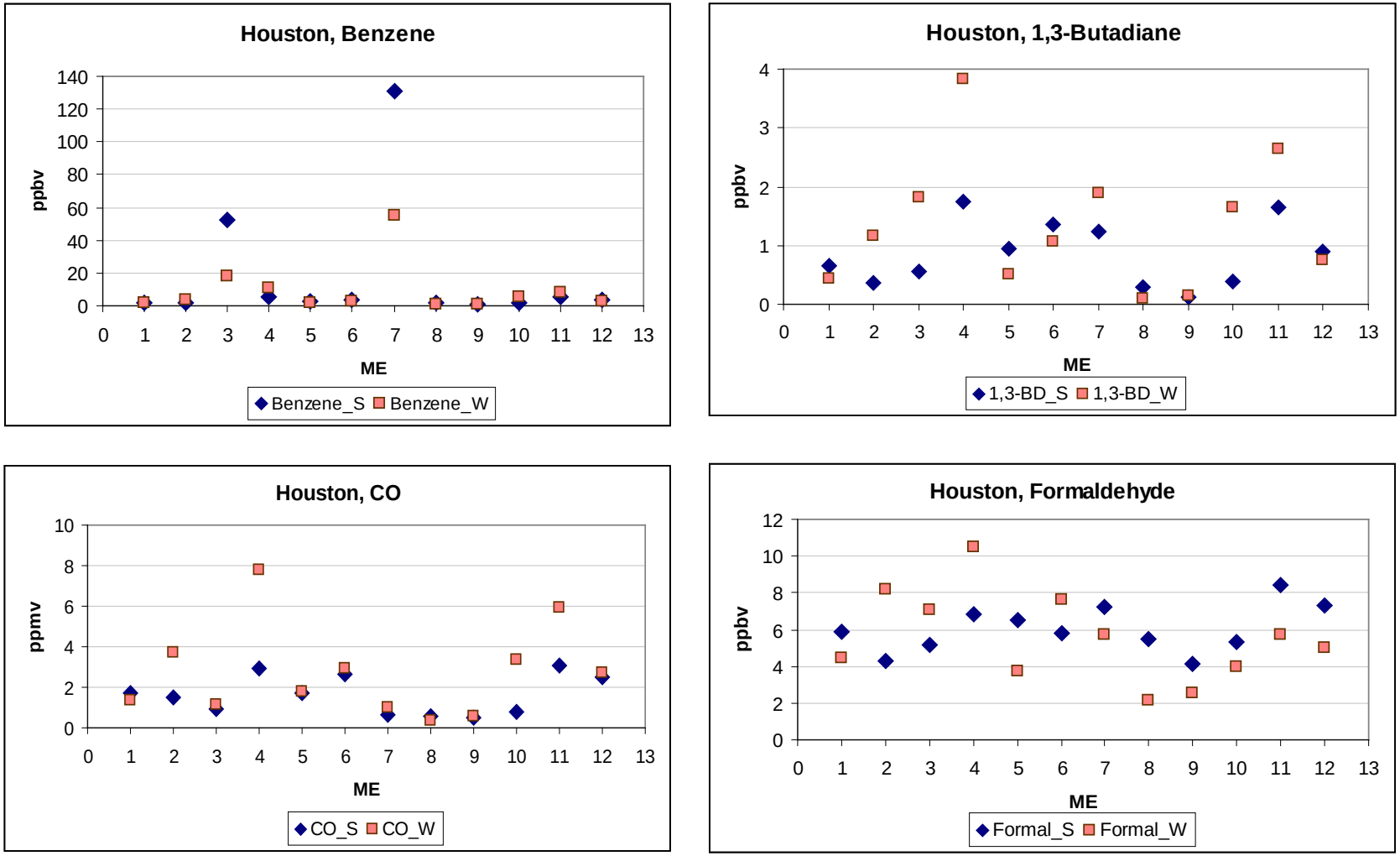


Figure 1.3.5-3. Time integrated average exposure levels in different MEs in Houston in Summer and Winter season

ME1: In-cabin congested freeway; **ME2**: In-cabin urban canyon; **ME3**: In-cabin refueling; **ME4**: In-cabin underground garage; **ME5**: In-cabin toll plaza; **ME6**: In-cabin roadway tunnel; **ME7**: Out-of-cabin refueling; **ME8**:Out-of-cabin sidewalk; **ME9**: Out-of-cabin sidewalk/bus stop; **ME10**: Out-of-cabin surface parking; **ME11**: Out-of-cabin underground garage; **ME12**: Outside toll plaza; **ME13**: In-cabin trailing high-emitter vehicle

1.3.6 Correlations to breath concentrations

Figures 1.3.6-1 and 1.3.6-2 shows the average concentrations of BTEX, 1,3-BD, MTBE, EtOH and CO_2 measured in pre- and a post-peak exposure breath for three MEs in each city and season. Detailed data are submitted in the electronic form. As it can be seen from these figures, a considerable increase in concentrations of measured species occurs in all cases immediately after a peak exposure. In Atlanta and Chicago, the highest breath concentrations of BTEX and 1,3-BD were observed in ME7 (refueling) and ME11 (underground garage). In Houston, high concentrations of MTBE were measured in ME7 in summer and winter. Although high concentrations of EtOH were measured in breath in all Chicago MEs, it is not clear if this is due wholly to the presence of EtOH in Chicago fuel, since pre-exposure breath concentrations were occasionally higher than the post-exposure concentrations. Subjects were cautioned against consuming alcoholic beverages or using alcoholic personal care products prior to breath testing but EtOH may also be a metabolic product for certain other food types. For example, it has been reported (Turner et al., 2006) that increased ethanol levels were observed in the breath of healthy individuals if sweet drinks/food had been consumed within 2 hr prior to providing breath samples.

Figure 1.3.6-3 (upper panel) shows the correlations between 1-minute maximum surrogate values for benzene and 1,3-BD and post-exposure breath concentrations of these species. The correlation is somewhat better for 1,3-BD ($R^2 = 0.46$) than for benzene ($R^2 = 0.26$); however, benzene concentrations in these MEs are much higher than breath concentrations. As shown in the lower panel of Figure 1.3.6-3, both benzene and 1,3-BD concentrations in breath track well these compound concentrations in all MEs. Note that the logarithmic scale was used for benzene and that no ME3 and ME7 data were included in 1,3-BD correlations for Houston. Also, some 1-minute surrogate 1,3-BD and benzene values are missing for certain MEs. As explained in Section 1.3.2, if the CO or NMVOC values were below the approximate detection limits of the continuous CO and PID instruments (0.5 ppmv and 25 ppbv, respectively), no 1-min surrogate data were calculated. Data used for these plots are submitted in electronic form.

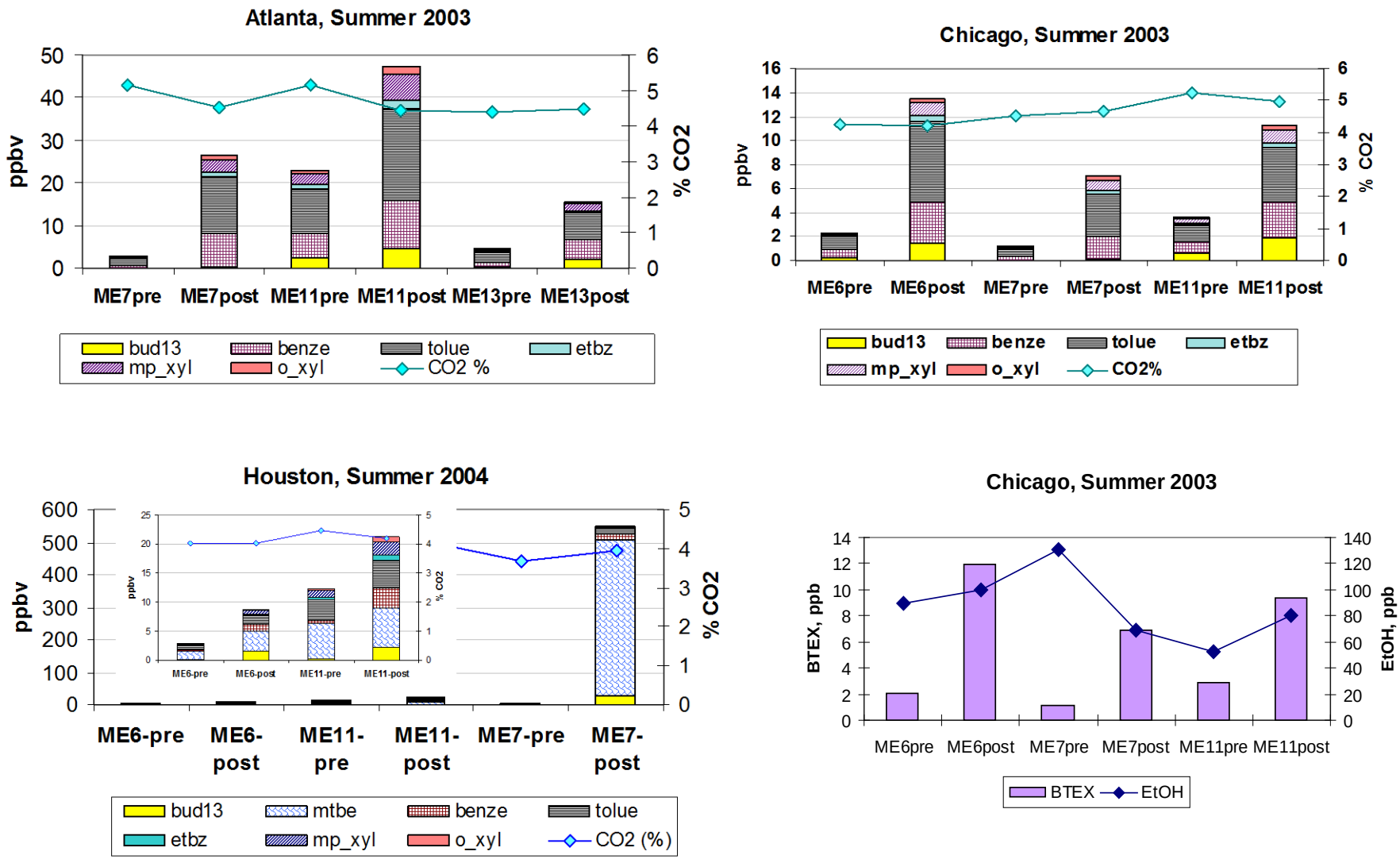


Figure 1.3.6-1. Average breath BTEX, 1,3-BD, MTBE, EtOH, and CO2 concentrations in three cities in Summer

ME1: In-cabin congested freeway; **ME2**: In-cabin urban canyon; **ME3**: In-cabin refueling; **ME4**: In-cabin underground garage; **ME5**: In-cabin toll plaza; **ME6**: In-cabin roadway tunnel; **ME7**: Out-of-cabin refueling; **ME8**:Out-of-cabin sidewalk; **ME9**: Out-of-cabin sidewalk/bus stop; **ME10**: Out-of-cabin surface parking; **ME11**: Out-of-cabin underground garage; **ME12**: Outside toll plaza; **ME13**: In-cabin trailing high-emitter vehicle

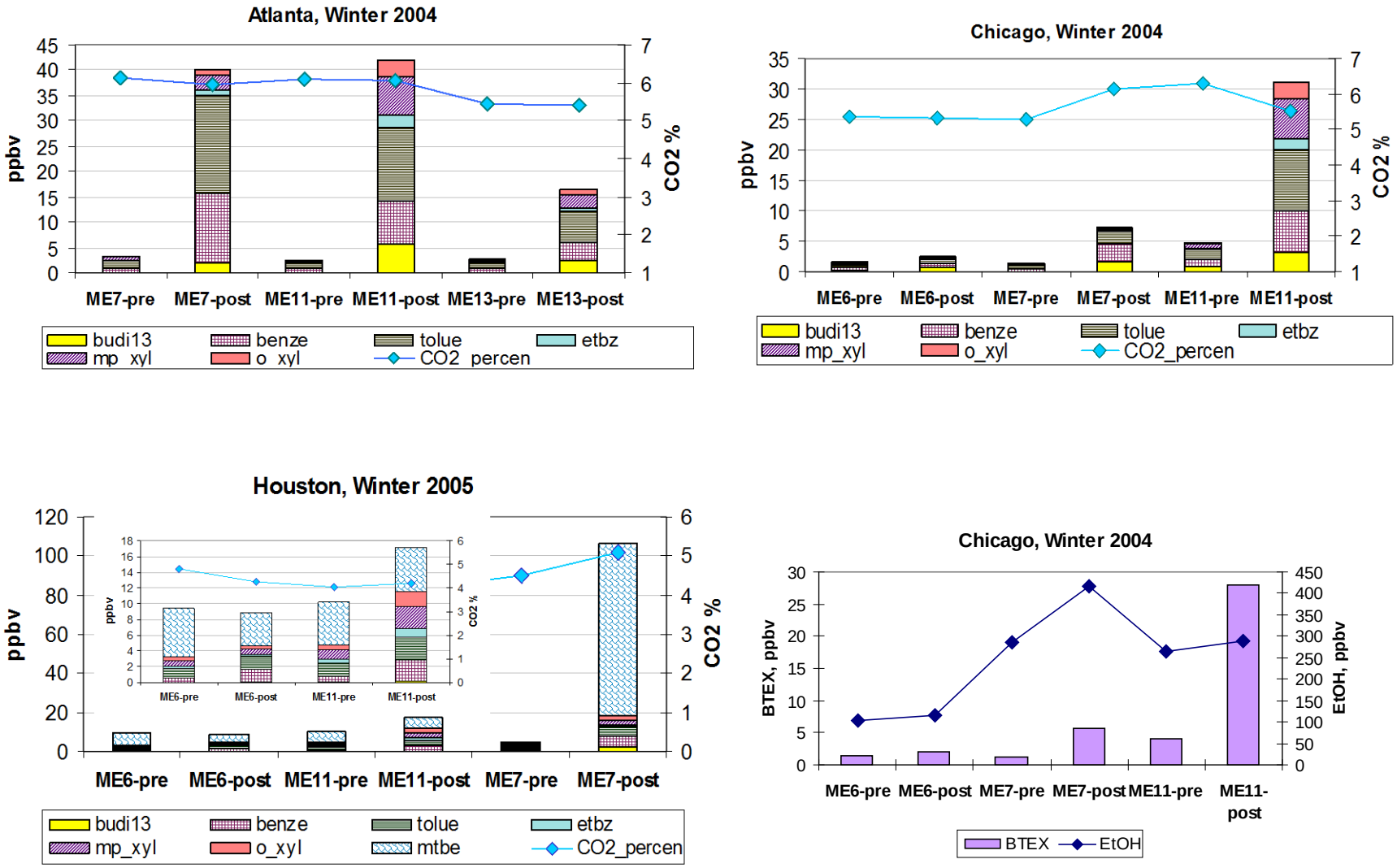


Figure 1.3.6-2. Average breath BTEX, 1,3-BD, MTBE, EtOH, and CO2 concentrations in three cities in Winter

ME1: In-cabin congested freeway; **ME2**: In-cabin urban canyon; **ME3**: In-cabin refueling; **ME4**: In-cabin underground garage; **ME5**: In-cabin toll plaza; **ME6**: In-cabin roadway tunnel; **ME7**: Out-of-cabin refueling; **ME8**:Out-of-cabin sidewalk; **ME9**: Out-of-cabin sidewalk/bus stop; **ME10**: Out-of-cabin surface parking; **ME11**: Out-of-cabin underground garage; **ME12**: Outside toll plaza; **ME13**: In-cabin trailing high-emitter vehicle

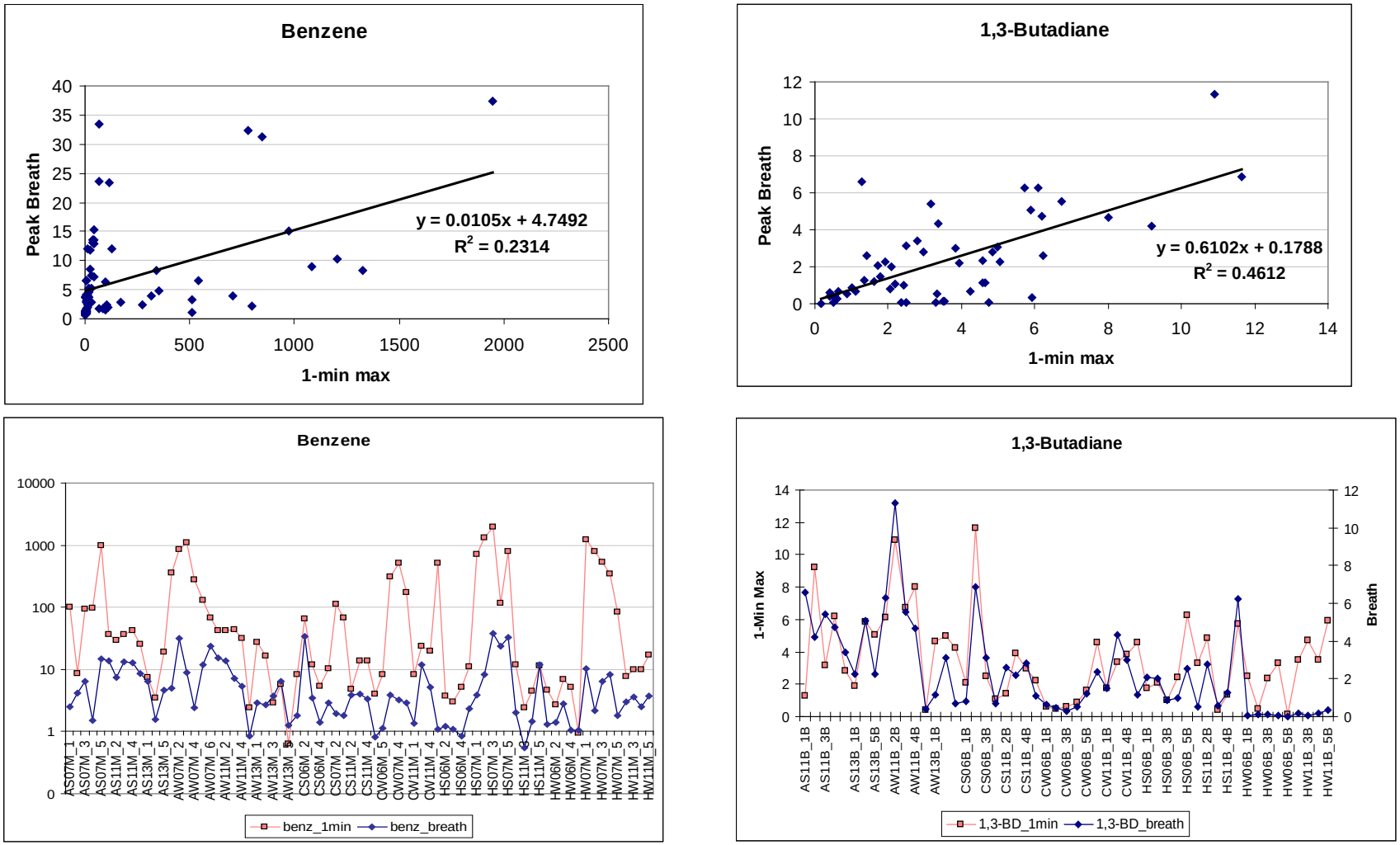


Figure 1.3.6-3. Correlations between 1-minute surrogate benzene and 1,3-BD max values and post-exposure breath concentrations (upper panel) and comparison of these concentrations in different ME and cities (lower panel)

ME1: In-cabin congested freeway; **ME2**: In-cabin urban canyon; **ME3**: In-cabin refueling; **ME4**: In-cabin underground garage; **ME5**: In-cabin toll plaza; **ME6**: In-cabin roadway tunnel; **ME7**: Out-of-cabin refueling; **ME8**:Out-of-cabin sidewalk; **ME9**: Out-of-cabin sidewalk/bus stop; **ME10**: Out-of-cabin surface parking; **ME11**: Out-of-cabin underground garage; **ME12**: Outside toll plaza; **ME13**: In-cabin trailing high-emitter vehicle

1.4 Conclusions

Summary findings related to the three city study are as follows:

- Day-to-day variations in high-end (99+th percentile) benzene, 1,3-BD, HCHO, and CO concentrations in different MEs are substantial and independent of city and season, but related to the activity and emission rates of sources in the given MEs which differ from day to day.
- With the exception of refueling, exposure levels are generally lower in outdoor MEs and higher in enclosed MEs.
- The 20-min average refueling benzene exposures range up to few hundred ppbv and show substantial day-to-day variability.
- In-cabin exposures during on-road vehicle operation are more consistent and uniform than for other in-cabin MEs.
- BTEX species show the highest concentrations in refueling MEs dominated by evaporative emissions whereas CO, HCHO, and 1,3-BD are the highest in the cold-start dominated MEs.
- BTEX and 1,3-BD measured by time-integrated canister method show good correlations with continuous NMVOC and CO measurements, respectively. HCHO correlation with continuous CO is modest, probably due to photochemical production of this compound.
- Continuous NMVOC (PID) and CO (NDIR) data can be used to reconstruct 1-minute time series for benzene and 1,3-BD, respectively, provided that the averaged continuous measurements are above the detection limits of the instruments (25 ppbv and 0.5 ppmv, respectively). CO data can also be used to reconstruct 1-minute HCHO data; however, less reliably so due to poorer correlation between these species.
- Reconstructed 1-minute time-series data for benzene and 1,3-BD, averaged over the five minute time frame corresponding to the collection of 5-minute canister samples, correlate well after excluding the Houston refueling ME with relatively high TVOC levels that distort typical correlation coefficients and elevated MTBE levels which bias 1,3-BD measurements.
- The concentrations of benzene and 1,3-BD measured in post peak exposure breath samples track corresponding ME 1-minute maximum reconstructed surrogate values well.
- Increases in concentrations of measured species occur in all breath samples collected within a minute of a peak exposure. In Atlanta and Chicago, the highest breath concentrations of BTEX and 1,3-BD were observed in ME7 (refueling) and ME11 (underground garage), respectively. In Houston, high concentrations of MTBE were measured in ME7.
- The largest differences in benzene, 1,3-BD, and CO concentrations between summer and winter seasons are observed in Chicago, consistent with the largest ambient temperature differences for this city. These concentrations are higher in winter. For Atlanta and Houston such differences are less pronounced. HCHO is consistently higher in summer season in outdoor environments, probably due to the photochemical production of this compound.

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2. Relative Contributions of Vehicle Evaporative and Exhaust Emission to Concentrations of Volatile Air Toxics in High Exposure Microenvironments in Houston

2.1 Introduction

The Desert Research Institute (DRI) conducted measurements to quantify exposures to automotive emissions in microenvironments representing the upper-end (> 99th percentile) of the distribution of inhalation exposures to evaporative and exhaust emissions of conventional- and oxygenated-gasoline. The study was conducted as part of the Section 211(b) Tier 2 High-End Exposure Study of Conventional and Oxygenated Gasoline. DRI and SwRI conducted measurements under controlled conditions to establish quantitative relationships between tailpipe and evaporative emission rates to exposure levels in a vehicle cabin and attached residential garage. Field exposures also were measured in several high-end exposure microenvironments in Atlanta, Chicago, and Houston during winter and summer. Target species (TVOC, CO, BTEX, HCHO,1,3-BD, MTBE, EtOH) were measured within microenvironments, breathing zones, and breath. This section apportions the relative contributions of fuel combustion and evaporative emissions to exposures measured various high-end microenvironments, based on differing abundances of MTBE and benzene in exhaust and evaporative emissions. This particular analysis approach was applied to the exposure data from Houston because it is the only city included in the Section 211(b) exposure screening study to use MTBE as the oxygenated additive.

Federal reformulated gasoline (RFG) was introduced in 1995 in nine metropolitan areas of the United States that were not in attainment of the ambient air quality standard for ozone. The RFG program is implemented year-round in these areas as an emission reduction program to control ambient ozone and mobile source air toxics (MSAT). Non-oxygenated conventional gasoline was used in Atlanta during the period of study. Ethanol was used to oxygenate reformulated gasoline in Chicago and MTBE in the Houston area. Table 2-1 summarizes the major differences in fuel composition between conventional and RFG. Exhaust emissions include a mixture of un-combusted fuel components (e.g., BTEX, MTBE, EtOH, TVOC) and species produced during combustion (e.g., benzene, 1,3-BD, HCHO, CO). The relative abundances of combustion by-products in the exhaust profile vary with emission control technology, level of vehicle maintenance, and operating mode.

Liquid gasoline contains many target compounds (BTEX, MTBE, EtOH, TVOC) in common with gasoline-vehicle exhaust. Gasoline headspace vapor, vapor in equilibrium with liquid gasoline, also contains these combustion compounds but is enriched in the more volatile species such as benzene, MTBE, and EtOH. Composite liquid and headspace vapor profiles across different brands and grades of gasoline were developed in conjunction with the Tuscarora, Fort McHenry, and SOS on-road exhaust experiments, for the Auto-Oil program, COAST, the Paso del Norte Study, and the 1995/96 RFG Study (Zielinska et al., 1997). Gasoline compositions were also determine for western Washington (Fujita et al., 1997c), Austin (Fujita, et al. 1999a), San Francisco Bay Area (Kirchstetter et al., 1999), Houston (Fujita et. al., 2001), and Los Angeles (Fujita et al, 1997; Fujita et al., 2003).

There are several sources of evaporative emissions including hot soak emissions driven by residual engine heat following cessation of vehicle operation, diurnal emissions associated with fuel tank 'breathing' during diurnal temperature and barometric pressure cycling, running losses resulting from fuel tank radiant heating by roadways or from injector fuel recirculation during vehicles operation, resting losses from gasoline permeation through rubber and plastic components of the fuel lines, and simple fuel system leakage. From an analysis of ambient air samples and reconciliation with VOC source profiles, Pierson et al. (1999) conclude that 71 ± 9% of motor vehicle VOC emissions are emitted from tailpipes, 17 ± 6% result from non-tailpipe liquid fuel emissions (fuel system leakage) , and 12 ± 4% are due to headspace vapor emissions.

2.2 Experimental Approach

The profiles for vehicle exhaust, liquid gasoline, and gasoline headspace vapor include many of the same species but notable differences in the ratio of species, a difference that can be used to apportion tailpipe and evaporative emission source strengths. The proportion of MTBE in exhaust is reduced during combustion relative to its proportion in the fuel. Conversely, benzene is enriched in exhaust relative to its proportion in the fuel due to toluene and xylene dealkylation. Consequently, MTBE to benzene ratios are substantially lower in exhaust than in liquid fuel or headspace vapors. MTBE and benzene were measured in all microenvironments in Houston as well as in fuel and vehicle exhaust samples. The fractional evaporative contribution, X, was estimated using following formula.

$$X = (R_{ME} - R_{EXH}) / (R_{VAP} - R_{EXH})$$

R_{ME} is the measured microenvironmental MTBE/benzene ratio, R_{EXH} is the exhaust MTBE/benzene ratio, and R_{VAP} is the evaporative MTBE/benzene vapor ratio; either of whole gasoline or headspace vapor depending upon type of evaporative emissions expected in a particular ME (e.g., whole liquid gasoline for hot soak, leaks, or spills and headspace vapors if refueling). Some MEs are influenced by a combination of whole gasoline and headspace vapor emissions.

For the present study, the Southwest Research Institute (SwRI) procured two test vehicles and determined their evaporative/tailpipe emissions in the normal/malfunction modes using the three test fuels. The test vehicles, a sedan and full-sized V8 truck, were chosen within the 1993-1996 model years from vehicles with 90,000-110,000 odometer miles. The chosen 1993 Toyota Camry (2.2L 4-cylinder engine) and 1995 Ford F150 Pickup truck (5.0L V8 engine) were operated in normal, as purchased, modes and in "high emitter" modes with the catalytic converter removed and emission levels above 2 grams per mile NMHC as measured on the FTP driving cycle. While converter removal sufficed for the F150 truck, a calibrated manifold leak was also needed to achieve the ≥ 2g/mile Camry emissions. SwRI determined dynamometer FTP emissions for each vehicle with all three fuels in the two emission modes (24 tests). Emission control components could be reproducibly adjusted to represent normal and reasonable high-end approximations (≥ 2g/mile) of real world exhaust emissions.

The FTP exhaust emission test uses the 1372 second Urban Dynamometer Driving Schedule (UDDS) that is divided into cold/start transient 505 (Bag 1) and cold stabilized 867

(Bag 2) second segments. This portion of the FTP is followed by a 10-minute soak and a hot/start transient 505 (Bag 3) test. The FTP evaporative emission test includes one hour Diurnal Heat Build (DHB) and Hot Soak Loss (HSL) tests. THC/VOC emissions are recorded during the HSL segment of the test. Prior to the FTP cold-start exhaust test, the DHB is conducted by fueling the test vehicle to 40 percent of tank capacity with fuel < 55°F, attaching a heating blanket outside the fuel tank, placing a thermocouple in the tank fuel, hooking it up to computer control, and beginning the test as fuel reaches 60°F (increasing at 0.4°F per minute for the 60-minute test to a 84°F final temperature). In the HSL segment, conducted immediately following exhaust emission testing, the vehicle is driven into an evaporative emission enclosure and allowed to "soak" in the enclosure for one hour. THC/VOC emissions are measured at the beginning and end of the one-hour segment and hot soak evaporative emissions are calculated.

Test fuel samples were subject to standard tests for Reid Vapor Pressure (RVP), distillation range, Specific Gravity, Sulfur, Benzene, HC Category (saturates, olefins, aromatics), Oxygenated species (MTBE/EtOH), carbon weight percent, hydrogen weight percent, oxygen weight percent, and octane number. Gasoline headspace vapor compositions were predicted from the measured composition of liquid gasoline using the Raoult's Law method described by Kirchstetter et al. (1999). This method is based on the proportionality between the compound headspace partial pressure and its liquid mole fraction times the vapor pressure of the pure species. The individual vapor pressures are determined using the Wagner equation (Reid et al. 1987).

DRI measured seasonal in-cabin breathing zone exposures for urban roadways and other high-end MEs in Houston (6/3-7/9/04; 2/1-2/8/05), Chicago (8/5-8/20/03; 3/3-3/17/04), and Atlanta (7/28-8/8/02; 8/23-9/3/03; 2/10-2/29/04) using a combination of time-integrated samples and continuous instruments listed in Table 2-2. Three replicate exposure measurements were made for low variability MEs and five for MEs with higher variability (i.e., ME13-trailing high emitting vehicles, ME11-underground garages, and ME7-outdoor refueling). Measurements in each ME were taken over a period of 20-40 minutes beginning at the top of the hour. Shorter sampling times were used for refueling events and parking garage exits after sporting events. Sampling and analytical methods are described in Section 1 of the report and in the study plan (Zielinska et al., 2003).

2.3 Results

The measured MTBE/benzene ratios are summarized in Table 2-3 for the Houston MEs. Exposures at the two refueling MEs (3 & 7) were dominated by evaporative emissions as expected, with MTBE/benzene ratios of 20 to 30. Ratios for all other MEs were between 1 and 4. The exhaust, headspace, and liquid fuel MTBE/benzene ratios measured in this and other recent studies are shown in Table 2-4. MTBE/benzene exhaust ratios among the dynamometer tests average slightly less than 1 with the tunnel ratios nearer 2, possibly due to the added running loss emissions in tunnels. The MTBE/benzene ratios in liquid gasoline and vapor are similar, averaging 15-20. Ratios for the SwRI SHED tests vary somewhat with calculated headspace compositions and values from earlier listed studies.

The estimated fractional contributions of evaporative emissions to total motor vehicles emissions for the various Houston MEs, using the above method, are summarized in Table 2-5 and Figure 2-1. Uncertainties are the standard deviation of the ratios calculated from replicate test measurements for each ME (represents the variability of ratio within observed sample set). Exposures during refueling (ME3, ME7) are 100% due to evaporative emissions within the uncertainties associated with the measurements and method. All other MEs are dominated by tailpipe emissions with fractional evaporative contributions < 10%.

2.4 Conclusions

The results presented in Table 2-5 indicate that evaporative emissions are only substantial components of high end ME exposures during vehicle refueling operations, where they are dominant. Since refueling MEs have the highest relative levels of these components (see sections 1 and 3), they constitute the peak exposures, although overall the average population time spent in these high end MEs is likely the shortest. The contribution of evaporative emissions for all other MEs was typically about 5% of the total measured exposure. Results were similar for both seasons, although evaporative contributions during refueling were marginally less during summer, possibly due to more rapid dispersion of vapors and evaporation of fuel spilled during each refueling test at higher summer temperatures. The clear distinction in evaporative contribution between refueling and non-refueling MEs, along with the relative consistency in MTBE/benzene ratios shown in Table 2.4, gives some confidence in the approach.

These results suggest that the contemporary Houston vehicle fleet contains relatively few carbureted or leaking vehicles given that evaporative emissions are not a substantial source in the non-refueling MEs tested. Refueling emissions released from pressurized fuel systems and spilled fuels appear to be the primary source of peak evaporative exposures. The lack of a seasonal variability in the evaporative contribution is also consistent with this supposition. Although it was not feasible to try to distinguish further between liquid and headspace vapor contributions by the method used, the extremely low MTBE/benzene ratios observed for the roadway, sidewalk, and parking MEs suggest that the contributions of emissions from leaking liquid gasoline is relatively small.

The contributions of exhaust and evaporative emissions to ambient volatile air toxics were estimated for Houston only since it is the only city among the three in the study with oxygenated gasoline containing MTBE. While the contributions of evaporative emissions relative to exhaust emissions may vary with differences in average prevailing meteorological conditions, such differences are unlikely to result in significantly different conclusions in other cities with regard to the relative contributions of exhaust and evaporative emissions to ambient concentrations of volatile air toxics. It must also be noted that the vehicle used in this study for the refueling tests was a 1996 vehicle. All vehicles prior to the 1998 model year do not have onboard refueling vapor recovery (ORVR) systems, and therefore higher refueling emissions. Although refueling stations in Houston had Stage II vapor recovery systems, the ORVR system also reduces vapor losses when the fuel cap is opened by lowering the internal pressure of the fuel tank. The implementation of ORVR systems may further reduce the relative contributions of evaporative emissions.

Table 2-1. Conventional gasoline versus reformulated gasoline RFG (from EPA OTAQ web page http://www.epa.gov/OMSWWW/rfgnew.htm, updated by S. Romanow, OTAQ).

	Fuel Parameter Values (national basis)				
	Conventional Gasoline		Gasohol	Oxyfuel (2.7% wt)	"Summer" Phase I RFG
	Average[a]	Range[b]	Average	Average	Average[e]
RVP[c] (PSI)	8.7-S 11.5-W	6.9-15.1	9.7-S 11.5-W	8.7-S 11.5-W	7.0-7.9[f]
T50 (°F)	207	141-251	202	205	199
T90 (°F)	332	286-369	316	318	325
Aromatics (volume %)	28.6	6.1-52.2	23.9	25.8	22.3
Olefins (volume %)	10.8	0.4-29.9	8.7	8.5	12.5
Benzene (volume %)	1.60	0.1-5.18	1.60	1.60	0.64
Sulfur (ppm)	338	10-1170	305	313	269
MTBE[d] (volume %)	--	0.1-13.8	--	15	11[g]
$EtOH_d$ (volume %)	--	0.1-10.4	10	7.7	10[h]

a As defined in the Clean Air Act.
b 1990 Motor Vehicle Manufacturer's Association (MVMA) survey.
c Winter (W) Reid Vapor Pressure (RVP) higher than Summer (S) to maintain vehicle performance.
d Oxygenate concentrations shown are for separate batches of fuel; combinations of both methyl tertiary butyl ether (MTBE) and ethanol (EtOH) in the same blend can never be above 15 volume percent total.
e Except as noted, values in this column are volume-weighted average based on preliminary analysis of a portion of 1996 RFG batch reporting data submitted to EPA by refineries and importers. Numbers are subject to change.
f The lower RVP number is average for RFG designated for sale in VOC Control Region 1; the higher RVP number for VOC Control Region 2. In general, Region 1 areas are to the south and/or west.
g This is a "typical" value for an RFG batch containing MTBE as the sole oxygenate; this provides about 2% oxygen by weight.
h This is a "typical" value for an RFG batch containing ethanol. Ethanol is not combined with other oxygenates in VOCcontrolled RFG. There are economic incentives for blending ethanol at this level, which provides about 3.5% oxygen by weight
i. T(50) and T(90) refers to temperatures at which 50% and 90%, respectively, of gasoline volume is distilled.

Table 2-2. Summary of sample collections in urban MEs

ME #	ME Description	Replicates	Biomarker	5 min Canister	Sampling Time (min)
1	In-Cabin Congested Freeway	5			40
2	In-Cabin Urban Canyon	3			40
3	In-Cabin Refueling	5			20
4	In-Cabin Underground Garage	5			40
5	In-Cabin Toll Plaza	3			40
6*	Roadway Tunnel	5			40
7	Outdoor Refueling	5	yes	yes	20
8	Sidewalk	3			40
8/9	Sidewalk/Bus Stop	3			40
10	Outdoor Surface Parking	3			40
11	Outdoor Underground Garage	5	yes	yes	40
12	Outdoor Toll Plaza	3			40
13*	In-cabin Trailing High-Emitting Vehicles	5	yes	yes	40

*ME13 was substituted for ME6 in Atlanta and Chicago.

Table 2-3. Mass ratios of MTBE to benzene in Houston by ME.

Microenvironment	ME	Summer	Winter
Freeway	1	1.72 ± 0.49	2.88 ± 1.33
Urban Canyon	2	1.10 ± 0.41	2.56 ± 0.80
In-Cabin Refueling	3	24.91 ± 12.19	41.96 ± 21.35
In-Cabin Underground Garage	4	3.22 ± 1.49	2.35 ± 1.78
In-Cabin Toll Plaza	5	2.49 ± 0.77	2.99 ± 1.14
Tunnel	6	2.74 ± 0.42	5.33 ± 6.63
Outdoor Refueling	7	28.82 ± 12.01	55.77 ± 26.83
Sidewalk	8	2.34 ± 0.19	1.15 ± 0.06
Bus Stop	9	2.87 ± 1.13	1.31 ± 0.18
Surface Parking	10	1.94 ± 0.36	6.93 ± 6.57
Outdoor Underground Garage	11	2.60 ± 0.37	3.30 ± 1.50
Outdoor Toll Plaza	12	2.48 ± 1.81	2.78 ± 1.18

Table 2-4. Mass ratios of MTBE to benzene in vehicle exhaust, gasoline vapor and liquid gasoline.

Test Set	Fuel	Year	Average	Stdev	Reference
Ratios in LDGV Exhaust					
CRPAQS/GDS dyno exhaust	Los Angeles	2001	0.62	1.35	Fitz et al. 2003
CRPAQS/GDS dyno warm-starts	Los Angeles	2001	0.43	1.43	Fitz et al. 2003
CRPAQS/GDS dyno hi-em	Los Angeles	2001	1.11	3.17	Fitz et al. 2003
SWRI FTP - summer	Houston	2004	0.44	0.24	Merritt, 2005
SWRI FTP - winter	Houston	2005	1.40	0.55	Merritt, 2005
SWRI FTP- normal	Houston	2004 and 2005	0.60	0.45	Merritt, 2005
SWRI FTP- malfunction	Houston	2004 and 2005	1.24	0.71	Merritt, 2005
Ratios in Tunnel and Roadway Samples					
WEO3 on-road	Los Angeles	2000	2.96	1.03	Fujita et al.2003a; Fujita et al., 2003b
LA tunnels-corrected for running loss	Los Angeles	1995 and 1996	0.32	0.99	Fujita et al., 2003b
LA tunnels, uncorrected	Los Angeles	1995 and 1996	1.69	0.54	Fujita et al., 2003b
API houston tunnel (ME6)	Houston	2004 and 2005	3.36	1.35	This study
Ratio in Gasoline Vapor					
LA vapor	Los Angeles	1995	16.63		Fujita et al., 2003b
WEO3 vapor	Los Angeles	2000	44.98		Fujita et al.2003a; Fujita et al., 2003b
SWRI shed - malfunction	Houston	2004 and 2005	20.52	29.20	Merritt, 2005
SWRI shed - malfunction, outlier removed	Houston	2004 and 2005	5.93	1.60	Merritt, 2005
estimated from fuel content - summer	Houston	2004	32.8		Merritt, 2005
estimated from fuel content - winter	Houston	2005	43.9		Merritt, 2005
Ratios in Liquid Gasoline					
LA gasoline - 1995 RFG	Los Angeles	1995	11.79		Fujita et al., 2003b
WEO3 gasoline	Los Angeles	2000	19.56	5.23	Fujita et al.2003a; Fujita et al., 2003b
gds gasoline	Los Angeles	2001	17.15	5.49	Gabele, 2003
API gasoline - summer	Houston	2004	13.28		Merritt, 2005
API gasoline - winter	Houston	2004	17.87		Merritt, 2005

Table 2-5. Fractional contributions of evaporative emissions to total motor vehicles emissions in Houston by ME.

Microenvironment	ME	Summer	Winter
Freeway	1	0.04 ± 0.02	0.03 ± 0.03
Urban Canyon	2	0.02 ± 0.01	0.03 ± 0.02
In-Cabin Refueling	3	0.76 ± 0.38	0.95 ± 0.50
In-Cabin Underground Garage	4	0.09 ± 0.05	0.02 ± 0.04
In-Cabin Toll Plaza	5	0.06 ± 0.02	0.04 ± 0.03
Tunnel	6	0.07 ± 0.01	0.09 ± 0.16
Outdoor Refueling	7	0.88 ± 0.37	1.28 ± 0.63
Sidewalk	8	0.06 ± 0.01	-0.01 ± 0.00
Bus Stop	9	0.08 ± 0.04	0.00 ± 0.00
Surface Parking	10	0.05 ± 0.01	0.13 ± 0.15
Outdoor Underground Garage	11	0.07 ± 0.01	0.04 ± 0.04
Outdoor Toll Plaza	12	0.06 ± 0.06	0.03 ± 0.03

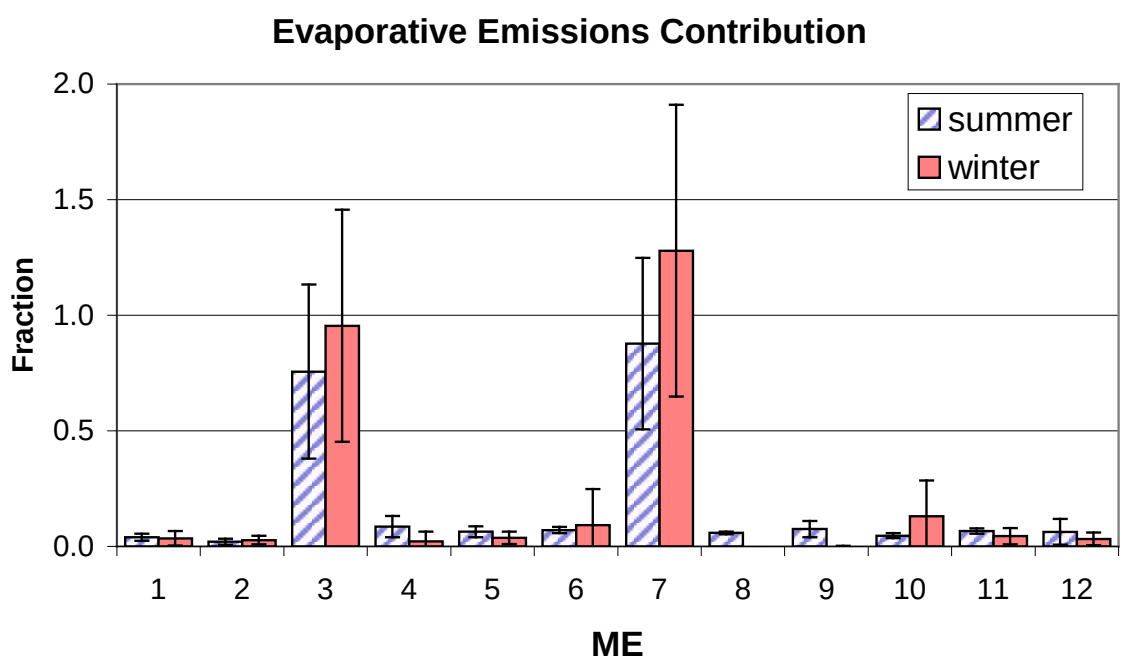

Figure 2-1.Fractional contributions of evaporative emissions to total motor vehicles emissions in Houston by ME.

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3. Determination of the Quantitative Relationships between Levels of Volatile Air Toxics and Carbon Monoxide Measured In High End Microenvironments and At Nearby Air Quality Monitoring Stations

3.1 Introduction

The U.S. Environmental Protection Agency conducts national-scale assessments of air toxics in order to set program priorities, characterize risks, and track progress towards achieving the goals of the national air toxics program as established by the 1990 Clean Air Act Amendments (CAAA). As part of the National Air Toxics Assessment (NATA), EPA conducted a national screening-level assessment for 1996 and 1999 to characterize the potential risks associated with inhalation exposures to 33 air toxics and diesel particulates. The screening-level assessment estimated outdoor air toxics concentrations across the US and related these concentrations to population exposures.

The Assessment System for Population Exposure Nationwide (ASPEN) model was used by EPA to estimate outdoor air toxics concentrations across for every census tract in the continental United States, Puerto Rico and the Virgin Islands. To enable the simulation of a large number of air toxics nationwide, a number of simplified approaches are incorporated into the model. The model uses a simplified approach to simulate atmospheric chemistry such as reactive decay and secondary formation (production of an air toxics compound due to chemical reactions in the atmosphere). A uniform background concentration is added for some pollutants for which information is available to compensate because the model simulates only pollutant transport within 50 kilometers of any individual source. For those air toxics with high levels of background concentrations, the model's ability to predict ambient concentrations are greatly impacted by the accuracy of background estimates. Past comparisons with limited monitoring data show that the modeled air toxics concentrations are generally within two orders of magnitude of measured concentrations.

For the exposure-modeling portion of the analysis, EPA used the Hazardous Air Pollutant Exposure Model (HAPEM). The HAPEM modeling approach simulates the movements of various population groups through zones of varying air quality. Each zone is defined by a geographic location (typically a census tract) and a microenvironment (ME). The patterns of movements among the zones are determined by diary-derived activity data and commuting data acquired from the U.S. census. Ambient concentrations are estimated by the ASPEN dispersion model based on local emissions and meteorological data. The pollutant concentration in a specific ME is estimated as a function of the ambient concentration by a linear expression containing three terms that vary with ME: the penetration factor (the indoor/outdoor ratio in the absence of indoor sources), the additive factor (accounts for contribution of indoor sources), and the proximity factor (accounts for distance to specific outdoor sources such as roadways). Estimates for these factors for 33 HAPS have been obtained from various field studies and from previous modeling exercises. In general, there is a high degree of uncertainty associated with HAPEM exposure estimates because of the limited data available for estimating the ME factors (Rosenbaum, 2005).

The DRI conducted measurements quantifying exposures to automotive emissions in microenvironments (MEs) representing the upper-end (> 99th percentile) of the distribution of inhalation exposures to evaporative and exhaust emissions of conventional and oxygenated-gasoline. The study was conducted as part of the Section 211(b) Tier 2 High-End Exposure Screening Study of Baseline and Oxygenated Gasoline. DRI and SwRI conducted measurements under controlled conditions to establish quantitative relationships between tailpipe and evaporative emission rates to exposure levels in a vehicle cabin and attached residential garage. Field exposures also were measured in several high-end exposure MEs in Atlanta, Chicago, and Houston during winter and summer. Target species (TVOC, CO, BTEX, HCHO,1,3-BD, MTBE, EtOH) were measured within MEs, breathing zones, and breath. This section examines the quantitative relationships between CO exposure levels in these MEs to the corresponding fixed site measurements at nearby air monitoring stations. These comparisons are extended for Houston to volatile organic mobile source air toxics, which was the only city among the three with available data. These relationships are compared to the HAPEM proximity factors (Long and Johnson, 2004) that were used in the National Air Toxics Assessments.

3.2 Experimental

DRI measured seasonal in-cabin breathing zone exposures for urban roadways and other high-end MEs in Houston (6/3-7/9/04; 2/1-2/8/05), Chicago (8/5-8/20/03; 3/3-3/17/04), and Atlanta (7/28-8/8/02; 8/23-9/3/03; 2/10-2/29/04) using a combination of time-integrated samples and continuous instruments for thirteen different MEs listed in Table 3-1. Three replicate exposure measurements were made for low variability MEs and five for MEs with higher variability (i.e., ME13-trailing high emitting vehicles, ME11-underground garages, and ME7-outdoor refueling). Measurements in each ME were taken over a period of 20-40 minutes beginning at the top of the hour. Shorter sampling times were used for refueling events and parking garage exits after sporting events.

The integrated samples included whole-air canister samples for CO, BTEX, MTBE, and 1,3-BD, acidified 2,4-diphenylhydrazine (DNPH) cartridges for HCHO and CH_3CHO, and a multi-bed (TenaxTA-Carbotrap-Carbosieve) solid adsorbent tube for EtOH. Continuous measurements included both non-dispersive infrared (NDIR) and passive electrochemical (Langan T-15) devices for CO and an active photo-ionization detector (PID) for TVOC with an ionization potential below 10.6 eV (principally olefins and aromatic species). Sampling and analytical methods are described in Section 1 and in the study plan (Zielinska et al., 2003).

Ambient CO and VOC data were retrieved from EPA's Air Quality System (AQS) for the specific periods of the field study in each city and compared to the ME measurements. The ambient monitoring and ME locations are mapped for each city in Figures 3-1a to 3-1c although some ME locations are overlapped by adjacent MEs. AQS VOC data were not available for Atlanta; incomplete data were available for a single site (Northbrook, IL) in Chicago located 20 miles N/NW of city center that is unlikely representative of urban Chicago. Speciated hourly GC/FID VOC data were available from two sites in Houston for both summer and winter. All sites reporting CO and VOC data within each metropolitan area were averaged together for the purposes of comparison. The average CO and benzene concentrations did not show substantial spatial variation within each city.

3.3 Results and Discussion

Exposure levels are directly related to source emission rates in the ME and inversely related to source distance and the extent of dilution, itself a function of meteorology and any physical obstructions that inhibit dilution. Hourly values from air quality monitoring stations in urban areas typically represent neighborhood scale exposure levels while 20-40 minute measures from MEs listed in Table 3-1 are intended to represent the high end exposures exceeding the 99th percentile. Consequently, the tabulated ME ratios reflect exposures scripted to reflect 'worst-case' conditions rather than population-average ME factors for these locations. Such information should be used solely to evaluate extreme exposures and not misinterpreted as 'typical' ME exposures encountered by the general population.

Quantitative relationships for CO between ME measures and fixed site measurements at nearby air monitoring stations are examined first. CO is non-reactive and commonly measured year-round as a primary mobile source emission that is generally correlated with BTEX and 1,3-BD. Table 3-2 shows the averages and standard deviations of the ratios of time-integrated CO from canister samples to the corresponding hourly CO from the ambient air monitoring stations in Houston, Atlanta, and Chicago by season and ME. As expected, the ratios are higher in MEs that are nearer to operating vehicle engines, especially in underground garages where dispersion of pollutants is limited. The average ratios for in-cabin exposures in congested freeway traffic ranged from 2 to 9 with lower ratios in the winter. Ratios were highest in Atlanta and lowest in Chicago. The seasonal and city-specific differences hold for most of the other MEs. Notable exceptions to the seasonal differences are the underground garages where the ratios are higher in the winter in all three cities, most likely due to the higher cold-start emissions. Garage size, ventilation, and spatial-temporal vehicle activity patterns account for the variance differences between underground garages. The garage in Atlanta is smaller, less ventilated, and more used than the garages in Houston or Chicago. While CO is a good exhaust species tracer, correlation with evaporative emissions is less. ME/ambient ratios are generally lower for CO than most of the other pollutants. This is most likely due to higher urban background levels of CO.

Table 3-3 shows average Houston BTEX and 1,3-BD ME/ambient ratios (± SD), i.e., the time-integrated canister value to the corresponding hourly monitoring station GC/FID value. In contrast to CO, BTEX ME/ambient ratios are substantially higher for refueling (ME 3, ME 7). The BTEX ratios are closer to corresponding ratios derived for CO during winter but higher during summer. Since 1,3-BD is an exhaust species, the relative variation of ME/ambient ratios is similar to CO. 1,3-BD measures in MEs with high MTBE were invalid due to interferences (see Section 1).

The integrated exposure measurements are 20-40 minute averages. Continuous CO and VOC PID measurements show higher peak (1-5 minutes) exposures. Continuous instruments provide sensitive proportionate measures of short-term target species variability since continuous time-averaged traces are well correlated to the corresponding time-integrated measurements. Consequently, the normalized continuous CO or VOC PID measures were used to reconstruct 1-minute time-series concentrations for specific components. Either CO or VOC PID traces are suitable surrogates in exhaust-dominated MEs; VOC PID values are suitable surrogates in evaporative emissions-dominated MEs such as refueling. Reconstructed time-series and ranges

of estimated 1-minute values are summarized in Section 1. Figures 3-2a through 3-2c show 20-40 minute average and maximal estimated 1-minute values for benzene, 1,3-BD, and HCHO, respectively. Short-term exposures from evaporative-dominated ME3 and ME7 range more widely than those from other exhaust-dominated MEs.

3.4 Conclusions

MEs in close proximity to running vehicle engines have enhanced CO relative to ambient levels with enrichment ratios approaching 40 where ventilation is limited, as in underground garages. Average in-cabin CO/ambient ratios in congested freeway traffic range from 2-9 with lower winter ratios. ME locations less proximate to operating vehicles, such as gas stations and urban sidewalks, have CO/ambient ratios of 0.5-2.

The Houston benzene ME1/ambient ratio of 9.8 ± 3.8 for exceed the HAPEM5 median proximity factor of 4.9 (triangular distribution mode:range 1.9:0-14.3) and HAPEM4 proximity factor of 6.9 for this ME (Rosenbaum, 2005; Long and Johnson, 2004), although by less than expected. The HAPEM4 factors may be elevated compared to present conditions since measurements occurred before 1991 when benzene fuel levels and roadway fleet emissions were higher than today. HAPEM5 proximity factors may also need to be adjusted since they were based on a 1998 scoping study where measurements ‘highlighted trailing behind heavy duty diesel vehicles and diesel city buses when possible’. Houston ME/ambient ratio comparisons also generally exceed the other HAPEM factors listed in Table 3-4. Refueling ratios (ME3, ME7) for benzene were substantially higher than the corresponding HAPEM factors also as expected. Concentrations of exhaust compounds such as CO and 1,3-BD were enhanced under reduced ventilation situations.

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Table 3-1. Summary of sample collections in urban microenvironments

ME #	ME Description	Replicates	Biomarker	5 min Canister	Sampling Time (min)
1	In-Cabin Congested Freeway	5			40
2	In-Cabin Urban Canyon	3			40
3	In-Cabin Refueling	5			20
4	In-Cabin Underground Garage	5			40
5	In-Cabin Toll Plaza	3			40
6*	Roadway Tunnel	5			40
7	Outdoor Refueling	5	yes	yes	20
8	Sidewalk	3			40
8/9	Sidewalk/Bus Stop	3			40
10	Outdoor Surface Parking	3			40
11	Outdoor Underground Garage	5	yes	yes	40
12	Outdoor Toll Plaza	3			40
13*	In-cabin Trailing High-Emitting Vehicles	5	yes	yes	40

*ME13 was substituted for ME6 in Atlanta and Chicago.

Table 3-2. Average and standard deviation in ratios of the time-integrated CO from canister samples to the corresponding hourly CO from regional ambient air monitoring sites for Houston, Atlanta and Chicago by season and microenvironment.

		Summer			Winter		
Microenvironment		**Houston**	**Atlanta**	**Chicago**	**Houston**	**Atlanta**	**Chicago**
1	Congested Freeway, In-Cabin	4.6 ± 1.0	9.1 ± 6.5	2.6 ± 0.4	4.0 ± 1.0	5.4 ± 1.9	1.7 ± 0.4
2	Urban Canyon, In-Cabin	5.2 ± 2.5	3.9 ± 3.9	2.9 ± 1.4	12.1 ± 10.9	2.7 ± 5.6	1.0 ± 0.5
3	Refueling, In-Cabin	3.6 ± 0.9	1.4 ± 2.7	0.7 ± 0.3	4.1 ± 3.2	1.3 ± 0.6	0.5 ± 0.1
4	Underground Garage, In-Cabin	8.4 ± 8.0	16.9 ± 0.8	7.9 ± 3.4	21.4 ± 12.5	38.8 ± 0.2	12.6 ± 5.8
5	Toll Plaza, In-Cabin	4.1 ± 1.0	6.4 ± 0.0	1.6 ± 0.5	3.6 ± 0.6	2.7 ± 0.0	1.0 ± 0.1
6	Tunnel, In-Cabin	8.4 ± 1.7		6.3 ± 1.5	9.7 ± 5.2		2.5 ± 0.4
7	Refueling, Outdoor	1.9 ± 0.8	1.2 ± 1.8	0.9 ± 0.3	3.3 ± 2.5	2.1 ± 1.4	0.8 ± 0.9
8	Sidewalk	1.9 ± 0.5	1.9 ± 0.5	1.1 ± 0.2	1.3 ± 0.6	1.9 ± 0.9	0.9 ± 0.0
9	Sidewalk/BusStop	1.5 ± 0.3	2.4 ± 0.3	1.6 ± 0.6	1.8 ± 0.1	1.9 ± 0.2	1.1 ± 0.2
10	Surf Parking, Outdoor	3.3 ± 1.2	5.3 ± 0.7	2.1 ± 1.3	4.7 ± 2.9	3.3 ± 0.6	1.4 ± 0.5
11	Underground Garage, Outdoor	8.6 ± 7.4	26.8 ± 3.6	3.9 ± 2.3	17.1 ± 11.2	32.9 ± 2.0	12.4 ± 7.2
12	Toll Plaza, Outdoor	7.6 ± 2.7	6.5 ± 8.8	3.2 ± 0.2	6.2 ± 4.3	7.4 ± 16.5	1.8 ± 0.3
13	Following High Emitter, In-Cabin		8.4 ± 2.6			12.0 ± 4.2	

Table 3-3. Average and standard deviations in ratios of BTEX and 1,3-BD from time-integrated canister samples to the corresponding hourly automated GC data from the ambient air monitoring sites in Houston.

Microenvironment		Benzene	Toluene	Etbenzene	m&p-Xylene	o-Xylene	1,3-Butadiene
Summer							
1	Congested Freeway, In-Cabin	9.8 ± 3.8	7.8 ± 1.9	5.4 ± 1.8	5.2 ± 0.6	6.6 ± 1.5	8.1 ± 3.6
2	Urban Canyon, In-Cabin	7.4 ± 3.0	6.8 ± 1.1	5.6 ± 3.3	5.6 ± 1.4	5.8 ± 2.4	7.3 ± 1.2
3	Refueling, In-Cabin	565 ± 791	446 ± 666	140 ± 188	115 ± 136	117 ± 147	
4	Underground Garage, In-Cabin	19.4 ± 13.9	17.2 ± 15.0	16.0 ± 13.7	14.2 ± 12.8	17.1 ± 17.0	50.0 ± 66.4
5	Toll Plaza, In-Cabin	9.1 ± 4.4	7.8 ± 3.6	6.8 ± 4.9	6.2 ± 3.4	7.1 ± 3.8	7.8 ± 5.2
6	Tunnel, In-Cabin	25.9 ± 14.1	12.4 ± 6.8	7.8 ± 2.9	7.5 ± 2.7	8.9 ± 2.7	37.9 ± 20.0
7	Refueling, Outdoor	1312 ± 1811	974 ± 1356	335 ± 479	219 ± 227	197 ± 198	
8	Sidewalk	15.4 ± 10.6	10.6 ± 4.4	12.5 ± 15.3	11.9 ± 14.0	14.2 ± 17.1	5.8 ± 2.4
9	Sidewalk/BusStop	4.7 ± 2.0	2.9 ± 1.3	1.8 ± 0.4	1.9 ± 0.5	2.3 ± 0.6	2.0 ± 1.3
10	Surf Parking, Outdoor	11.5 ± 5.5	8.3 ± 2.8	7.4 ± 2.1	6.7 ± 3.1	7.0 ± 3.2	5.5 ± 1.9
11	Underground Garage, Outdoor	16.7 ± 5.3	15.7 ± 7.2	13.8 ± 7.2	11.1 ± 7.2	14.4 ± 9.6	39.6 ± 29.5
12	Toll Plaza, Outdoor	14.7 ± 8.5	11.3 ± 10.2	9.2 ± 8.3	8.5 ± 7.6	11.0 ± 10.6	13.4 ± 13.1
Winter							
1	Congested Freeway, In-Cabin	4.6 ± 1.6	6.4 ± 3.7	6.4 ± 3.0	8.8 ± 5.2	9.7 ± 5.1	0.36 ± 0.06
2	Urban Canyon, In-Cabin	17.0 ± 21.7	22.7 ± 27.7	22.1 ± 26.4	31.1 ± 36.9	26.7 ± 28.9	
3	Refueling, In-Cabin	35.0 ± 25.4	36.5 ± 27.2	22.7 ± 18.2	25.3 ± 19.2	24.2 ± 16.3	
4	Underground Garage, In-Cabin	37.2 ± 15.8	32.3 ± 12.9	24.0 ± 9.4	23.2 ± 8.5	25.0 ± 9.7	
5	Toll Plaza, In-Cabin	3.5 ± 1.7	3.7 ± 1.5	4.3 ± 1.7	4.6 ± 2.0	5.3 ± 2.1	
6	Tunnel, In-Cabin	8.5 ± 6.7	9.0 ± 6.9	7.0 ± 4.5	8.9 ± 6.4	9.9 ± 7.2	1.91 ± 0.54
7	Refueling, Outdoor	160 ± 148	119 ± 92	49.1 ± 39.2	56.1 ± 54.3	44.6 ± 33.7	
8	Sidewalk	2.8 ± 0.8	2.6 ± 1.0	2.7 ± 0.7	3.6 ± 1.7	3.7 ± 1.3	0.09 ± 0.10
9	Sidewalk/BusStop	3.3 ± 0.3	3.6 ± 0.3	3.5 ± 1.1	4.2 ± 0.7	4.3 ± 0.8	
10	Surf Parking, Outdoor	4.3 ± 3.0	7.5 ± 6.4	5.7 ± 2.9	6.1 ± 2.1	6.0 ± 2.5	
11	Underground Garage, Outdoor	28.3 ± 16.5	25.0 ± 13.0	20.8 ± 11.3	21.9 ± 11.1	22.9 ± 10.7	0.60 ± 0.03
12	Toll Plaza, Outdoor	4.8 ± 0.7	4.5 ± 1.4	4.5 ± 1.8	4.9 ± 1.6	5.4 ± 1.9	

Table 3-4. Houston benzene ME/ambient ratio comparison with HAPEM benzene ME factors

ME	Summer	Winter	HAPEM4 PROX	HAPEM5 PROX Distribution (mode;median)	*HAPEM5 PROX Range*
1 Congested Freeway, In-Cabin	9.8	4.6	5.2, 6.9*	Triangular 1.9; 4.9	*0-14.4*
2 Urban Canyon, In-Cabin	7.4	17	4.4	Triangular 1.9; 4.9	*0-14.4*
3 Refueling, In-Cabin	565	35	4.4	Triangular 1.6; 2.7	*0-7.1*
4 Underground Garage, In-Cabin	19	37	1.0	Triangular 1.6; 2.7	*0-7.1*
5 Toll Plaza, In-Cabin	9.1	3.5	4.4	Triangular 1.9; 4.9	*0-14.4*
6 Tunnel, In-Cabin	26	8.5	4.4	Triangular 1.9; 4.9	*0-14.4*
7 Refueling, Outdoors	1300	160	4.4	Triangular 1.6; 2.7	*0-7.1*
8 Sidewalk	15	2.8	4.4	Triangular 1.6; 2.7	*0-7.1*
9 Sidewalk, BusStop	4.7	3.3	4.4	Triangular 1.6; 2.7	*0-7.1*
10 Surface Parking, Outdoors	12	4.3	4.4	Triangular 1.6; 2.7	*0-7.1*
11 Underground Garage, Outdoors	17	28	1.0	Triangular 1.6; 2.7	*0-7.1*
12 Toll Plaza, Outdoors	15	4.8	4.4	Triangular 1.6; 2.7	0-7.1

* truck, car

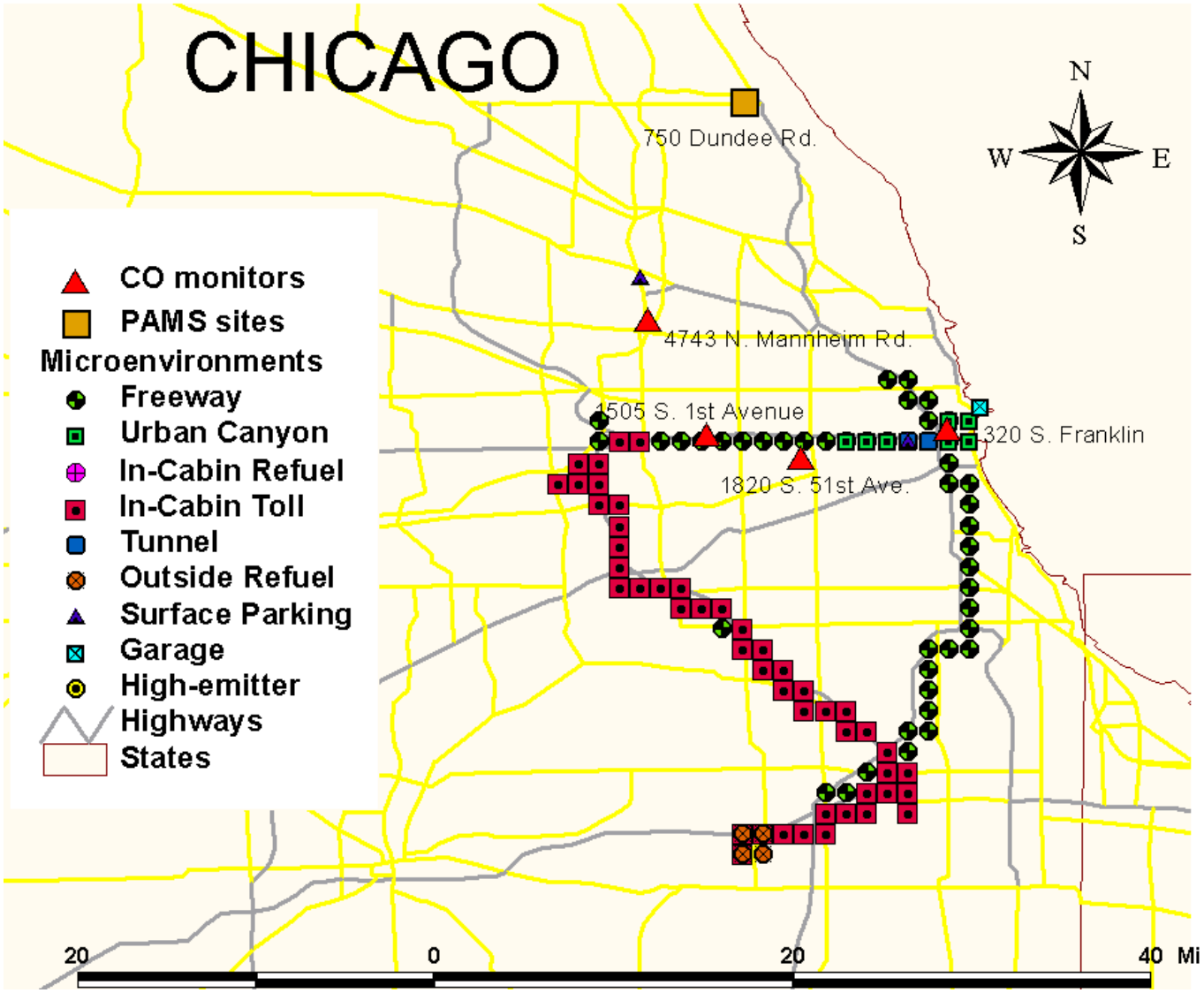


Figure 3.1a. Location of ME sampling and fixed monitoring stations in Chicago Metro Area.

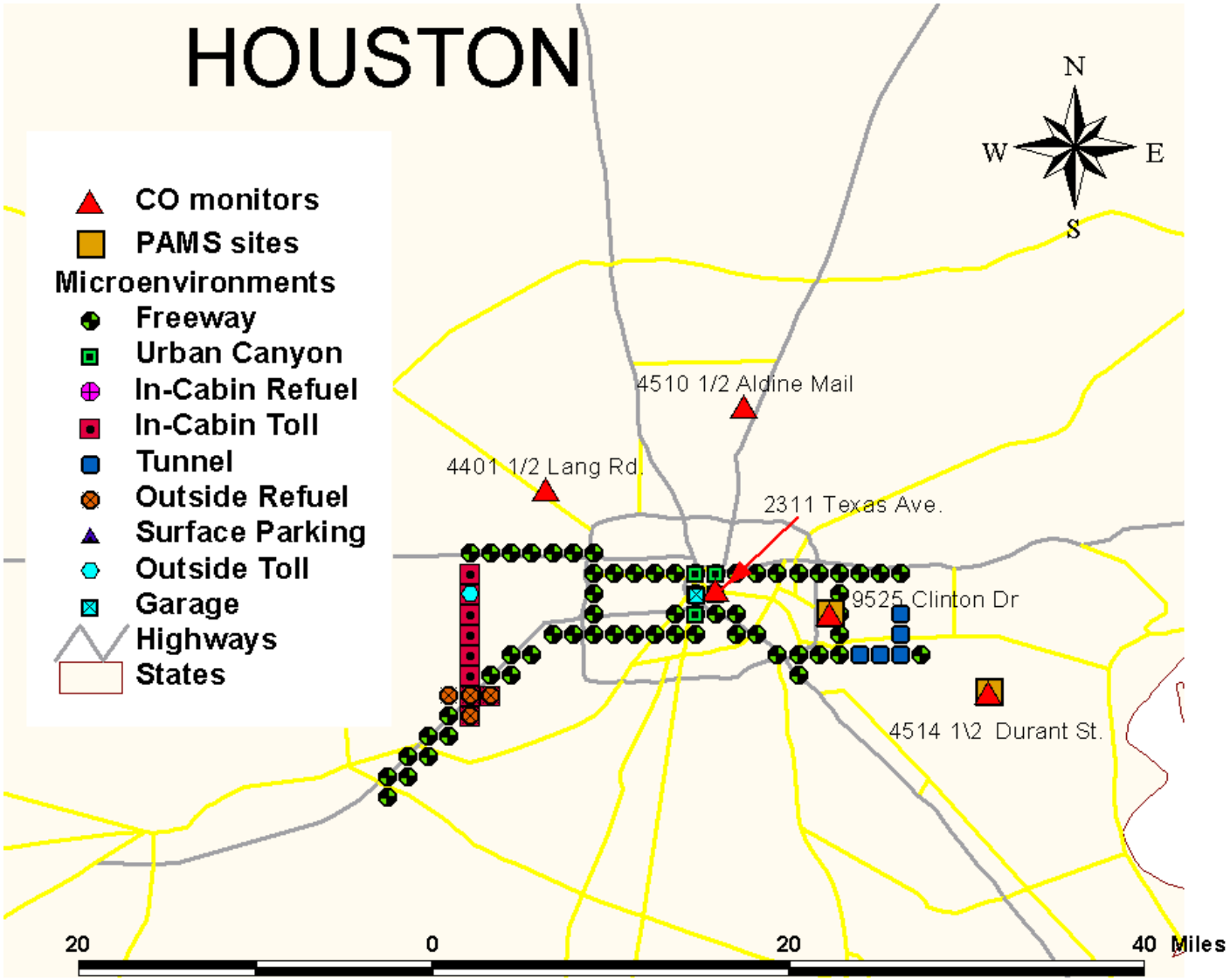


Figure 3.1b. Location of ME sampling and fixed monitoring stations in Houston Metro Area.

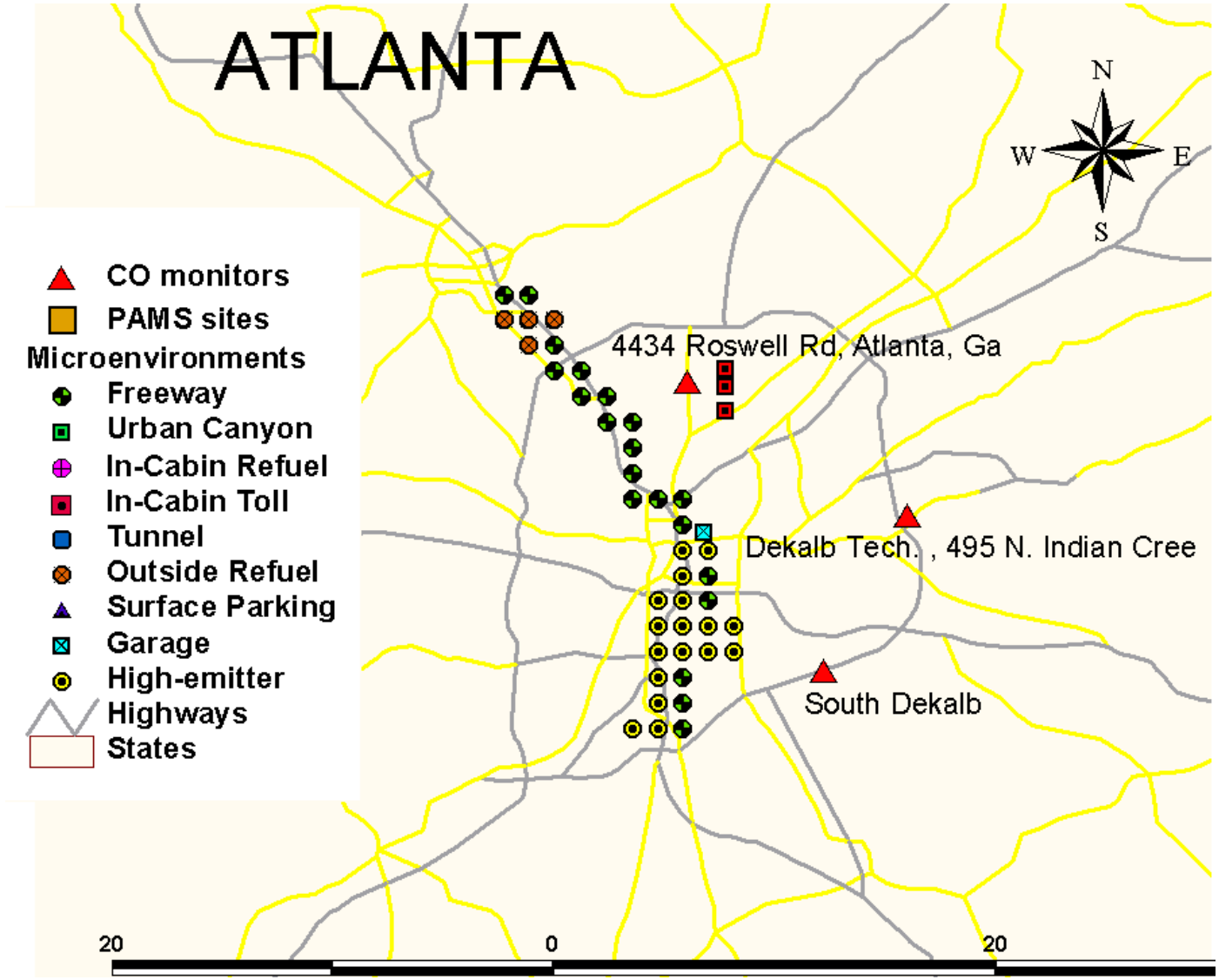
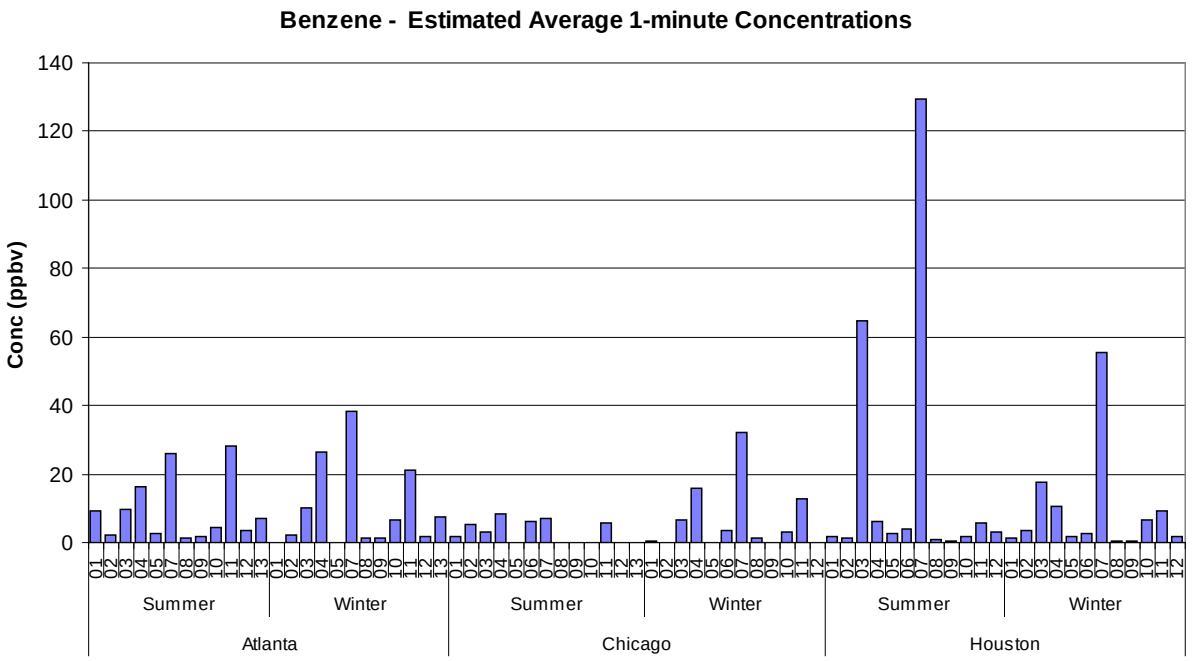


Figure 3.1c. Location of ME sampling and fixed monitoring stations in Atlanta Metro Area.



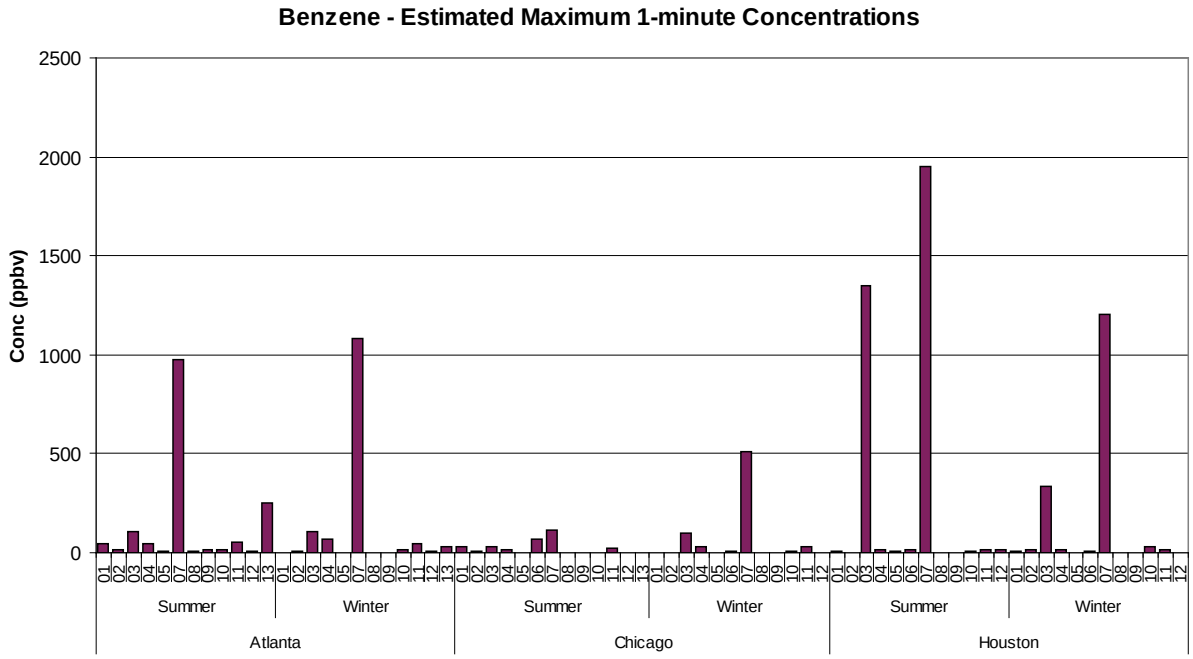


Figure 3-2a. Comparison of average versus the maximum 1-minute benzene levels by city, season and microenvironment.

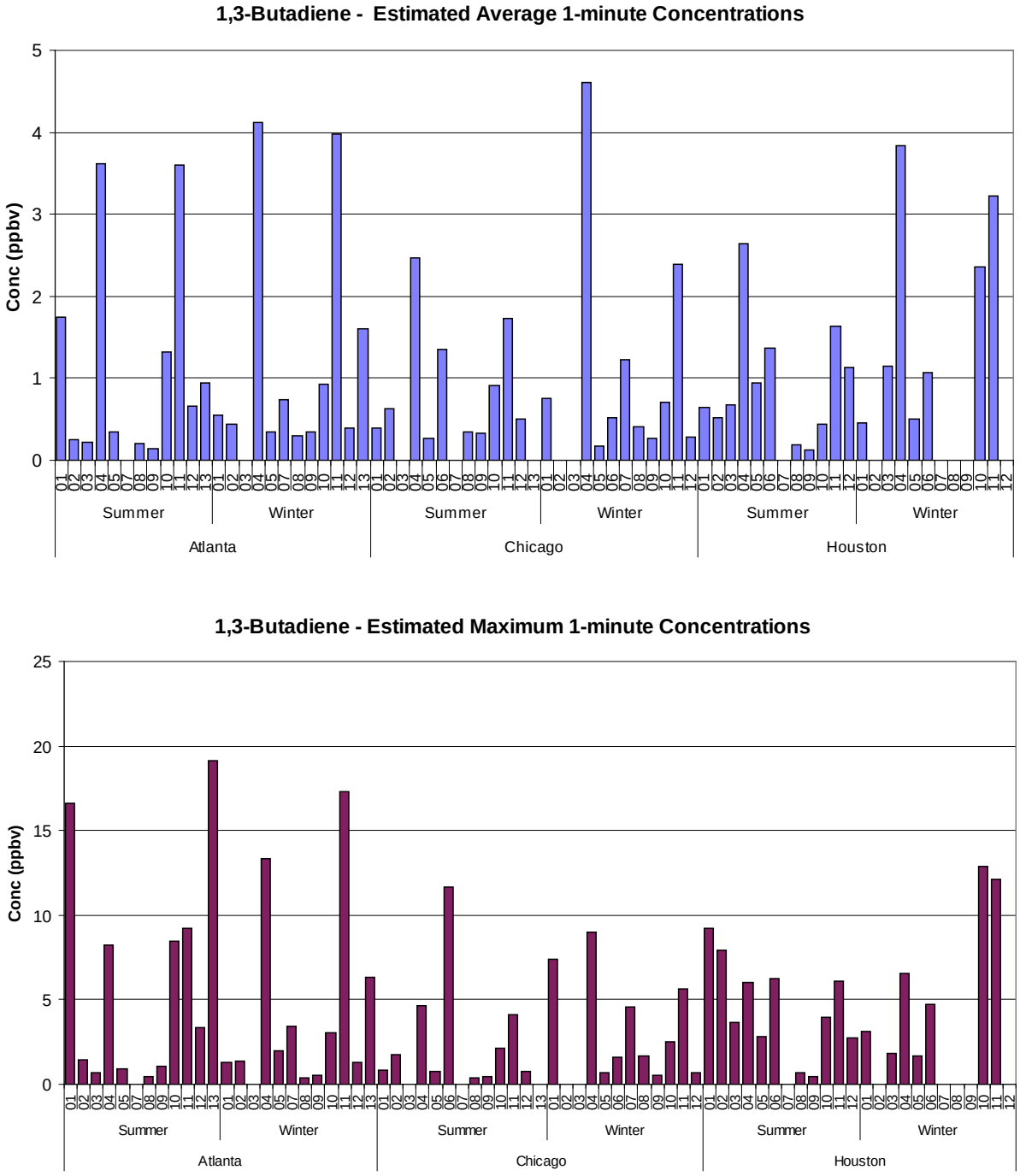


Figure 3-2b. Comparison of average versus the maximum 1-minute 1,3-butadiene levels by city, season and microenvironment.

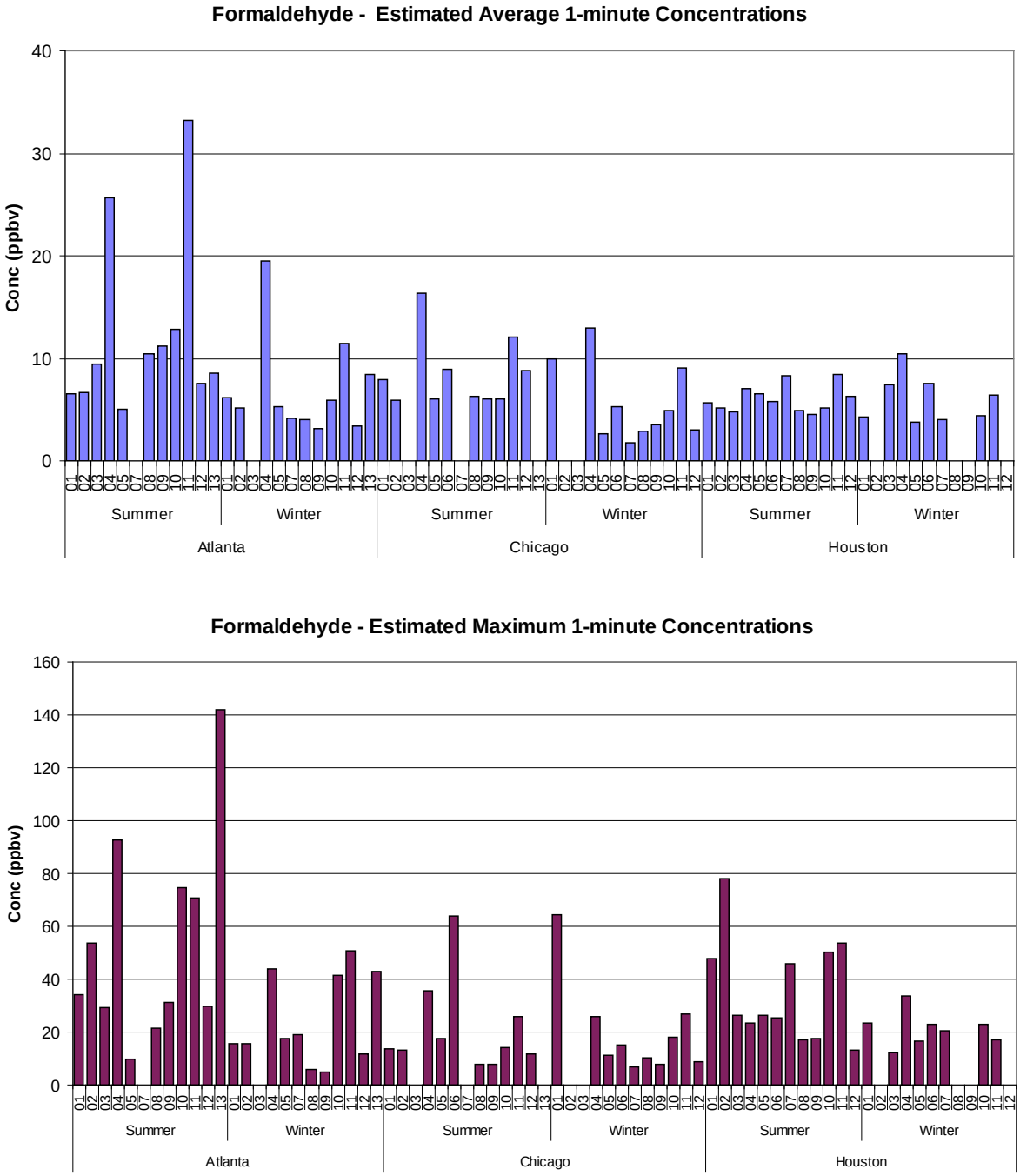


Figure 3-2c. Comparison of average versus the maximum 1-minute formaldehyde levels by city, season and microenvironment.

4. Relationships of Attached Garage and Home Exposures to Fuel Type and Emission Levels of Garage Sources

4.1 Introduction

This chapter describes experiments to determine relationships between measured fuel and exhaust components in the attached garage, adjacent room (kitchen), and garaged vehicle emission levels. The same vehicles, fuels and vehicle malfunctions used here are used in Chapter 5 to explore the effects of ventilation, proximity, and leading vehicle emission levels on trailing vehicle in-cabin exposures. These measurements are also described in the executive summary and Chapter 1.

Measurements were performed during June-July 2002 and February-March 2005 in San Antonio, TX on a sedan and a pickup truck using either non-oxygenated conventional gasoline, gasohol (E10), or an MTBE-oxygenated gasoline. The vehicles were tested in both a normal emissions mode and a malfunctioning high emitter mode where emissions were adjusted to exceed 2 grams of non-methane hydrocarbons (NMHC) per mile as measured by the Federal Test Procedure (FTP).

4.2 Experimental

Methods and procedures specific to the attached garage experiments are summarized below. Sampling and analyses methods are described in Chapter 1 and Appendix B.

4.2.1 Vehicles and Vehicle Test Methods

The Southwest Research Institute (SwRI) procured two test vehicles and determined their evaporative/tailpipe emissions in the normal/malfunction modes using the three test fuels. The test vehicles, a sedan and full-sized V8 truck, were chosen within the 1993-1996 model years from vehicles with 90,000-110,000 odometer miles. The chosen 1993 Toyota Camry (2.2L 4-cylinder engine) and 1995 Ford F150 Pickup truck (5.0L V8 engine) were operated in normal, as purchased, modes and in “high emitter” modes with the catalytic converter removed and emission levels above 2 grams per mile NMHC as measured on the FTP driving cycle. While converter removal sufficed for the F150 truck, a calibrated manifold leak was also needed to achieve the ≥ 2g/mile Camry emissions. SwRI determined dynamometer FTP emissions for each vehicle with all three fuels in the two emission modes (24 tests). Emission control components could be reproducibly adjusted to represent normal and reasonable high-end approximations (≥ 2g/mile) of real world exhaust emissions. The vehicle properties are summarized in Table 4.2-1 and included in the SwRI report (Appendix F).

Table 4.2-1. Summary of vehicles used.

Vehicle	Make	Model	Year	Engine	Malfunction
Truck	Ford	F150	1995	5.0 L V8	Removed Catalyst.
Sedan	Toyota	Camry	1993	2.2 L 4 cylinder	Removed Catalyst and added leak to manifold.

Regulated exhaust emissions (THC, NMHC, CO, NOx), fuel economy, and specific VOCs (MTBE, EtOH, BTEX, 1,3-BD, HCHO) were determined in dynamometer FTP tests. During hot-soak SHED tests, THC and specific VOCs (minus HCHO) were also determined.

The FTP exhaust emission test uses the 1372 second Urban Dynamometer Driving Schedule (UDDS) that is divided into cold/start transient 505 (Bag 1) and cold stabilized 867 (Bag 2) second segments. This portion of the FTP is followed by a 10-minute soak and a hot/start transient 505 (Bag 3) test. The FTP evaporative emission test includes one hour Diurnal Heat Build (DHB) and Hot Soak Loss (HSL) tests. THC/VOC emissions are recorded during the HSL segment of the test. Prior to the FTP cold-start exhaust test, the DHB is conducted by fueling the test vehicle to 40 percent of tank capacity with fuel < 55°F, attaching a heating blanket outside the fuel tank, placing a thermocouple in the tank fuel, hooking it up to computer control, and beginning the test as fuel reaches 60°F (increasing at 0.4°F per minute for the 60-minute test to a 84°F final temperature).

In the HSL segment, conducted immediately following exhaust emission testing, the vehicle is driven into an evaporative emission enclosure and allowed to “soak” in the enclosure for one hour. THC/VOC emissions are measured at the beginning and end of the one-hour segment and hot soak evaporative emissions are calculated.

4.2.2 Fuel Testing

Test fuel samples were subject to standard tests for Reid Vapor Pressure (RVP), distillation range, Specific Gravity, Sulfur, Benzene, HC Category (saturates, olefins, aromatics), Oxygenated species (MTBE/EtOH), carbon weight percent, hydrogen weight percent, oxygen weight percent, and octane number. These results are presented in Table 4.3-1.

4.2.3 Test House

Fuel component levels were measured in the garage and in a room (kitchen) adjacent to an attached garage using the fuels and test vehicles in normal and high emitter modes. Appendix I shows the layout of the house. The double garage contained an active ceiling fan that minimized emissions stratification and hot spots within the garage. The garage also contained a plastic gasoline container and gasoline-powered lawnmower filled with the test fuels. The exhaust fan over the kitchen’s stove was not used during the

experiments. However, the central air conditioning was active during the summer tests. Garage and kitchen monitoring was conducted according to the scenarios described in Table 4.2-2. Window and door openings, of the garage vehicle door, the kitchen door between the garage and kitchen, and kitchen window were scripted. Time-integrated canister, DNPH and solid adsorbent (for EtOH) cartridges, and SPME samples were collected for each test. EtOH was measured for Chicago fuel only. Continuous or semi-continuous measurements were also operated during the exposure periods. Measurements were taken over scripted 30-minute scenario intervals through collocated sampling inlets at breathing height (1.5 m) a meter distant from nearby walls in the kitchen and unventilated garage. Continuous PID TVOC and Langan CO instruments sampled from the kitchen before (background) and during 2002 tests. For the winter 2005 samples, a second PID TVOC and the NDIR CO instrument were used to monitor the garage continuously. In the summer 2002 samples, the continuous MS200 BTEX and A-Ω HCHO monitors sampled cyclically through collocated inlets in the garage and kitchen every 10 minutes.

A half-filled two-gallon plastic gasoline storage container with vent opened was placed adjacent to a fueled lawnmower, with gas tank half filled, against the center of the rear garage wall common with the kitchen. The container and lawnmower filled with the appropriate fuel were placed in the garage one day before the series of vehicle tests for that fuel began and remained there over the duration of the tests. Scenario conditions were changed every 30 minutes over the 3-hour protocol as described in the Table 4.2-2. Ambient garage temperatures were recorded each 30 minutes. Tests were conducted daily (excluding weekends) over a two week period.

Table 4.2-2. Protocol for attached garage experiments.

Condition	**Time (min)**	**Garage Door**	**Kitchen Door**	**Kitchen Window**	**Inlet Location**	**Continuous Instruments**	**SPME**	**Integrated Canisters/ Cartridges**
Background No vehicle, but lawn mower & gas	10	closed	closed	closed	garage	yes	2	2
	10				kitchen	yes		
	10				garage	yes		
Hot soak vehicle, lawnmower, & gas	10	closed	opened 1 min & closed	closed	kitchen	yes	2	2
	10				garage	yes		
	10				kitchen	yes		
Cooling vehicle, lawnmower, & gas	10	closed	closed	closed	garage	yes	2	
	10				kitchen	yes		
	10				garage	yes		
Cold vehicle, lawnmower, & gas	10	closed	closed	open	kitchen	yes	2	
	10				garage	yes		
	10				kitchen	yes		

Cold start, idling, lawnmower, & gas	10	open	opened 1 min & closed	closed	garage	yes	2	
	10				kitchen	yes		
	10				garage	yes		
No vehicle, but lawnmower, & gas	10	closed	closed	closed	kitchen	yes	2	
	10				garage	yes		
	10				kitchen	yes		

The first scenario condition, background, assesses levels in the kitchen and garage prior to the beginning of vehicle testing. In the garage, background will include emissions from the gasoline container and lawn mower. The hot soak condition should most closely reflect the hot soak SHED tests performed by SwRI. In this condition, the exposure scenario is that of a person coming home from shopping and conveying purchases through the kitchen-garage door into the home, allowing some enhanced air exchange between the garage and the kitchen. The next condition, cooling vehicle, reflects a period where the trapped garage air remains in the kitchen. The cold vehicle condition is performed with the kitchen window open to allow outside fresh air exchange within the kitchen (keeping the garage door closed). The cold start condition simulates a person warming up his car in an open garage prior to leaving; the kitchen door is open for one minute to account for the extra trips to and from the vehicle. The vehicle is started and then idled for the entire 30 minutes. The final condition, no vehicle, represents kitchen exposures after the vehicle has left. One integrated canister and cartridge samples were collected over background test and another one over all five phases of the garage experiments, as shown in Table 4.2-2.

4.3 Results

4.3.1 Fuel Analyses

The results of the fuel analyses are presented in Table 4.3-1. Fewer tests were run on the Summer 2002 fuels.

The results confirm that there was no oxygenate in the Atlanta conventional fuel, that MTBE was present in the Houston fuel, and that ethanol was present in the Chicago fuel. Across seasons total aromatics were similar in the oxygenated fuels but higher in the conventional fuel. Benzene levels range from 0.5-1.2 % with the conventional summer fuel highest. The Reid Vapor Pressure (RVP) is higher in the winter fuels to ensure cold start reliability.

Table 4.3-1. Summary of properties for the six test fuels.

Parameter, method	Summer 2002			Winter 2005		
	Houston GA-4614	Atlanta GA-4637	Chicago GA-4640	Houston GA-5427	Atlanta GA-5437	Chicago GA-5440
ASTM D5845 Petrospec®						
MeOH, wt%	N/A	N/A	N/A	0	0	0
EtOH, wt% (D5599)	N/A	(0)	(10.75)	0	0	10
MTBE, wt% (D5599)	(9.86)	N/A	N/A	10.7	0.4	0.6
ETBE, wt%	N/A	N/A	N/A	0	0	0
TAME, wt%	N/A	N/A	N/A	1.4	0	0
DIPE, wt%	N/A	N/A	N/A	0	0.2	0.5
TBA, wt%	N/A	N/A	N/A	0.3	0	0
O_2 Total wt% (D5599)	(1.81)	(0.01)	(3.73)	2.23	0.1	3.66
Benzene, vol% (D5580)	(0.62)	(1.24)	(0.84)	0.5	1.06	1.03
Aromatic, vol% (D1319)	(19.9)	(38.4)	(17.1)	17.5	21.4	16.3
Olefins, vol%	(17.3)	(10.5)	(9.1)	9.4	6.0	15.2
Saturate, vol%	(52.8)	(51.1)	(70.9)	60.8	72.0	58.0
RON	N/A	N/A	N/A	92.2	90.5	92.3
MON (D2700)	N/A	(81.9)	(83.0)	83.5	82.9	82.8
R+M/2	N/A	N/A	N/A	87.8	86.7	87.5
T50, degF (D86)	(190)	N/A	N/A	184	208	164
T90, deg F (D86)	(327)	N/A	N/A	330	336	319
E200, %	N/A	N/A	N/A	52	40	59
E300, %	N/A	N/A	N/A	82	83	83
RVP, ASTM D5191	7.01	6.29	6.93	10.20	10.87	14.16
API Gravity, ASTM D4052	61.1	55.5	63.7	62.1	60.3	62.8
Specific Gravity, ASTM D4052	0.7347	0.7568	0.7390	0.7308	0.7379	0.7282
Carbon content, wt%, ASTM D5291	84.77	86.76	82.30	83.99	86.28	80.85
Hydrogen content, wt%, ASTM D5291	14.04	13.14	13.71	13.95	13.25	13.64

In some instances, two different methods were utilized to determine fuel properties. In these instances, the second method and corresponding results are presented in parentheses.

O2 Total wt% = total oxygen weight %
MeOH = methanol; EtOH = ethanol

4.3.2 Vehicle Regulated and Hot Soak Emissions

The vehicle emission tests were conducted as described in Section 4.2. The details of these tests are described in the SwRI Report, attached in Appendix F. Tables 4.3-2 through 4.3-5 show the measured regulated exhaust and hot soak emissions from the test vehicles for summer and winter test fuels. The FTP results show that all emissions increased and the high emitter target of ≥ 2 grams NMHC per mile was achieved.

Table 4.3-2. Regulated and Hot Soak Emissions from the Ford F-150, Summer 2002.

Parameter	Units	Houston Fuel		Atlanta Fuel		Chicago Fuel	
		Normal	Mal-function	Normal	Mal-function	Normal	Mal-function
HC	g/mi	0.397	2.19	0.469	2.45	0.430	2.27
NMHC	g/mi	0.296	2.09	0.366	2.35	0.281	2.17
CO	g/mi	2.19	15.6	1.88	16.89	1.66	15.2
NOx	g/mi	0.989	2.11	1.05	2.13	1.40	2.07
Fuel Economy	mi/gal	14.9	15.0	15.3	15.1	14.5	14.8
Hot Soak HC	g	0.00	2.60	0.07	2.18	0.00	1.95

Table 4.3-3. Regulated and Hot Soak Emissions from the Ford F-150, Winter 2005.

Parameter	Units	Houston Fuel		Atlanta Fuel		Chicago Fuel		
		Normal	Mal-function	Normal	Mal-function	Normal	Normal	Mal-function
HC	g/mi	0.570	2.39	0.588	2.63	0.795	0.794	2.41
NMHC	g/mi	0.464	2.23	0.487	2.54	0.637	0.637	2.31
CO	g/mi	2.95	16.3	2.90	17.2	9.32	8.19	16.4
NOx	g/mi	1.04	2.02	1.08	2.20	1.12	1.26	2.27
Fuel Economy	mi/gal	13.6	14.1	14.2	14.0	13.4	13.5	13.8
Hot Soak HC	g	0.21	6.83	0.28	13.9	0.42	N/C*	21.0

*N/C = not conducted

Table 4.3-4. Regulated and Hot Soak Emissions from the Toyota Camry, Summer 2002

Parameter	Units	Houston Fuel		Atlanta Fuel		Chicago Fuel	
		Normal	Mal-function	Normal	Mal-function	Normal	Mal-function
HC	g/mi	0.227	4.05	0.288	3.89	0.244	4.21
NMHC	g/mi	0.186	3.55	0.249	3.49	0.208	3.71
CO	g/mi	3.18	64.4	2.64	59.5	2.61	60.4
NOx	g/mi	0.525	2.56	0.581	2.64	0.516	2.44
Fuel Economy	mi/gal	26.8	19.5	22.2	19.9	22.8	19.7
Hot Soak HC	g	0.09	0.77	0.01	0.62	0.05	2.16

Table 4.3-5. Regulated and Hot Soak Emissions from the Toyota Camry, Winter 2005

Parameter	Units	Houston Fuel		Atlanta Fuel		Chicago Fuel	
		Normal	Mal-function	Normal	Mal-function	Normal	Mal-function
HC	g/mi	0.268	3.99	0.384	4.03	0.388	3.75
NMHC	g/mi	0.199	3.47	0.346	3.58	0.276	3.29
CO	g/mi	2.72	64.5	3.78	63.0	3.89	55.0
NOx	g/mi	1.15	1.98	0.877	2.46	0.873	2.76
Fuel Economy	mi/gal	24.3	19.8	23.2	20.1	21.9	19.3
Hot Soak HC	g	0.02	8.02	0.00	4.84	0.11	8.66

4.3.3 Garage and Kitchen Exhaust/Evaporative Fuel Component Levels

This section summarizes emission component concentrations observed in the kitchen and attached garage. As discussed in Chapter 1, measured 1,3-BD levels are biased upwards in the presence of high MTBE concentrations. In addition, a single garage sample (sedan with gasohol in normal mode) was invalidated. The sample contained high anomalous levels of BTEX, BTEX/1,3-BD and BTEX/CO ratios were 25- and 88-fold higher, respectively, in the normal mode than the high emitter tests, suggesting an anomalous source of BTEX such as an unrecorded garage fuel spill.

BTEX and 1,3-butadiane data presented in Tables 4.3-6 to 4.3-12 are from the canister samples and ethanol is from the sorbent cartridges, as described in Chapter 1 and Appendix B..

4.3.3.1 Background and Overall Concentrations

The background samples, taken before the vehicle was brought into the garage, are presented in Table 4.3-6 for both the average (top section, separated for summer and winter) and ranges of the data. Note that the max-min ranges denote the single highest values for each species individually across tests. Gaps indicate missing samples. Both HCHO and EtOH show relatively higher levels in the kitchen. HCHO off-gases from residential furnishings and construction materials. EtOH is emitted from people, foods, cleaning & personal care products, domestic garbage, and alcoholic beverages.

Table 4.3-6. Summary of Background Concentrations in Kitchen and Garage. Units are ppbv, except as noted.

	Budi13	Benze	Tolue	Etbz	Mp_xyl	O_xyl	MTBE	CO,ppm	Formal	EtOH	Acetal
Kitchen Backgrounds											
Summer	0.08	1.70	6.50	0.67	2.30	1.05	0.42	0.35	49.83	1215.58	13.57
Winter	0.21	3.93	7.47	4.82	7.47	4.32	1.31	0.87	13.51		5.47
Garage Backgrounds											
Summer	0.02	2.68	8.87	0.92	3.25	1.14	0.20	0.15	20.29		6.28
Winter	0.12	2.29	5.40	0.85	3.13	1.21	1.11	0.78	7.70		2.65
Kitchen, all											
Min	0.02	0.73	3.33	0.37	1.25	0.50	0.00	0.15	5.50	53.60	3.00
Max	1.33	11.76	15.49	38.21	32.27	24.64	6.16	5.29	106.63	2194.10	24.56
Garage, all											
Min	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.85	0.90	1.20
Max	0.90	11.47	25.72	3.19	11.33	4.27	3.78	7.01	35.63	1475.60	13.89

Budi13 = 1,3BD; Benze = benzene; Tolue = toluene, Mp_xyl = m,p-xylene; o_xyl = o-xylene, Formal = formaldehyde; EtOH = ethanol, Acetal = acetaldehyde

The ranges of all samples taken during the vehicle-related scenario portions are presented in Table 4.3-7. As expected, the lower concentrations stem from normal mode vehicles and higher levels from the high emitter mode.

Table 4.3-7. Summary of Test Concentration Ranges in Kitchen and Garage. Units are ppbv, except as noted.

		Budi13	Benze	Tolue	Etbz	Mp_xyl	O_xyl	MTBE	CO,ppm	Formal	EtOH	Acetal
Kitchen, all												
	Min	0.02	0.18	2.49	0.25	0.78	0.43	0.00	0.00	0.00	158.80	0.00
	Max	1.64	11.17	15.58	3.02	9.06	5.12	13.27	10.85	95.59	670.20	23.86
Garage, all												
	Min	0.03	1.33	2.48	0.39	1.25	0.51	0.00	0.20	0.00	5.80	0.00
	Max	36.35	65.44	93.67	18.23	50.72	19.36	185.63	39.16	174.20	27.70	30.79

Budi13 = 1,3BD; Benze = benzene; Tolue = toluene, Mp_xyl = m,p-xylene; o_xyl = o-xylene, Formal = formaldehyde; EtOH = ethanol, Acetal = acetaldehyde

4.3.3.2 Seasonal Impacts

Seasonal max trends are inconsistent. Table 4.3-8 shows that differences seen in the kitchen are smaller than in the garage. The garage has higher exhaust 1.3-BD and HCHO in the summer, but lower CO values than in the winter.

Table 4.3-8. Seasonal Impact on Observed Maximum Concentrations (Units are ppbv, except as noted).

.

		Budi13	Benze	Tolue	Etbz	Mp_xyl	O_xyl	MTBE	CO,ppm	Formal	EtOH	Acetal
Kitchen	Max-S	1.42	7.77	14.64	1.84	6.44	2.98	10.49	1.62	95.59	670.20	23.86
	Max-W	1.64	11.17	15.58	3.02	9.06	5.12	13.27	10.85	54.78		15.51
Garage	Max-S	36.35	65.44	93.67	18.23	50.72	19.36	93.63	28.60	174.20	27.70	30.79
	Max-W	8.47	24.68	34.61	6.05	22.78	8.04	185.63	39.16	54.78		15.51

Budi13 = 1,3BD; Benze = benzene; Tolue = toluene, Mp_xyl = m,p-xylene; o_xyl = o-xylene, Formal = formaldehyde; EtOH = ethanol, Acetal = acetaldehyde

Tables 4.3-9 and 4.3-10 provide max and average values for normal mode vehicles only. The maximum values for the normal vehicles are generally lower with winter mean values higher than summer.

Table 4.3-9. Seasonal Impact on Observed Maximum Concentrations (Units are ppbv, except as noted), Normal Mode Vehicles Only.

Normal Only		Budi13	Benze	Tolue	Etbz	Mp_xyl	O_xyl	MTBE	CO,ppm	Formal	EtOH	Acetal
Kitchen	Max-S	0.29	4.87	14.35	1.80	6.44	2.48	1.59	0.81	95.59	519.70	23.86
	Max-W	1.55	11.17	14.80	2.76	8.50	3.44	13.27	3.07	31.31		11.00
Garage	Max-S	4.76	21.02	48.73	6.99	19.92	7.73	8.95	3.86	58.53	27.70	13.79
	Max-W	8.47	24.68	34.61	6.05	22.78	8.04	185.63	39.16	54.78		15.51

Budi13 = 1,3BD; Benze = benzene; Tolue = toluene, Mp_xyl = m,p-xylene; o_xyl = o-xylene, Formal = formaldehyde; EtOH = ethanol, Acetal = acetaldehyde

Table 4.3-10. Seasonal Impact on Observed Average Concentrations (Units are ppbv, except as noted), Normal Mode Vehicles Only.

Normal Only		Budi13	Benze	Tolue	Etbz	Mp_xyl	O_xyl	MTBE	CO,ppm	Formal	EtOH	Acetal
Kitchen	Ave-S	0.16	3.25	11.54	1.39	4.58	1.97	0.56	0.39	53.33	339.25	13.48
	Ave-W	0.43	4.38	7.24	1.31	4.12	1.72	3.76	0.92	14.54		4.99
Garage	Ave-S	1.87	8.72	20.36	3.06	8.67	3.51	2.47	1.82	26.44	17.35	6.26
	Ave-W	2.35	8.15	14.44	2.54	9.00	3.39	36.64	6.45	18.72		4.79

4.3.3.3 Fuel and Vehicle Effects

This section addresses fuel, vehicle, and operational mode separately for all seasons. For the sedan, Table 4.3-11 indicates highest mean MTBE values for Houston fuel and EtOH for Chicago, as expected, with high-emitter/malfunction effects strongest in the garage.

Table 4.3-11. Effect of Fuel and Operational Mode of the Sedan on Observed Levels in the Kitchen and Garage (Units are ppbv, except as noted).

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	Location	Fuel	Budi13	Benze	Tolue	Etbz	Mp_xyl	O_xyl	MTBE	CO,ppm	Formal	EtOH	Acetal
Normal	Garage	Atlanta	0.55	2.40	6.09	0.98	3.24	1.38	0.82	0.31	7.16		1.78
		Houston	0.95	3.56	9.78	1.51	5.20	2.08	10.81	0.56	22.25		5.11
		Chicago	1.19	3.40	8.29	1.39	4.91	2.06	0.48	0.45	11.75	27.70	3.81
	Kitchen	Atlanta	0.06	2.01	8.42	1.03	3.61	1.45	0.10	0.10	63.45		16.78
		Houston	0.24	2.82	7.49	1.10	3.69	1.59	3.35	0.52	24.01		6.65
		Chicago	0.06	3.82	8.45	1.26	4.40	1.91	0.27	0.29	13.38	158.80	2.48
Malfunction	Garage	Atlanta	1.42	26.80	44.40	4.03	13.08	4.86	16.67	6.27	23.35		9.03
		Houston	2.54	12.45	25.68	4.20	14.11	5.53	49.97	13.29	30.72		7.35
		Chicago	1.92	9.54	11.26	1.65	5.64	2.18	1.13	12.16	13.08	19.00	7.35
	Kitchen	Atlanta	0.86	9.13	15.11	2.06	6.47	2.92	0.35	5.59	21.99		6.97
		Houston	0.23	4.14	9.68	1.74	5.42	2.65	10.19	1.30	26.19		8.37
		Chicago	0.23	2.81	6.04	1.03	3.51	1.53	0.30	0.76	25.93	670.20	9.88

Budi13 = 1,3BD; Benze = benzene; Tolue = toluene, Mp_xyl = m,p-xylene; o_xyl = o-xylene, Formal = formaldehyde; EtOH = ethanol, Acetal = acetaldehyde

For the truck, Table 4.3-12 indicates lesser fuel impacts on normal mode garage levels than for the sedan. For the malfunction mode, Houston fuel garage values exceed those of the other two fuels.

Table 4.3-12. Effect of Fuel and Operational Mode of the Truck on Observed Levels in the Kitchen and Garage (Units are ppbv, except as noted).

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	Location	Fuel	Budi13	Benze	Tolue	Etbz	Mp_xyl	O_xyl	MTBE	CO,ppm	Formal	EtOH	Acetal
Normal	Garage	Atlanta	2.40	11.28	26.45	3.79	11.05	4.32	0.44	2.13	38.17		8.25
		Houston	1.39	9.69	24.99	3.83	11.12	4.46	10.46	2.15	38.12		8.85
		Chicago	2.55	9.64	15.61	2.99	8.56	3.41	1.74	2.87	0.00	7.00	0.00
	Kitchen	Atlanta	0.12	1.65	8.23	0.83	2.58	1.04	0.10	0.28	35.68		8.88
		Houston	0.37	4.57	9.68	1.62	4.85	2.28	7.20	0.82	45.47		13.40
		Chicago	0.92	8.02	14.08	2.27	6.97	2.78	1.95	1.94	21.61	519.70	7.25
Malfunctior	Garage	Atlanta	3.74	16.19	26.42	3.87	12.22	4.58	0.38	8.03	45.11		9.79
		Houston	22.41	45.06	64.14	12.14	36.75	13.70	139.63	33.88	114.49		23.15
		Chicago	2.73	7.72	11.55	1.85	5.87	2.16	0.06	2.52	32.96	5.80	17.28
	Kitchen	Atlanta	0.24	3.25	7.65	1.99	5.67	3.15	0.13	0.68	42.56		10.91
		Houston	0.80	4.23	9.05	1.42	4.25	1.89	4.57	1.33	52.72		14.55
		Chicago	0.11	4.11	7.29	1.45	4.67	1.92	0.03	0.28	29.37	414.10	7.65

Figure 4.3-1 illustrates the effect of fuel and mode (N-normal, F-malfunction) on mean garage values averaged across vehicle and season. Figure 4.3-2 shows the kitchen values. Both figures report relatively high 1,3-BD values for the Houston fuel high emitter mode. Since both are also associated with high MTBE values, these 1,3-BD values are suspect as discussed earlier and in Chapter 1. The same caveat applies to Figures 4.3-3 and 4.3-4.

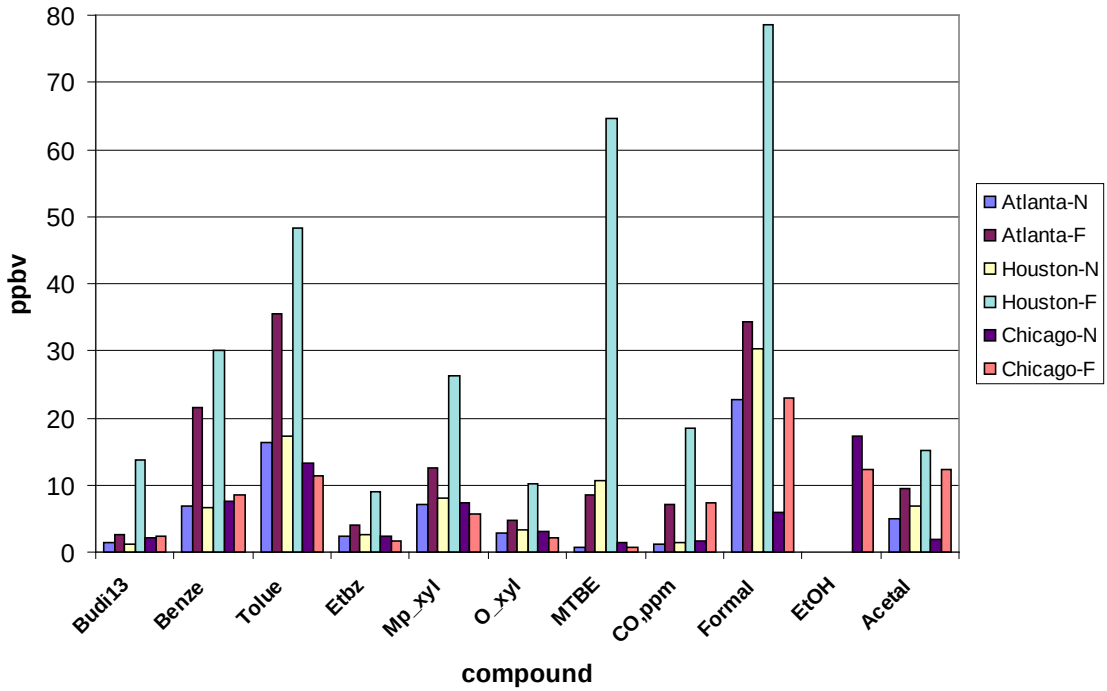


Figure 4.3-1. Effect of fuel and mode on observed concentrations in the garage. The legend “N” is normal and “F” is malfunction. The 1,3-BD value for Houston-F is suspect.

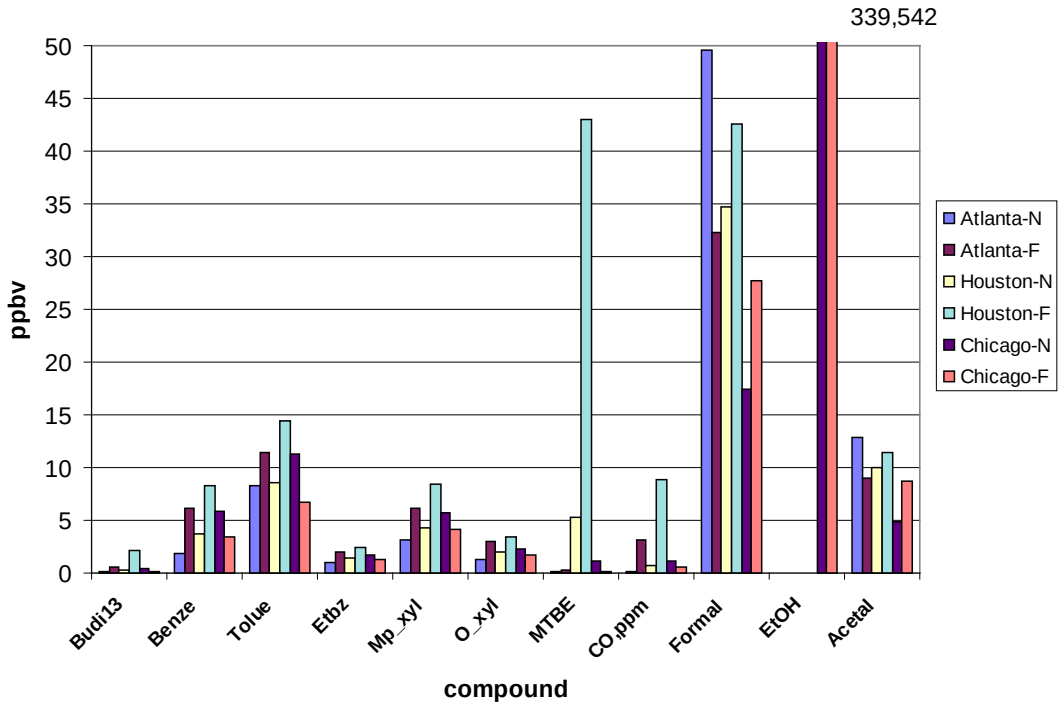


Figure 4.3-2. Effect of fuel and mode on observed concentrations in the kitchen. The legend "N" is normal and "F" is malfunction. The 1,3-BD value for Houston-F is suspect.

The kitchen concentrations are dominated by HCHO and EtOH, but high background levels indicate kitchen sources rather than the garaged vehicles.

The effect in the garage is expected to be more directly correlated with the vehicle. Figure 4.3-3 shows the concentrations seen in the garage only for the sedan, looking at the effect of the fuel and operational mode. The same presentation for the truck only is in Figure 4.3-4.

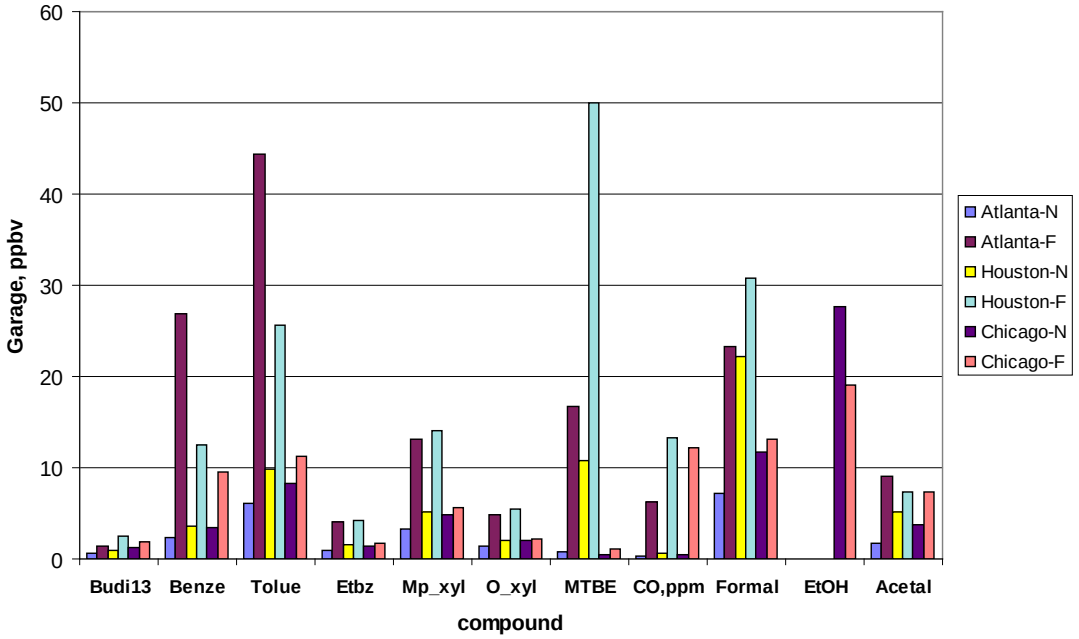


Figure 4.3-3. Effect of fuel and mode on observed sedan garage levels. The legend "N" is normal and "F" is malfunction. The 1,3-BD level for Houston-F is suspect, see text.

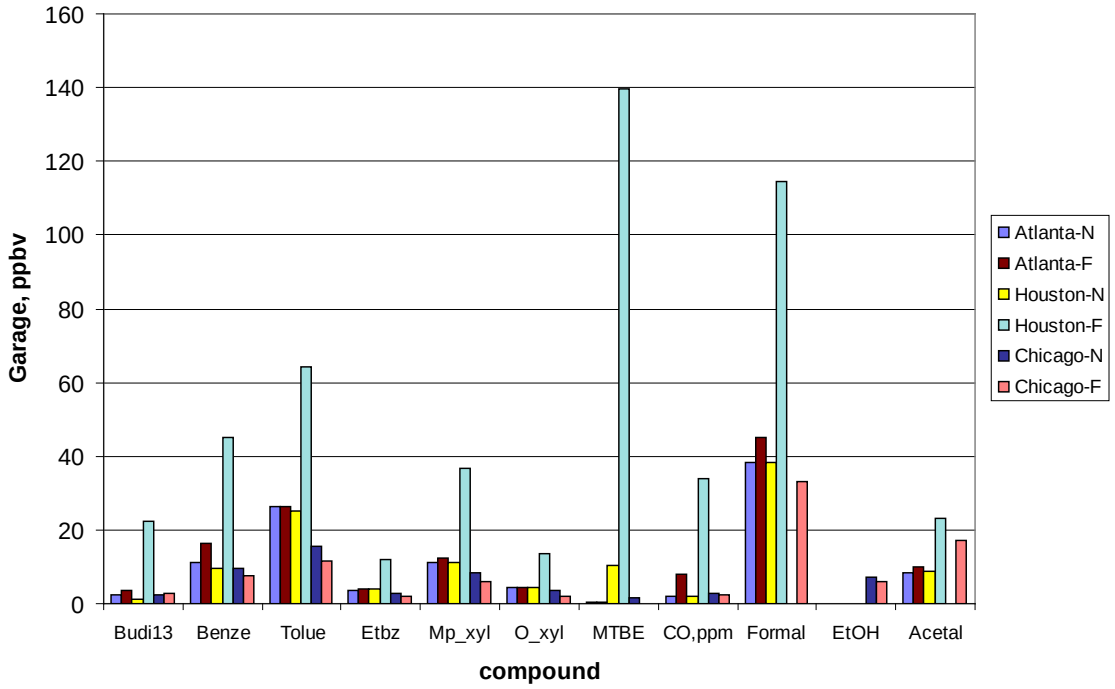


Figure 4.3-4. Effect of fuel and mode on observed truck garage levels. The legend "N" is normal and "F" is malfunction. The 1,3-BD level for Houston-F is suspect, see text.

Comparison of 1,3-BD, BTEX and CO background concentrations with garage and kitchen concentrations for each test is shown in Figure 4.3-5 and Figure 4.3-6 for Summer 2002 and Winter 2005, respectively. In general, these figures indicate compound range rankings of garage » kitchen ~ background, especially for vehicle in the normal mode. For vehicles in high emitting mode, the increase in kitchen levels could be seen. In Winter 2005, a few high background samples were observed, possibly due to a prolonged storage of a plastic gasoline container in the garage.

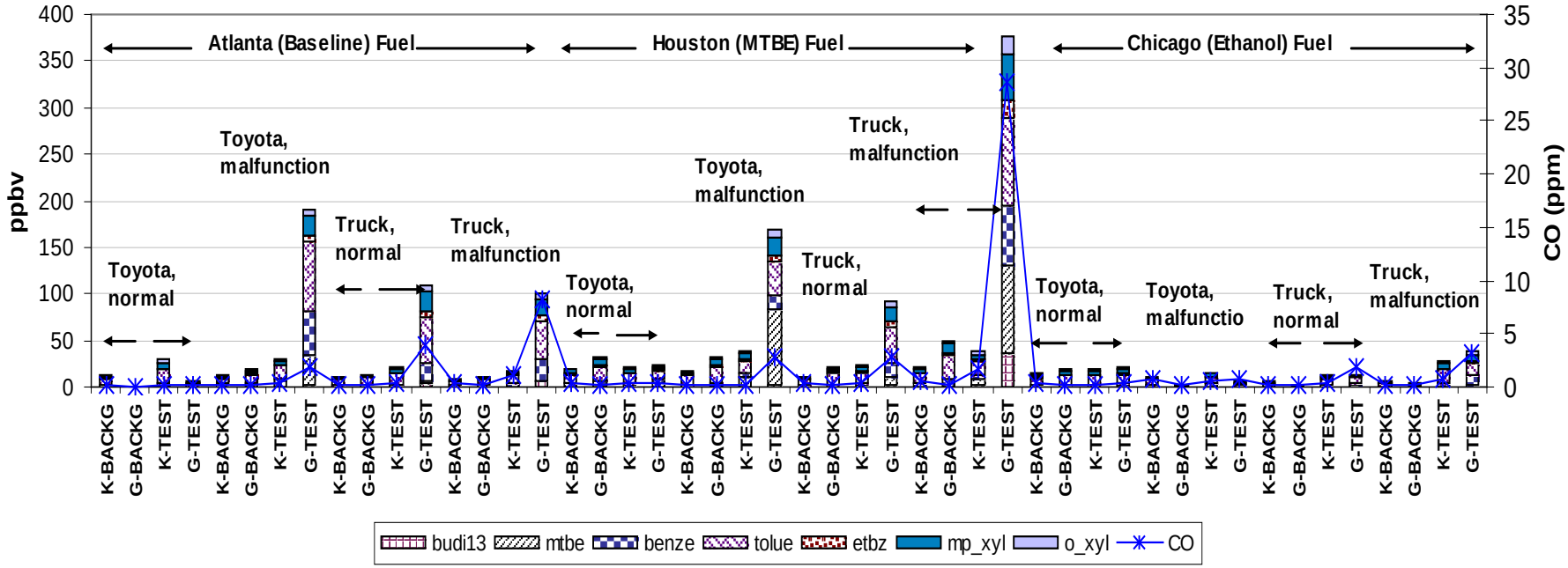


Figure 4.3-5. Concentrations of 1,3-butadiene, MTBE and BTEX and CO as measured from canisters in the garage and the adjacent kitchen in Summer 2002

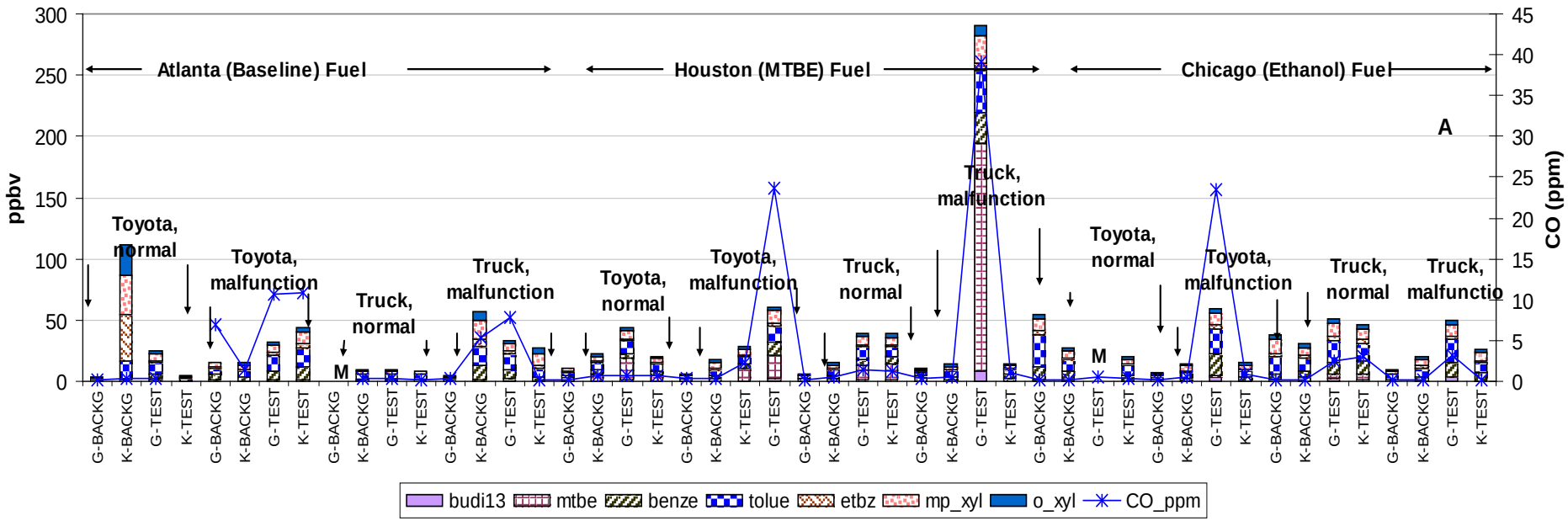


Figure 4.3-6. Concentrations of 1,3-butadiene, MTBE and BTEX (A) and CO (B) as measured from canisters in the garage and the adjacent kitchen in Winter 2005. M=sample missing or invalid.

4.3.3.4 Comparison with Emissions Data

There are five distinct garage scenario phases after the background sample as described in Table 4.2-2. The first phase, hot soak, is best compared to the hot soak SHED test run by SwRI. Benzene canister values are compared in Figure 4.3-7. While there does not appear to be a strong correlation, the canister samples collected in the garage average over all five scenarios, not only hot soak. The high outlying points come from the truck in high emitter mode and are expected to be high. SPME samples taken every half-hour correspond better with the phases of the experiment. Benzene winter SPME values for hot soak phase are compared with SHED values in Figure 4.3-8A (all samples) and 4.3-8B (outliers removed). Although the correlation is not very good for all samples (A), it improves after removing two outliers from the truck in high emitter mode (B). The high emitting vehicles are generally not stable and the SHED results may be very different from the garage, due to different time and location.

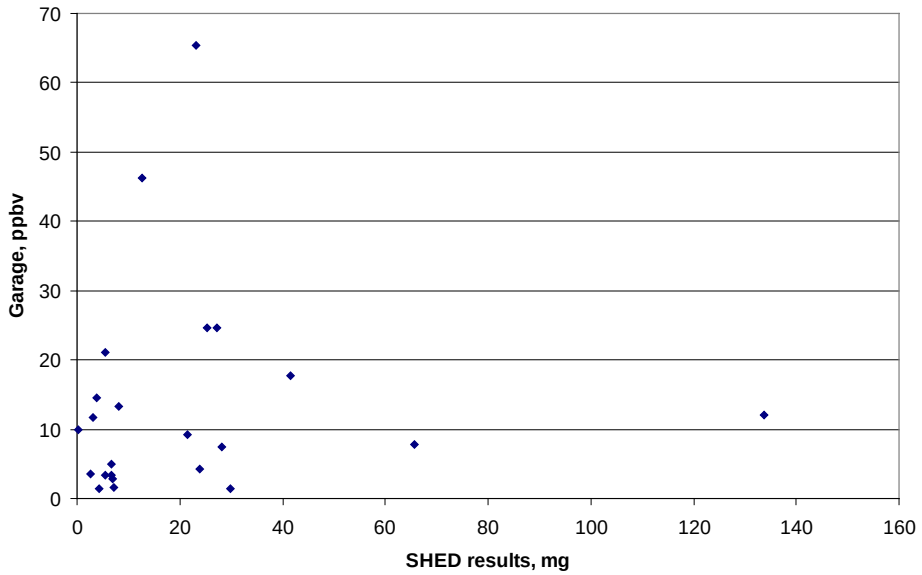


Figure 4.3-7. Comparison of SHED results with the observed canister concentration in the garage for benzene.

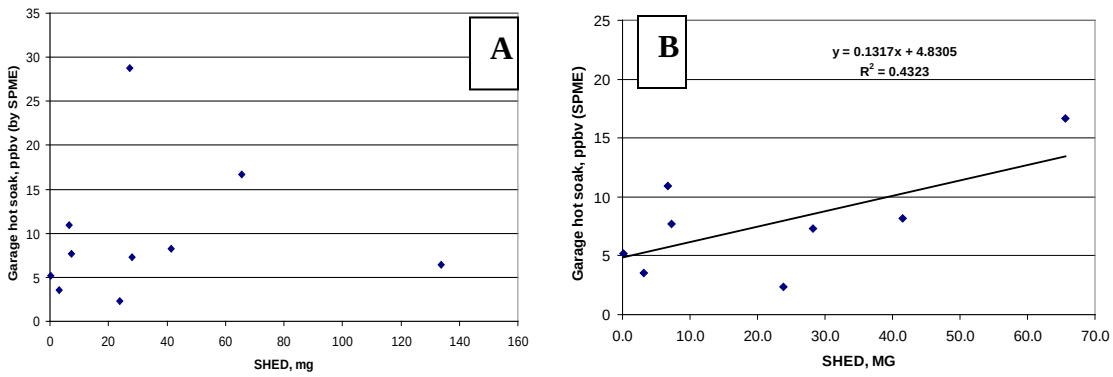


Figure 4.3-8. Comparison of the SHED results with the observed SPME hot soak concentration in the garage for benzene A: all data, B: two outliers removed.

Cold start 1,3-BD and benzene canister values can be compared to the FTP Bag 1 data in Figures 4.3-9 and 4.3-10, respectively. Garage 1,3-BD values appear insensitive to FTP levels. It is possible that this may reflect another 1,3-BD analytical challenge from NO2 scavenging in the FTP sample; the high point in Figure 4.3-7 is also suspect since 1,3-BD occurs concurrent with high MTBE levels. The Figure 4.3-8 garage benzene scatter is similar to 1,3-BD and also appears insensitive to FTP levels; however, benzene is stable in canisters and these values should be accurate. Figure 4.3-11 compares garage SPME cold start values to FTP Bag 2 values. This comparison trends upwards with garage values increasing with increasing FTP emissions, although not strongly.

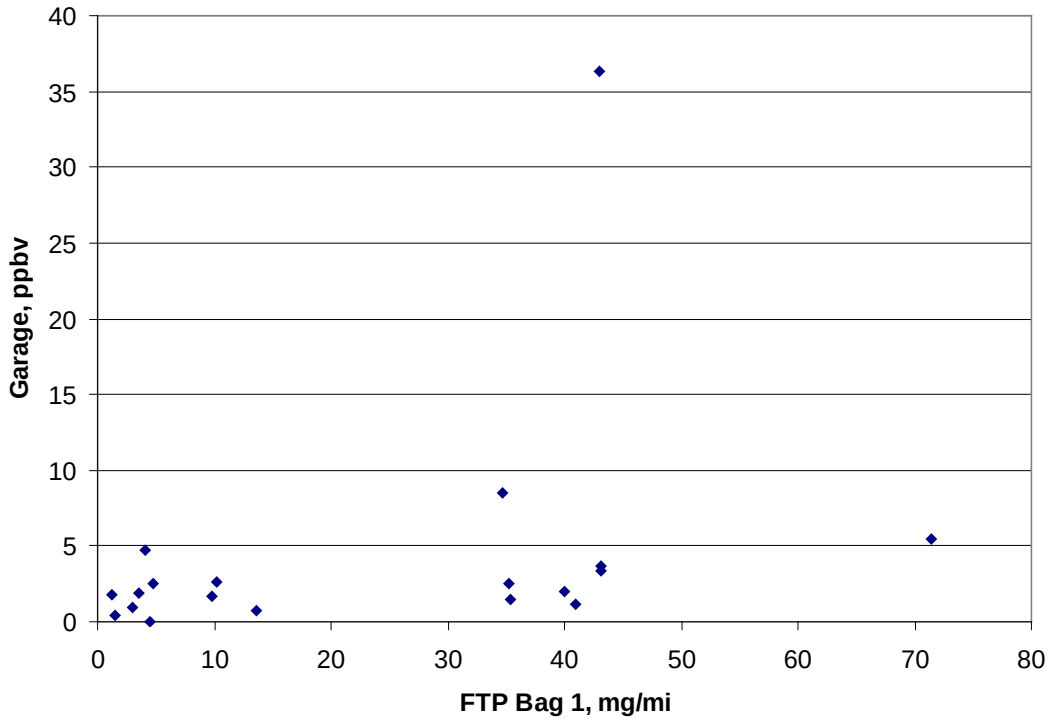


Figure 4.3-9. Comparison of FTP Bag 1 emissions and observed garage levels of 1,3-BD.

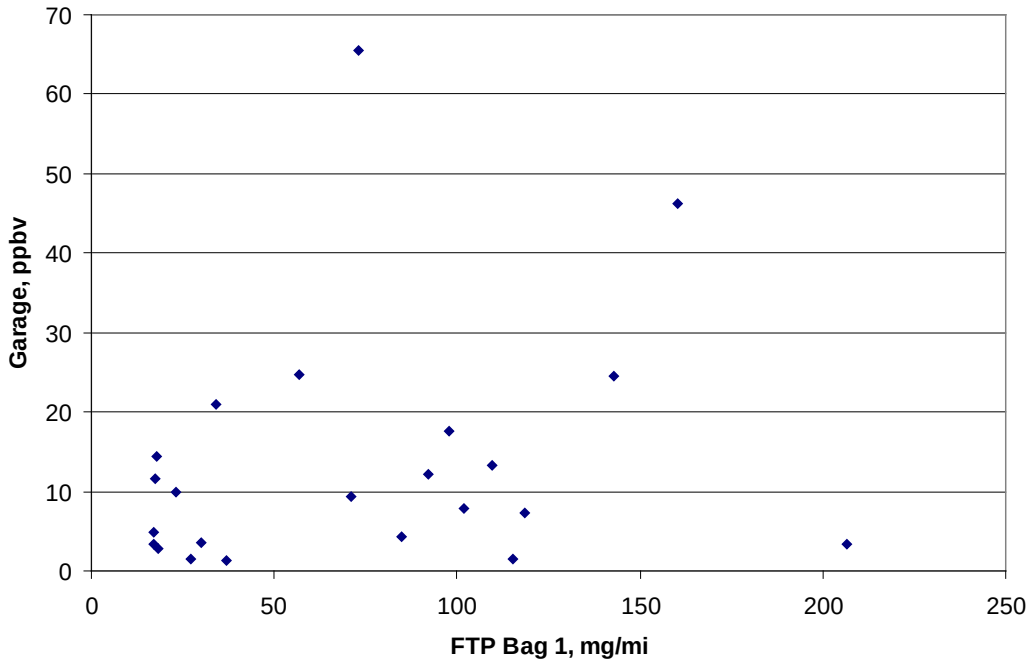


Figure 4.3-10. Comparison of FTP Bag 1 benzene emissions and observed garage levels.

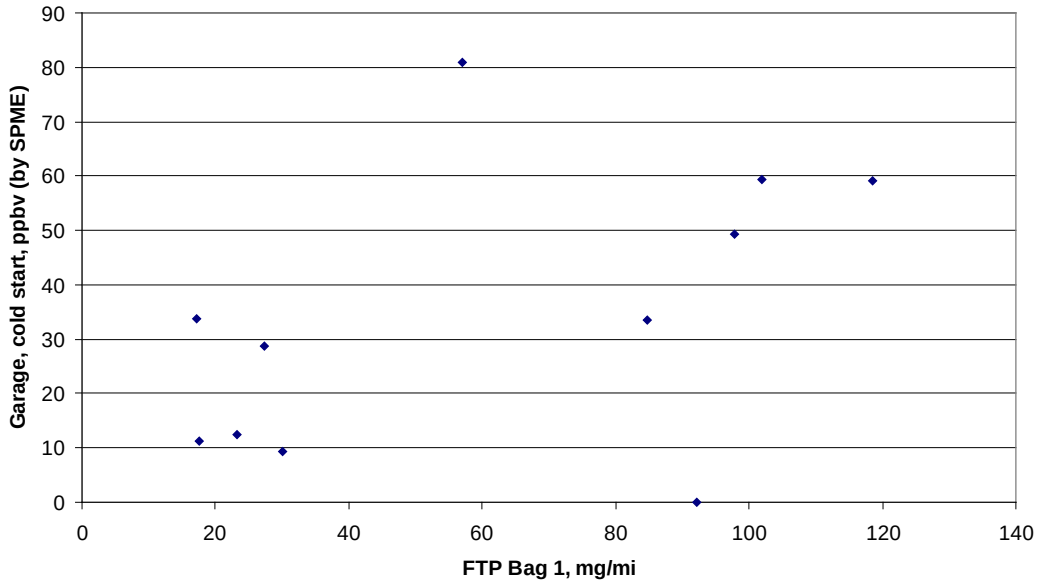


Figure 4.3-11. Comparison of hot soak FTP Bag 1 benzene emissions and observed SPME garage values.

4.3.3.5 Relationships of Garage and Kitchen Concentrations

Kitchen values would be expected to increase with increasing garage levels from vehicle and fuel container sources. Based on their high background levels, EtOH and HCHO would not be good candidates for tests. Three other species 1,3-BD, CO, and benzene are plotted in Figures 4.3-12, 4.3-13 and 4.3-14, respectively.

Figure 4.3-12A shows a weak 1,3-BD trend which seems to be driven mostly by outliers associated with high level MTBE interference. As explained in Chapter 1 (page 1-6) elevated MTBE concentrations biases measured 1,3-BD levels upwards, due to the thermal decomposition of MTBE (in the order of 1 to 5 %) in a GC injector. The removal of two outliers (for the truck with MTBE fuel in malfunction mode) eliminates any correlation between garage and kitchen concentrations (Figure 4.3-12B).

Figure 4.3-13 trends toward a CO insensitivity to garage concentrations. The high value occurred for the sedan in malfunction mode; the continuous data show a 100 ppm CO spike at the beginning of the cold-start phase that may have penetrated through a briefly opened kitchen door. Figure 4.3-14 shows that there is no correlations between kitchen and garage benzene concentrations. However, it has to be pointed out that these kitchen – benzene correlations are shown for the time-integrated canister samples that were collected over 2.5 hr duration of the experiment. During this time several 30-min scenarios were executed, as shown in Table 4-2.2. The differences in ventilation conditions between garage and kitchen are the most probably responsible for the lack of correlations between species measured from canisters.

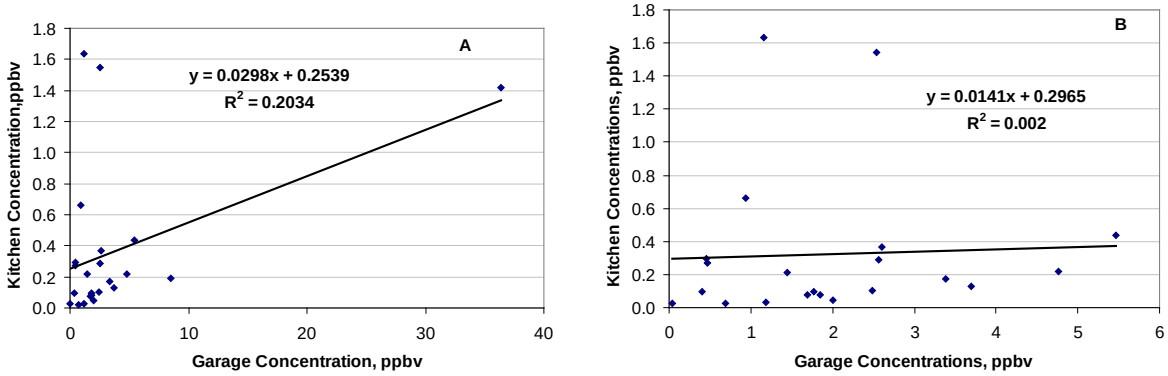


Figure 4.3-12. Comparison of garage and kitchen concentrations for 1,3-BD. A – all data, B- with two outliers removed (see text).

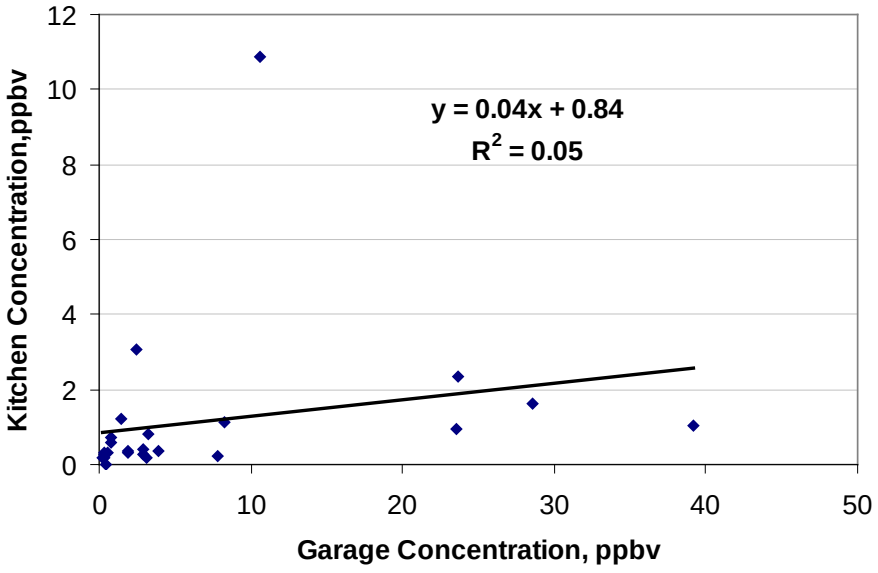


Figure 4.3-13. Comparison of garage and kitchen concentrations of carbon monoxide.

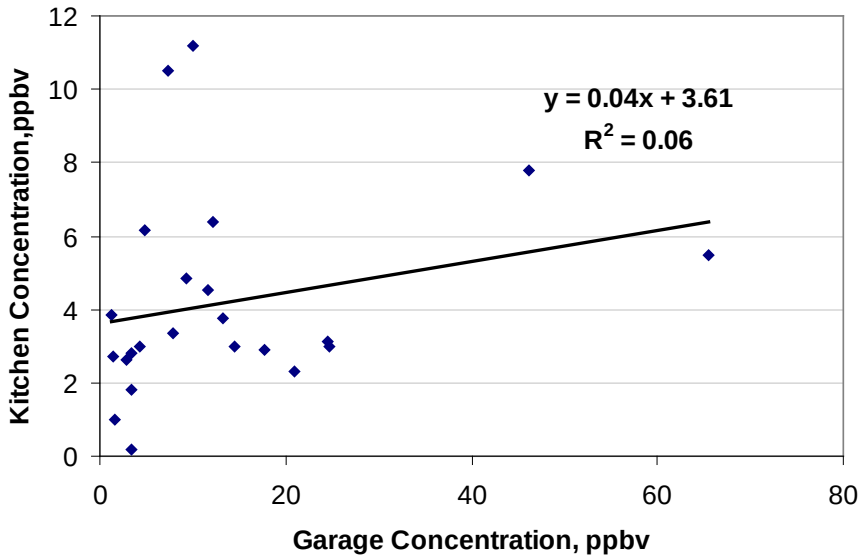


Figure 4.3-14. Comparison of garage and kitchen concentrations of benzene.

4.4 Discussion

The objective of this section was to test the effects of attached garage on indoor home levels of fuel and exhaust components. The experiment simulates common activities such as coming home with a warm car or leaving home after starting a cold vehicle.

Various parameters are assessed in section 4.3 to determine their effects on air levels in the adjacent room (here a kitchen) connecting to the garage. Two target components, HCHO and EtOH, had high kitchen background values indicating indoor sources of these materials. Average HCHO levels were higher in summer than winter, consistent with enhanced off-gassing of building materials and/or penetration of ambient photochemical HCHO. It has been also reported (Reiss et al, 1995; Wang and Morrison, 2006; Weschler, 2006) that a larger fraction of indoor HCHO and other oxygenated-low molecular weight hydrocarbons can result from heterogeneous processes. Ozone originating from outdoors can be deposited onto indoor surfaces and react with different materials to produce low molecular weight organic acids and aldehydes. The concentrations of these species are higher during the summer when more ozone penetrates indoors.

Tables 4.3-8 to 4.3-10 show a seasonal impact where kitchen BTEX, MTBE and CO species are higher in winter than summer. The exception is toluene which shows a minimal difference that actually averages higher in summer for normal mode vehicles. This is consistent with indoor toluene emissions from paints, adhesives, cleaning, and personal care products. Tables 4.3-8 and 4.3-9 focus on normal mode vehicles to remove the variability of high emitter modes in assessing the seasonal effect. Since many species higher in the winter come from both evaporative and exhaust emissions, it is possible that winter enhanced fuel RVP contributes to the apparent seasonal effect. In addition, a large number of studies have shown that home air exchange rates are typically lower during the winter. This would result in longer residence times (thus accumulation) of pollutants generated in the garage and further infiltration to the kitchen area.

Tables 4.3-10 and 4.3-12 show vehicle data separately for each fuel. MTBE and ethanol are highest for fuels containing those species, as anticipated. Otherwise, there is not a strong fuel effect across vehicles.

FTP exhaust and SHED evaporative emissions were tested for each vehicle, fuel, and emissions mode, and compared to observed levels in the garage. These comparisons are challenging in that canisters integrate across hours covering not only hot soak, adjustments to the air exchange, and cold start. Concurrent SPME samples are collected for each condition. However, neither canister nor SPME samples show strong correlations with hot soak emissions (Figures 4.3-5 to 4.3-8), although cold-stabilized FTP Bag 2 benzene appears reasonably correlated to the cold-start SPME (Figure 4.3-9).

Correlations of kitchen levels with garage concentrations are presented in Figures 4.3-12 to 4.3-14. These plots evidence weak correlations and could not be used to predict kitchen exposures from garage levels. 1,3-BD (Figure 4.3-12) and benzene (Figure 4.3-14) may trend weakly upwards, with kitchen levels increasing with garage levels; however CO (Figure 4.3-13)

does not. Tables 4.3-6 and 4.3-7 indicate (HCHO & EtOH excepted) compound range rankings of garage » kitchen ~ background, especially for vehicle in the normal mode. For vehicles in high emitting mode, the increase in kitchen levels is seen from Figures 4.3-5 and 4.3-6.

4.5 References:

Reiss, R., Ryan, P., Tibbetts, S. E., and Koutrakis, P., Measurement of Organic Acids, Aldehydes, and Ketones in Residential Environments and their Relationship to Ozone, *Journal of the Air and Waste Management Association, 45*, 811 (1995).

Wang, H., G.C. Morrison. Ozone-initiated secondary emission rates of aldehydes from indoor surfaces in four homes. *ES&T* 40: 5262-68 (2006)

Weschler, C.J. Ozone's impact on public health: contributions from indoor exposures to ozone and products of ozone-initiated chemistry. *Environ.Health Perspective* 141: 1489-96 (2006).

5. Effect of Ventilation, Proximity, and Emission Levels on In-Cabin Exposures of Trailing Vehicle.

5.1 Introduction

This chapter describes experiments designed to determine the relationships between ventilation, proximity, fuel, and emission levels of a leading vehicle on in-cabin exposures within a trailing vehicle. The same vehicles, fuels and induced malfunctions used for this chapter are used for Chapter 4. These measurements are part of the program described in the executive summary and Chapter 1.

As in the preceding chapter, the vehicles used are a sedan and a pickup truck; the fuels used are either a conventional fuel (without oxygenate), an ethanol fuel, or an MTBE fuel. The vehicles are tested in a normal and induced-malfunction mode with non-methane hydrocarbon (NMHC) emissions of about 2 g/mile by Federal Test Procedure (FTP).

The experiments were performed in summer (June-July 2002) and winter (February-March 2005).

5.2 Experimental

The Southwest Research Institute (SwRI) procured two test vehicles and determined their evaporative/tailpipe emissions in the normal/malfunction modes using the three test fuels. The test vehicles, a sedan and full-sized V8 truck, were chosen within the 1993-1996 model years from vehicles with 90,000-110,000 odometer miles. The chosen 1993 Toyota Camry (2.2L 4-cylinder engine) and 1995 Ford F150 Pickup truck (5.0L V8 engine) were operated in normal, as purchased, modes and in “high emitter” modes with the catalytic converter removed and emission levels above 2 grams per mile NMHC as measured on the FTP driving cycle. While converter removal sufficed for the F150 truck, a calibrated manifold leak was also needed to achieve the 2g/mile Camry emissions. SwRI determined dynamometer FTP emissions for each vehicle with all three fuels in the two emission modes (24 tests). Emission control components could be reproducibly adjusted to represent normal and reasonable high-end approximations (2 g/mile) of real world exhaust emissions. Test vehicle evaporative emissions were also measured for test fuels in the two emission modes as reported in Chapter 4.

Regulated exhaust emissions (THC, NMHC, CO, NOx), fuel economy, and specific VOCs (MTBE, EtOH, BTEX, 1,3-BD, HCHO) were determined in the dynamometer FTP tests. During hot-soak SHED tests, THC and specific VOCs (minus HCHO) were determined.

The FTP exhaust emission test uses the 1372 second Urban Dynamometer Driving Schedule (UDDS) that is divided into cold/start transient 505 (Bag 1) and cold stabilized 867 (Bag 2) second segments. This portion of the FTP is followed by a 10-minute soak and a hot/start transient 505 (Bag 3) test. The FTP evaporative emission test

includes one hour Diurnal Heat Build (DHB) and Hot Soak Loss (HSL) tests. THC/VOC emissions are recorded during the HSL segment of the test. Prior to the FTP cold-start exhaust test, the DHB is conducted by fueling the test vehicle to 40 percent of tank capacity with fuel < 55°F, attaching a heating blanket outside the fuel tank, placing a thermocouple in the tank fuel, hooking it up to computer control, and beginning the test as fuel reaches 60°F (increasing at 0.4°F per minute for the 60-minute test to a 84°F final temperature).

In the HSL segment, conducted immediately following exhaust emission testing, the vehicle is driven into an evaporative emission enclosure and allowed to "soak" in the enclosure for one hour. THC/VOC emissions are measured at the beginning and end of the one-hour segment and hot soak evaporative emissions are calculated.

5.2.1 Fuel Testing

Test fuel samples were subject to standard tests for Reid Vapor Pressure (RVP), distillation range, Specific Gravity, Sulfur, Benzene, HC Category (saturates, olefins, aromatics), Oxygenated species (MTBE/EtOH), carbon weight percent, hydrogen weight percent, oxygen weight percent, and octane number. These results are presented in Chapter 4, Table 4.3-1.

5.2.2 Relationship between Exhaust Emission Rates and In-Cabin Exposure - Trailing Vehicle Test

5.2.2.1 Test Protocol

The two test vehicles were used as characterized sources of measured in-cabin exposures for an instrumented trailing vehicle. SwRI procured a 1996 Chrysler Minivan which DRI instrumented as the trailing vehicle (described in Chapter 1) that was driven behind the test vehicles over a remote, paved, two-lane, farm-to-market roadway loop (described below) for test periods up to 3 hours. Initial measurements made absent the test vehicles established background levels. Trailing vehicle tests then implemented far, near, and passing scenarios at low (30 mph) and high speeds (60 mph) as noted in Table 5.2-1. During 'far' scenarios, 'safe' vehicle spacing (defined as one car length - 10 feet - for each 10 mph) was maintained. During the 'near' scenario, the trailing vehicle tailgated the lead vehicle, following at a close distance deemed 'safe' by the professional drivers under prevailing traffic and meteorological conditions. During the "passing" scenario, the trailing vehicle split its time between tailgating the lead vehicle and 'passing,' immediately behind the lead vehicle but in the adjacent lane. A final idling test was conducted while the trailing vehicle was parked on the road shoulder downwind and closely behind the parked idling lead vehicle. High (10 min) and low (10 min) ventilation conditions were used during all (including idling) tests.

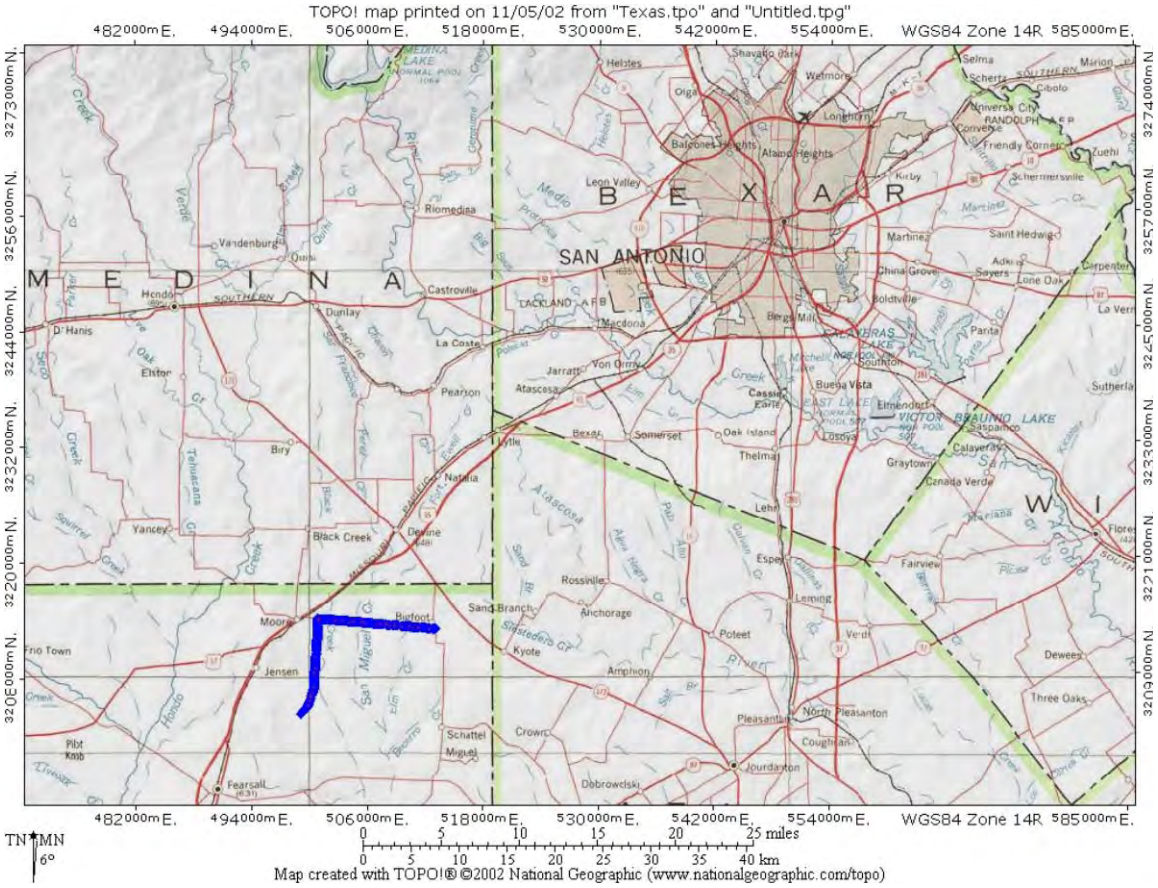
Table 5.2-1 details the trailing vehicle protocol. Trailing vehicle in-cabin TVOC [ppbRAE-PID (photoionization detector)], CO (Langan T15), BTEX (Kore200MS), and HCHO (A-Ω) were continuously monitored. Integrated VOC/NMHC (canister),

HCHO/CH_3CHO (DNPH cartridge), and EtOH (sorbent tube – EtOH fuel only) samples were also collected. SPME BTEX samples were collected every 10 min. Appendix B describes sampling and analytical methods in detail.

The trailing vehicle tests were conducted south of San Antonio, TX on county roads 462 and 2779 off IH 35 in the vicinity of Moore, Big Foot, and Jones Mound, Texas. The position of the trailing vehicle was recorded continuously by a Garmin 12XL GPS unit recording in UTM using NAD83/WGS84. Speed and direction of the vehicle between any two points can be located on a map as illustrated in the June 19, 2002 test Figures 5.2-1, -2. The mapping software also contains a digital elevation model that creates elevation profiles as shown in Figure 5.2-3. The change in elevation over the 14.5-mile driving route is approximately 100 feet.

Table 5.2-1. Protocol for Trailing Vehicle Tests

Time Min.	**Speed Mph**	**Ventilation Setting**	**Distance**	**Notes**	**Continuous Instruments**	**SPME**	**Time Integrated**
10	high	high		background	Y	1	1
10	low	high	far	Vehicles:Toyota Camry and Ford Pick-up truck, in normal and malfunction mode. Fuels: Atlanta (conventional), Houston (MTBE), Chicago (ethanol)	Y	1	One sample in Summer 2002. Two samples, at high/low ventilation, for Winter 2005.
10	low	high	near		Y	1	
10	low	high	passing		Y	1	
10	high	high	far		Y	1	
10	high	high	near		Y	1	
10	high	high	passing		Y	1	
10	low	low	far		Y	1	
10	low	low	near		Y	1	
10	low	low	passing		Y	1	
10	high	low	far		Y	1	
10	high	low	near		Y	1	
10	high	low	passing		Y	1	
10	idle	low	adjacent		Y	1	1
10	idle	high	adjacent		Y	1	


TOPO! map printed on 11/05/02 from "Texas.tpo" and "Untitled.tpg"
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494000mE.
506000mE.
518000mE.
530000mE.
542000mE.
554000mE.
WGS84 Zone 14R
585000mE.
3273000mN.
3256000mN.
3244000mN.
3232000mN.
3220000mN.
3209000mN.
3274000mN.
3257000mN.
3245000mN.
3233000mN.
3221000mN.
3209000mN.
M E D I N A
B E X A R
W I
SAN ANTONIO
Medina Lake
Helotes
Leon Valley
Riomedina
Vandenburg
Castroville
Dunlay
La Coste
Pearson
Hondo
D'Hanis
Elstor
Bry
Natalia
Yancey
Black Creek
Devine
Moore
Bigfoot
Jensen
Frio Town
Pibt Knob
Fearsall
Schattel
Miguel
Rossville
Sand Branch
Anchorage
Kyote
Amphion
Crown
Dobrowolski
Jourdanton
Poteet
Pleasanton
North Pleasanton
Coughran
Lehm
Lemmg
Verdi
Espe
Fairview
Dewees
Three Oaks
Thelma
Oak Island
Somerset
Bexar
Lytle
Atascosa
Jarrett
Von Ormy
Cassia Park
Buena Vista
Losoya
Elmendorf
Graytown
Calaveras
Cenaida Verde
Saspamco
Southton
Macdona
Lackland AFB
Berg Mill
Boldtville
China Grove
Martinez
Saint Hedwig
Adkins
Sayers
Lone Oak
Carpenter
La Vern
Panta
Sutherla
Selma
Scherts
Cibolo
Marion
Universal City
Converse
Friendly Corner
Zuehl
Schertzmersville
Kirby
Balcones Heights
Alamo Heights
Lonehurst
Shavano Park
Wetmore
Olga
Tieblas
Medio
Martinez
Salado
Cibolo
Leon
Medina
Verde
Hondo
Frio
Nueces
Atascosa
Alex Hogg
Pad
Galvan
Calaveras
Salado
Cibolo
Sandy
Sabinal
Leona
Frio
Dry
Seco
Oak
Squirrel
Tehuacana
Black
Devine
Hondo
San Miguel
Pleasanton
Cibolo
Creek
Medina Lake
Braunig Lake
Victor
East Lake
Mitchell Lake
Calaveras Lake
Southton
Lake
Pool
Normal Pool
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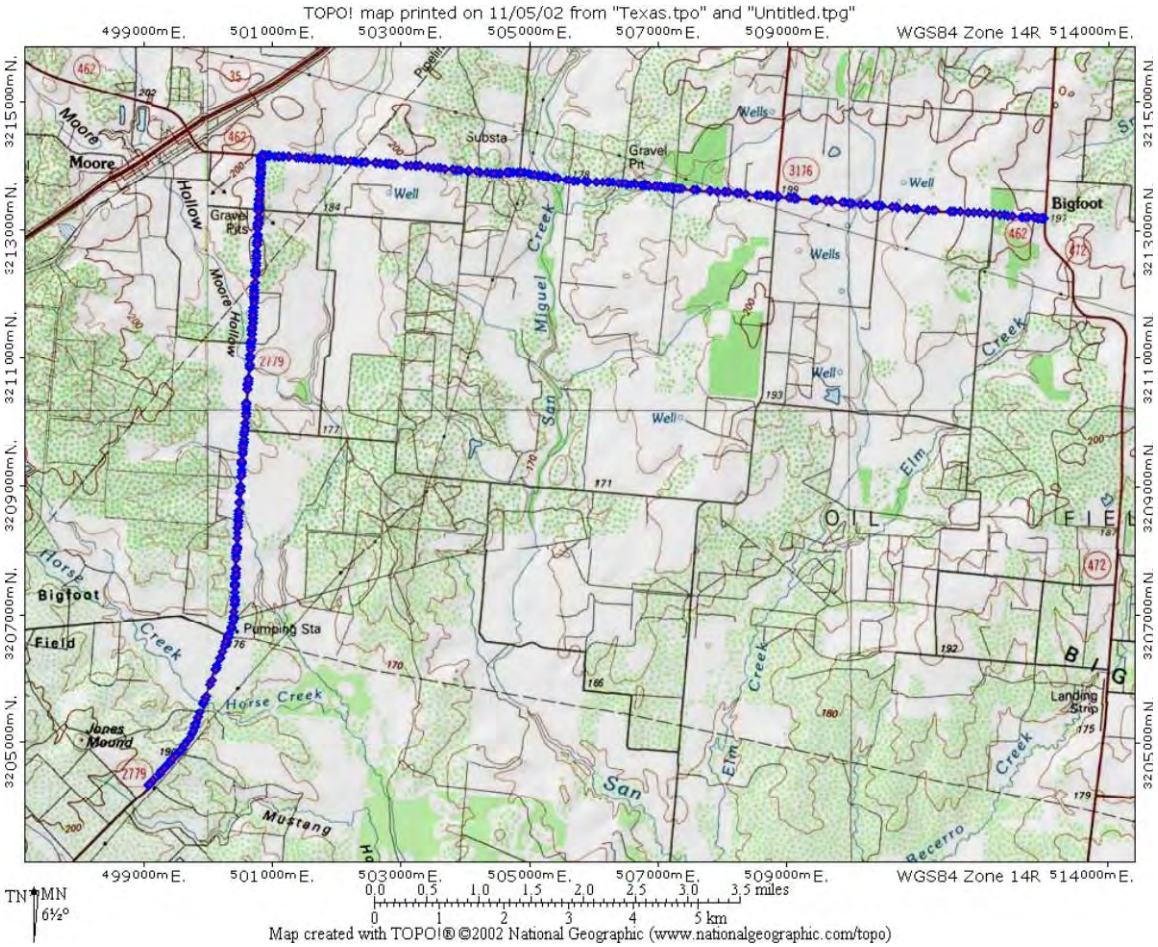

Figure 5.2-2. Map of Driving Test Location near Moore, TX.

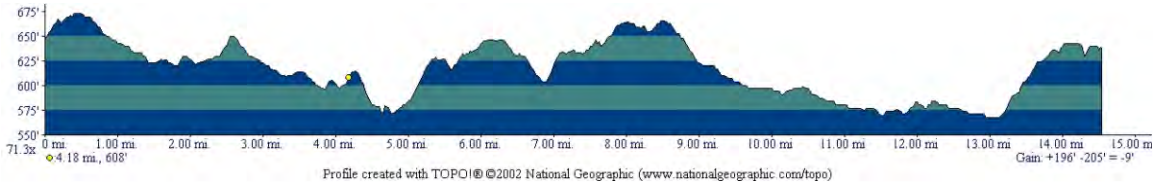

Figure 5.2-3. Elevation Profile of the Driving Route near Moore, TX.

5.3 Results

An initial summary of the trailing vehicle study findings, averaging across all vehicles, emission modes, and fuels, is presented below. The lead vehicles and fuels are the same as described in Chapter 4; Section 4.3.1 presents the fuel analyses and Section 4.3.2 the FTP exhaust and evaporative vehicle emissions tests.

Note the protocol changes between Summer 2002 and Winter 2005 tests: in the Summer tests only half the sample days were begun with a background sample; in the Winter tests separate in-cabin samples were taken for the high ventilation and low ventilation measurements as detailed in Table 5.2-1.

5.3.1 Background and Overall Concentrations

The background sample results from the summer and winter samples are presented in Table 5.3-1. The percent standard deviations are relatively low, suggesting that the backgrounds are relatively stable. The MTBE deviations are highest likely because this compound is principally present only in the Houston fuel. Background MTBE ranged from 0 to 0.21 ppbv. There was only one EtOH background measurement for the Summer 2002 (261 ppb) and three valid measurements for Winter 2005. The high 2002 EtOH value could be connected with the presence of four people in the vehicle cabin and/or the presence of the continuous formaldehyde analyzer. The winter values range from 9 to 44 ppb and seem to be more reliable.

Table 5.3-1. Summary of Summer and Winter Background Concentrations.

	Budi13	Benze	Tolue	Etbz	Mp_xyl	O_xyl	MTBE	CO, ppm	Formal	EtOH	Acetal
Mean Summer (n=6)	0.02	0.27	0.44	0.07	0.17	0.11	0.06	0.13	5.80	261	2.80
% std dev	54%	26%	15%	24%	46%	48%	131%	18%	84%	(n=1)	90%
Mean Winter (n=12)	0.03	0.32	0.52	0.11	0.38	0.16	0.08	0.21	5.62	22.07	4.05
% std dev	46%	46%	67%	61%	63%	62%	101%	38%	63%	88%	42%
Mean all	0.03	0.31	0.49	0.10	0.31	0.14	0.07	0.19	5.68	81.81	3.64
% std dev	50%	42%	58%	59%	72%	63%	107%	41%	68%	147%	56%

Budi13 = 1,3BD; Benze = benzene; Tolue = toluene, Mp_xyl = m,p-xylene; o_xyl = o-xylene, Formal = formaldehyde; EtOH = ethanol, Acetal = acetaldehyde

In Figure 5.3-1 the values for formaldehyde are divided by 10 to fit on the same scale as the rest of the species and the EtOH values are not shown. Generally speaking the in-cabin background values are < 1 ppbv, with the exception of HCHO and EtOH, and relatively consistent from summer to winter.

In-cabin HCHO measurements likely included contributions from photochemical formation from ambient VOCs and in-cabin fabric component degassing of this species. As mentioned in Chapter 1 and 4, EtOH may be emitted from people (as a metabolic product for certain food types), foods, cleaning& personal care products, etc.

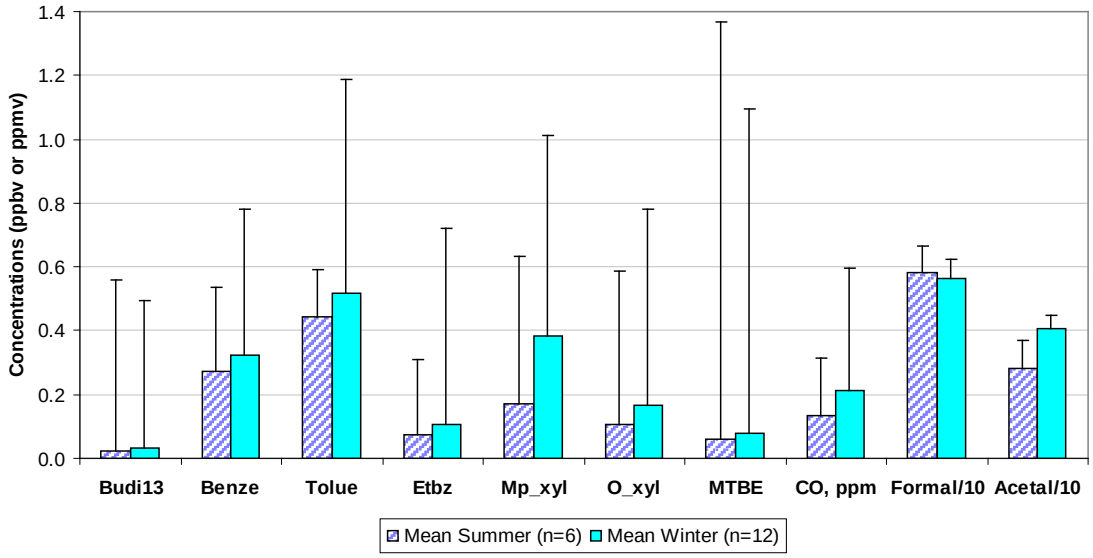

Figure 5.3-1. Comparison of Summer and Winter Background Concentrations with Standard Deviations. Formaldehyde and acetaldehyde divided by 10 for scale.

Mean concentrations over all tests are presented in Table 5.3-2. Standard deviations are expressed as a percent of test value. As with the background concentrations, MTBE likely shows the greatest variability since it was prominent in only one fuel. Also, EtOH Summer 2002 measurements (3 values) are most probably artifact, whereas Winter 2005 data (6 measurements) seem to be much more reliable.

Table 5.3-2. Summary of Test Concentrations for Summer, Winter and Overall. Units are ppbv, except CO as noted.

	Budi13	Benze	Tolue	Etbz	Mp_xyl	O_xyl	MTBE	CO, ppm	Formal	Acetal	EtOH
Mean Summer (n=12)	0.69	1.40	2.32	0.43	1.25	0.59	0.44	1.00	6.84	5.61	2308.07
% std dev	103%	69%	56%	65%	62%	63%	230%	72%	47%	71%	102%
Mean Winter (n=24)	0.59	1.20	1.99	0.37	1.30	0.50	0.83	1.72	4.82	2.54	1.70
% std dev	96%	76%	73%	77%	74%	76%	220%	91%	70%	75%	51%
Mean all	0.62	1.26	2.09	0.39	1.28	0.53	0.70	1.49	5.53	3.63	693.61
% std dev	100%	75%	67%	73%	70%	71%	233%	91%	63%	89%	250%

Budi13 = 1,3BD; Benze = benzene; Tolue = toluene, Mp_xyl = m,p-xylene; o_xyl = o-xylene, Formal = formaldehyde; EtOH = ethanol, Acetal = acetaldehyde

Figure 5.3-2 and 5.3-3 shows the CO, MTBE and BTEX concentrations for each test in the Summer 2002 and Winter 2005, respectively.

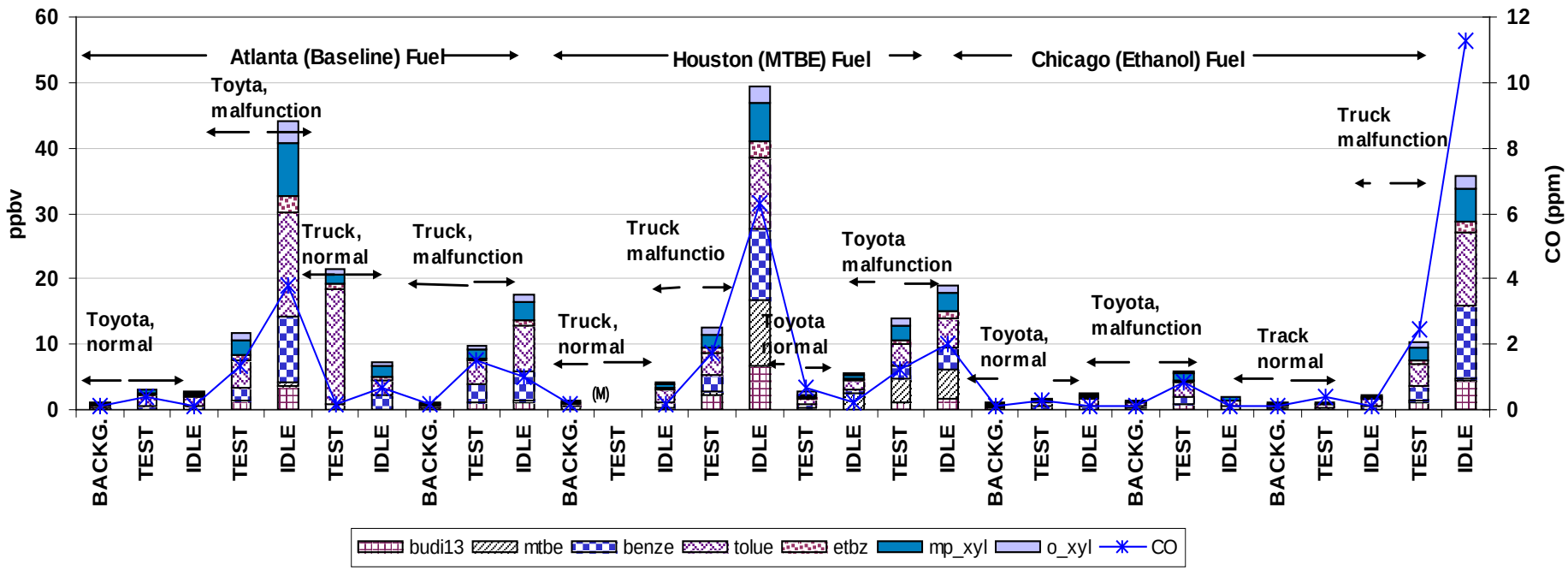

Figure 5.3-2. Concentrations of 1,3-BD, MTBE and BTEX (A) and CO (B) as measured in the cabin of the trailing vehicle, Summer 2002

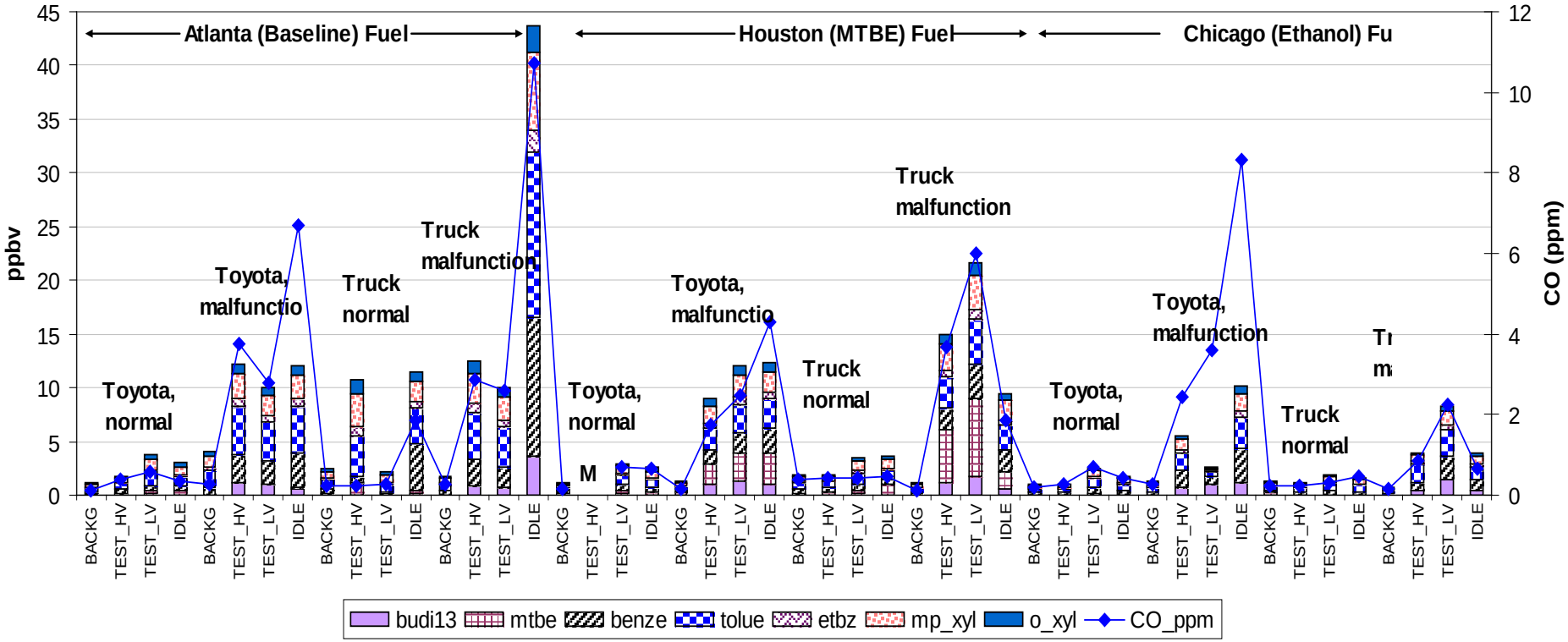

Figure 5.3-3. Concentrations of 1,3-BD, MTBE and BTEX and CO as measured in the cabin of the trailing vehicle, Winter 2005

Figure 5.3-4 compares summer and winter concentrations which, like background, are similar (EtOH data not shown).

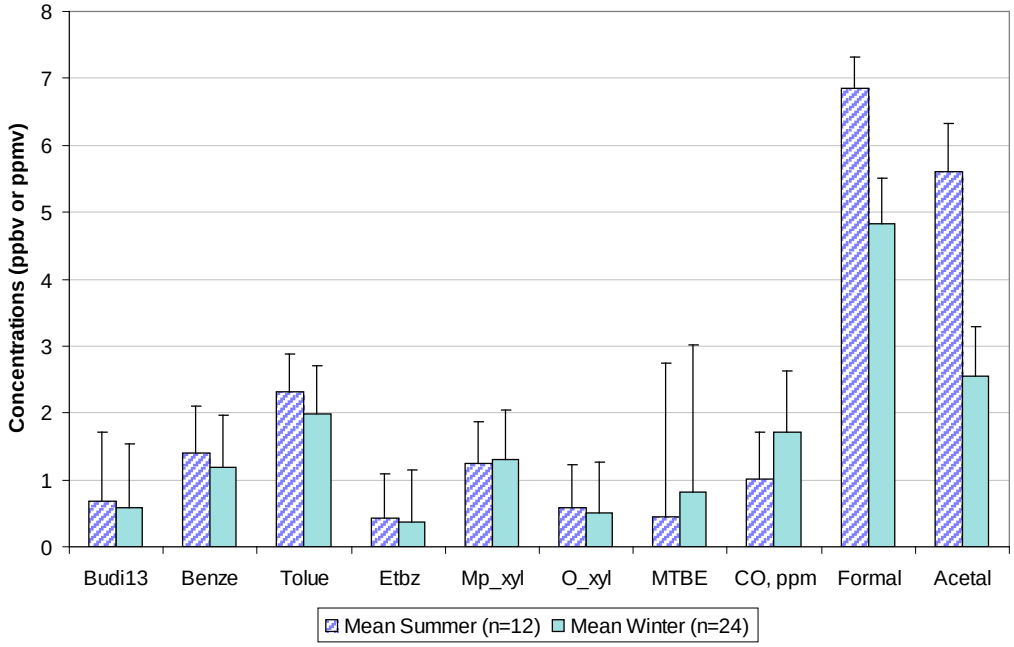

Figure 5.3-4. Comparison of Summer and Winter Concentrations for the Trailing tests.

Summer background and test values, excluding HCHO and EtOH, are compared in Figure 5.3-5. Test values show a substantial increase over background. Correlating all summer species except HCHO and EtOH against their background values gives a slope of 0.24 (r-square = 0.93).

Winter background and test values are presented in Figure 5.3-6, omitting HCHO and EtOH. The observation that the winter HCHO values were, on average, lower than background values suggests that most of the HCHO observed was not coming from the lead vehicle but possibly from photochemical or off-gassing sources (e.g., fabrics) inside the trailing vehicle. EtOH background values were higher than test values, which suggest some initial off-gassing of EtOH in the vehicle cabin (since background sample was collected at the beginning of each experiment). The correlation of all winter species values except HCHO and EtOH against their background values had a slope of 0.31 (r-square = 0.73).

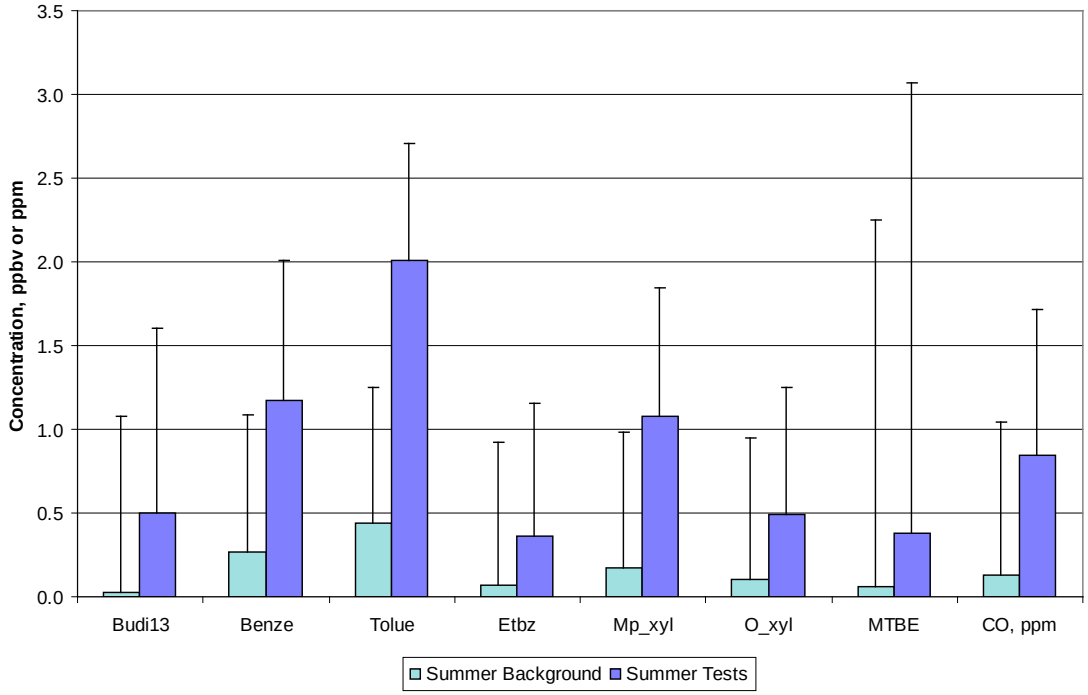

Figure 5.3-5. Comparison of Summer Background and Test Values.

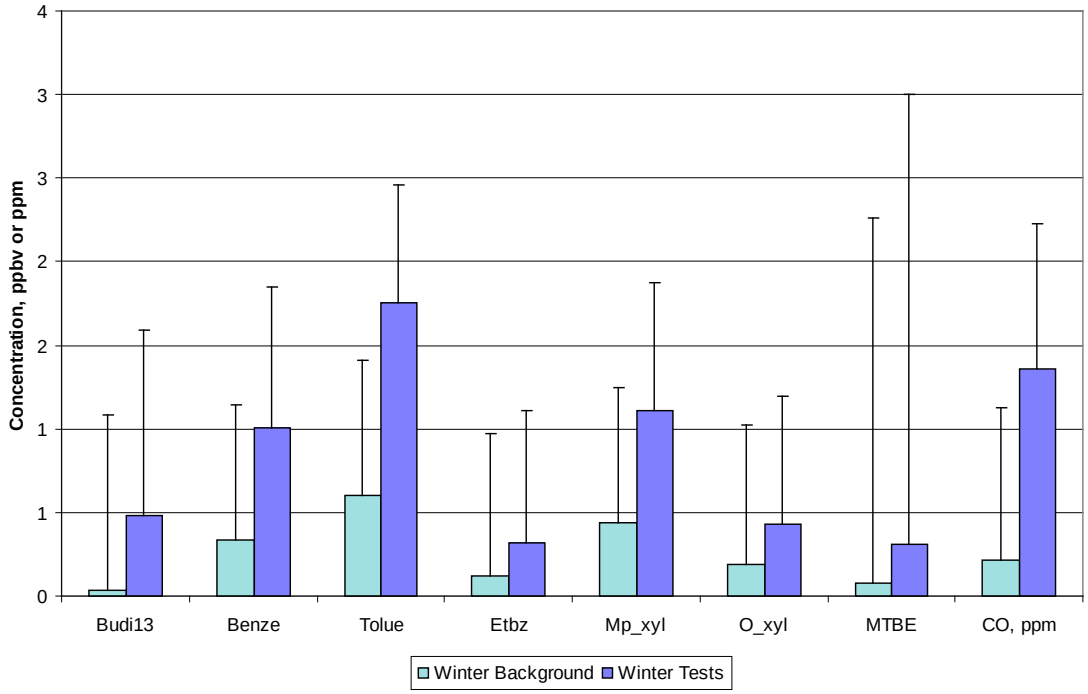

Figure 5.3-6. Comparison of Winter Background and Test Values.

Table 5.3-3 presents the concentrations and percent standard deviations observed during the idle tests. These values showed more of a range and larger deviations than either the background or the driving tests. HCHO again appears to be an outlier with the lowest deviation of any of the species, likely indicating that this species is not coming predominantly from the upwind lead vehicle. EtOH values for Summer 2002 (3 measurements) are most probably artifact and the Winter 2005 values (4 measurements) are more realistic. Since the main difference between the Summer 2002 and Winter 2005 experiments was the absence of the continuous formaldehyde and MS200 KORE mass spectrometer in the trailing vehicle, it is possible that one of these instruments (most probably the continuous formaldehyde analyzer, since it is based on the wet method) was out-gassing EtOH.

Table 5.3-3. Summary of Concentrations Observed During Idle Tests. Units are ppbv except CO as noted.

	Budi13	Benze	Tolue	Etbz	Mp_xyl	O_xyl	MTBE	CO, ppm	Formal	EtOH	Acetal
Mean Summer (n=11)	1.50	3.77	4.96	0.80	2.45	0.99	1.54	2.16	9.61	1030.68	9.04
% std dev	149%	116%	103%	110%	109%	104%	195%	160%	43%	59%	65%
Mean Winter (n=12)	0.66	2.57	3.01	0.48	1.71	0.65	0.54	3.06	6.53	3.86	3.37
% std dev	156%	137%	136%	111%	111%	96%	169%	118%	40%	61%	28%
Mean all	1.08	3.17	3.99	0.64	2.08	0.82	1.04	2.61	8.00	517.27	6.08
% std dev	163%	124%	116%	114%	110%	103%	214%	133%	46%	131%	81%

Budi13 = 1,3BD; Benze = benzene; Tolue = toluene, Mp_xyl = m,p-xylene; o_xyl = o-xylene, Formal = formaldehyde; EtOH = ethanol, Acetal = acetaldehyde

5.3.2 Vehicle and Fuel Effects

The preceding section assessed overall mean concentrations in the trailing vehicle cabin, averaging across vehicles, emission modes and fuels; this section will separately consider these parameters.

Table 5.3-4 details the effects of changing vehicle, fuel, and emission mode.

The first two rows distinguish the truck and the car, averaged over all fuels and modes. These values are very similar, showing little effect of the vehicle by itself.

The next three rows distinguish the fuels, averaging over the vehicles and modes. The Atlanta fuel results in higher BTEX concentrations in the trailing vehicle cabin, which is consistent with higher aromatic contents of Atlanta fuel, especially in summer (see Table 4.3-1).

The next two rows distinguish the normal and high emitter modes, averaging over the vehicles and fuels. The values clearly differ, with the high emitter mode values much higher than for the normal emitter mode.

The last line in this table presents the percent standard deviations of the high emitter values that are very similar, with the anticipated exception of MTBE which is larger due to its predominant occurrence in only one of the three fuels.

Figure 5.3-7 presents the effect of normal versus high emitter vehicle on the trailing vehicle in-cabin concentrations in a scatter plot for all species except HCHO and EtOH. Cabin levels of HCHO and EtOH were omitted since in-cabin upholstery and occupant sources of these compounds predominate penetration of outdoor levels. The slope indicates that in-cabin values measured during trailing the vehicle in high emitter mode are about twice those found for the normal mode. Since lead vehicles in these tests are converted between 'normal' and 'high emitter' states by disabling control devices, not by mis-tuning the engines or opening fuel line leaks, exhaust emissions should remain roughly proportionate between both operational modes.

Table 5.3.4. Effect of Vehicle, Fuel, and Operational Mode. Units are ppbv, except CO as noted. Number of measurements = n

	Budi13	Benze	Tolue	Etbz	Mp_xyl	O_xyl	MTBE	CO, ppm	Formal	Acetal
Truck only (n=12)	0.64	1.40	2.32	0.45	1.46	0.61	0.87	1.56	4.55	3.67
Car only (n=12)	0.59	1.13	1.87	0.33	1.11	0.45	0.53	1.42	5.90	3.59
Atl fuel only (n=8)	0.53	1.44	2.79	0.51	1.66	0.68	0.14	1.41	5.99	3.39
Hou fuel only (n=8)	0.89	1.52	2.20	0.48	1.58	0.66	2.17	1.91	5.61	4.37
Chi fuel only (n=8)	0.48	0.87	1.32	0.20	0.66	0.28	0.03	1.22	4.20	3.19
Normal only (n=12)	0.06	0.46	1.05	0.21	0.73	0.31	0.16	0.41	5.21	3.26
High emitter only (n=12)	1.06	1.95	2.99	0.55	1.77	0.71	1.21	2.50	5.37	3.37
St Dev high emitter only	28%	36%	38%	41%	44%	44%	177%	52%	52%	64%

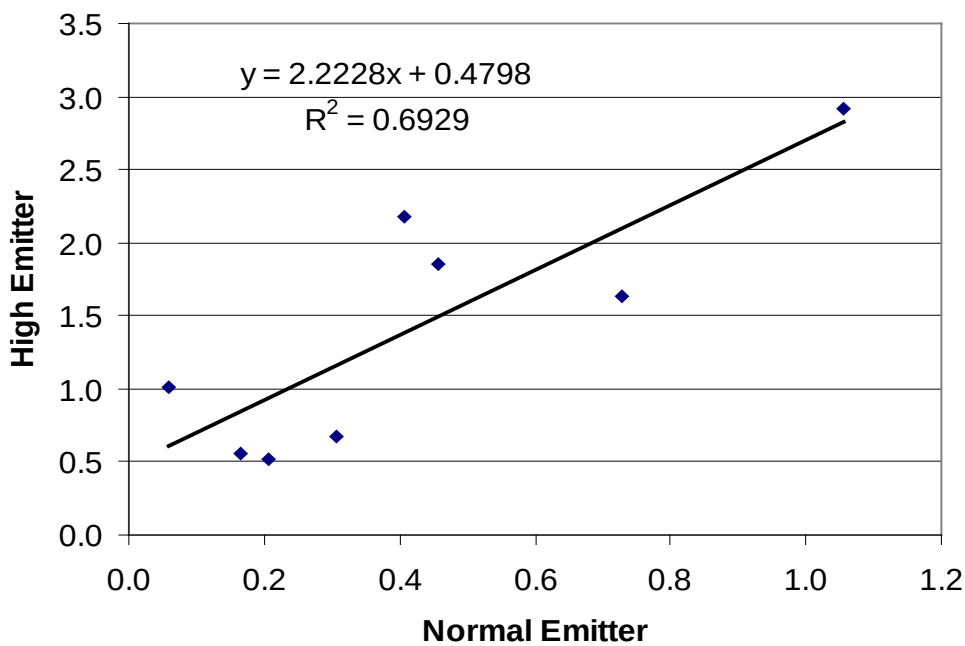

Figure 5.3-7. Scatter plot of Normal Emitter and High Emitter Mean In-cabin Values for all species except HCHO and EtOH.

Looking at the high emitter mode only, Table 5.3-5 presents high emitter mean in-cabin values for each fuel separately. MTBE values present the clearest difference. This is expected based on the fuel composition. The other species show relatively little difference. EtOH values are not shown, due to the Summer 2002 artifact.

Table 5.3-5. Influence of high emitting vehicles and each fuel on trailing vehicle in-cabin concentrations. Units are ppbv except CO as noted.

	Budi13	Benze	Tolue	Etbz	Mp_xyl	O_xyl	MTBE	CO, ppm	Formal	Acetal
High Emiter, Atl (n=4)	1.02	2.35	3.97	0.67	2.12	0.85	0.03	2.48	5.04	2.80
High Emiter, Hou (n=4)	1.43	2.18	3.08	0.69	2.24	0.93	3.45	2.81	6.00	5.77
High Emiter, Chi (n=4)	0.91	1.40	2.02	0.31	0.98	0.42	0.06	2.08	5.42	3.90

The high emitter values, averaged across fuels, are presented in Table 5.3-6 separated by season. HCHO has the largest difference, summer > winter, which is likely due to more rapid photochemical reactions or in-cabin off gassing rates during the summer. In addition, BTEX concentrations are consistently higher during the summer, which is consistent with higher aromatic contents of summer fuels, especially for Atlanta (see Table 4.3-1).

Table 5.3-6. Summary of Seasonal Differences in the High Emitter Samples.

	Budi13	Benze	Tolue	Etbz	Mp_xyl	O_xyl	MTBE	CO, ppm	Formal	Acetal
Summer High	1.23	2.15	3.33	0.61	1.79	0.82	0.76	1.52	8.02	7.66
Winter High	1.06	1.89	2.86	0.53	1.78	0.69	1.39	2.92	4.22	2.27

5.3.3 Trailing Vehicle Effects

In the winter 2005 tests, separate canisters were collected for the high and low cabin ventilation portions of the tests; in the summer 2002 tests, only a single canister was collected integrating these two periods. Table 5.3-7 shows the average values from the high and low ventilation winter 2005 canisters. Their values are similar across seasons. Table 5.3-7 shows that although mean canister (integrated) in-cabin values were similar under high and low ventilation conditions, the range of concentrations observed by continuous PID monitor was much larger under high ventilation conditions, as illustrated in Figure 5.3-8. The high ventilation condition continues up to 60 min and is then switched to low ventilation for the remaining 60 min. The outdoor ppbRAE-PID shows generally lower values and the two indoor peaks in the first 60 min are associated with the “near” tailgating portion of the driving sequence. The outdoor PID2 shows generally lower values that the indoor PID1, since it was mounted on the aerial on the right side of the van, thus its inlet was mostly opposite to the truck’s tailpipe (that was situated on the left side of the truck).

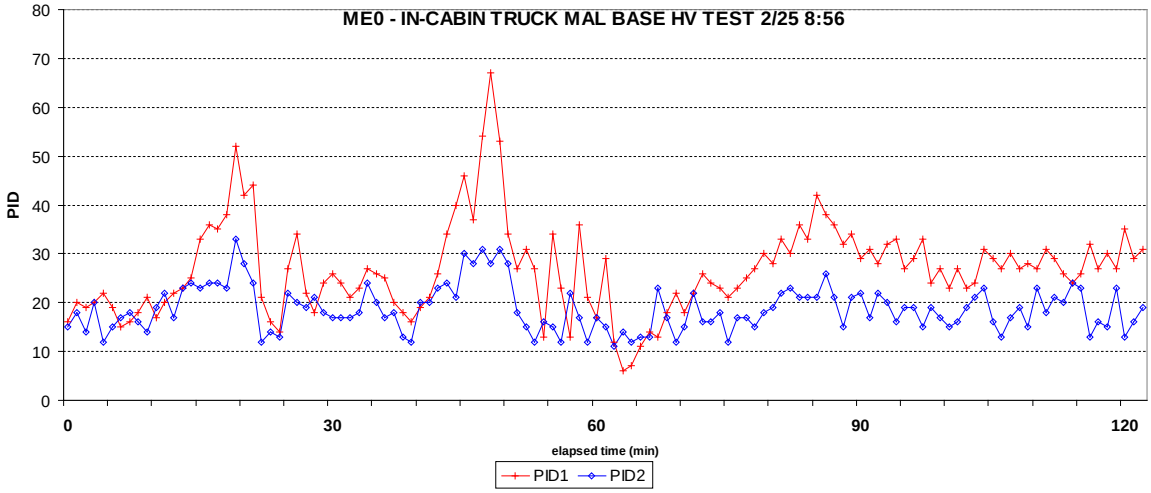

Figure 5.3-8. Time Series of In-Cabin (PID1) and Outside (PID2) PID Values. The first 60 min are under high ventilation conditions (0-60 min) and the next 60 min (60-120 min) are under low ventilation conditions.

Table 5.3-7. Comparison of High and Low In-cabin Ventilation Conditions, Winter 2005 only. Units are ppbv except CO as noted.

	Budi13	Benze	Tolue	Etbz	Mp_xyl	O_xyl	MTBE	CO, ppm	Formal	Acetal
High Vent only	0.52	1.15	2.07	0.40	1.35	0.54	0.74	1.54	4.38	2.13
Low Vent only	0.64	1.24	1.91	0.35	1.25	0.47	0.91	1.89	4.65	3.08

5.3.4 Comparison with FTP Data

The driving tests were all conducted while the vehicle was in a hot stabilized operating condition. The FTP test phase most comparable is phase 2 (Bag 2) and this section will examine the correlation of the Bag 2 components with observed values in the driving tests.

Figure 5.3-9 correlates Bag 2 and the trailing vehicle benzene values. There is a trend of increasing cabin benzene concentrations with increasing benzene FTP emissions (R^2=0.64). Figure 5.3-10 presents the same correlation for MTBE although there are fewer data points since only the Houston fuel contained substantial concentrations of MTBE. Figure 5.3-11 illustrates the same correlation for 1,3-BD. Unlike benzene and MTBE, 1,3-BD is primarily an exhaust component. The 1,3-BD plot shows the same correlation (R^2 =0.62) between the FTP emission level and the resulting trailing vehicle cabin concentration as benzene. The correlations are driven mostly by the vehicles in malfunction modes, since only these vehicle emissions result in significant concentrations in the trailing vehicle cabin.

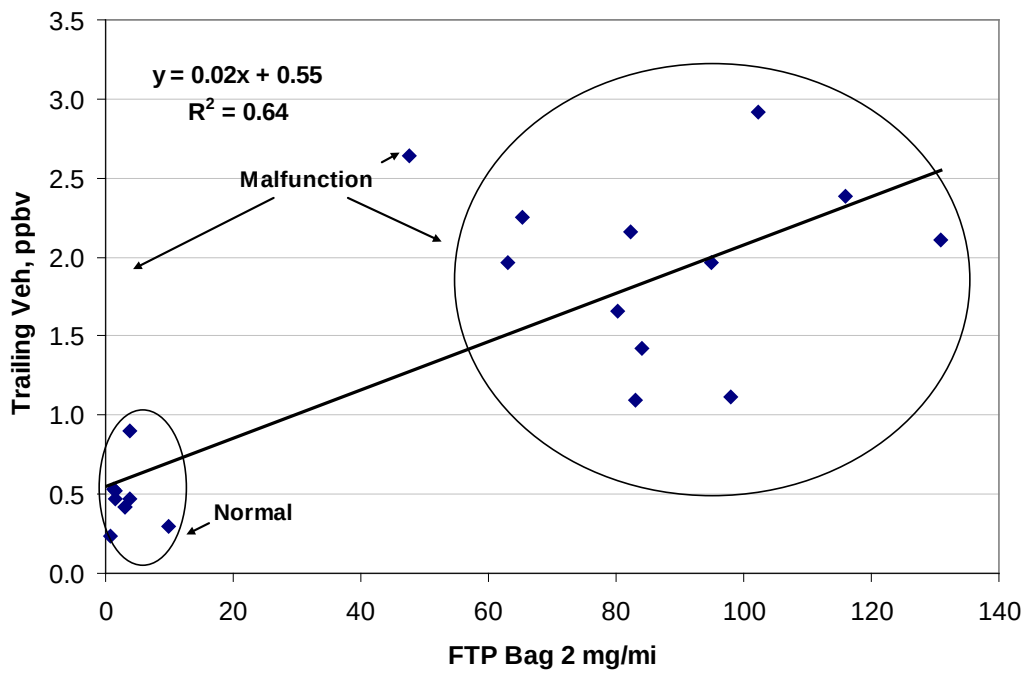

Figure 5.3-9. Comparison of FTP Bag 2 Benzene Emissions to In-cabin Concentration in the Trailing Vehicle.

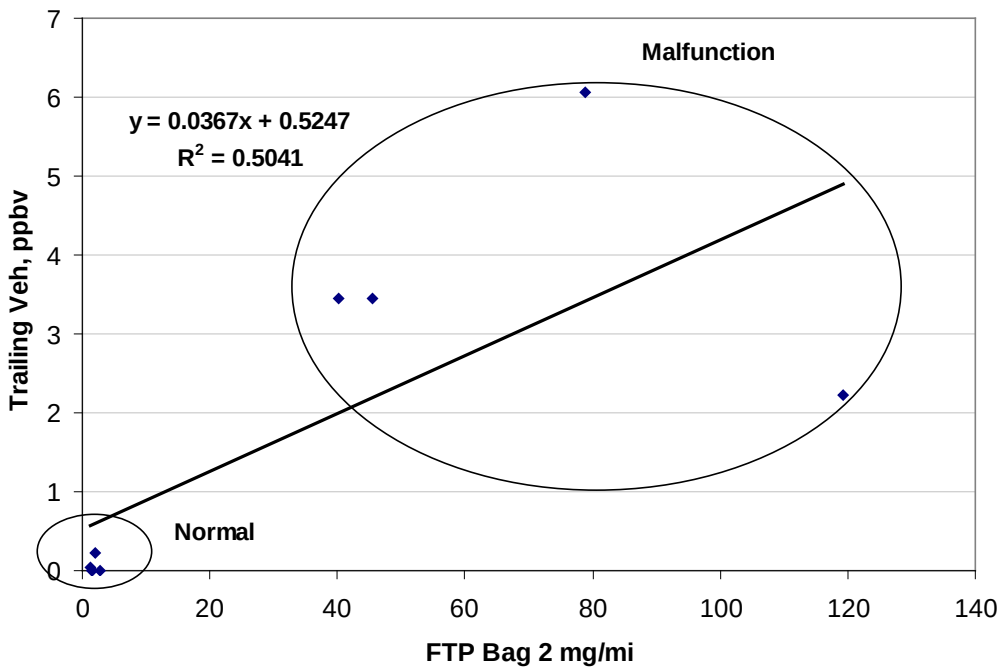

Figure 5.3-10. Comparison of FTP Bag 2 MTBE emissions to in-cabin concentrations in the trailing vehicle.

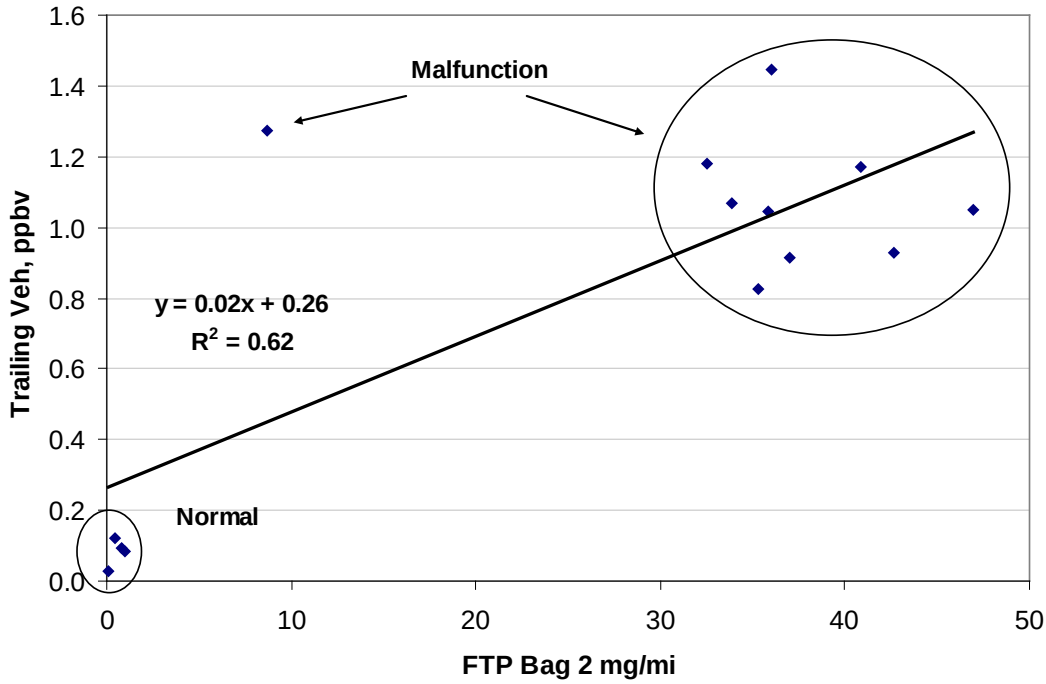

Figure 5.3-11. Comparison of FTP Bag 2 1,3-BD Emissions to In-cabin Concentrations in the Trailing Vehicle.

5.4 Discussion

The overall objective of this section is to assess the various effects that might impact trailing vehicle in-cabin levels of leading vehicle emissions. A rural test site with very little traffic was chosen to minimize non-lead vehicle influences on measured in-cabin values. Background samples were taken prior to the driving tests to quantify other possible sources. Measured component backgrounds were low and consistent from summer to winter although HCHO backgrounds were relatively high, suggesting in-cabin sources.

Summer and winter in-cabin values were similar in magnitude with the exception of HCHO which was higher in the summer, possibly due to higher photochemical activity and higher temperatures that led to more HCHO off-gassing of the vehicle cabin interior. EtOH values in Summer 2002 are much higher than in Winter 2005, most probably due to the off-gassing effect of the continuous formaldehyde analyzer that was located in the trailing vehicle cabin for Summer 2002 measurements.

Trailing vehicle cabin values were substantially larger than background values except for HCHO which was actually lower than background in winter tests. Idle test sample values were on average twice those encountered in driving tests, suggesting that proximity and proximity duration may substantially impact in-cabin trailing vehicle concentrations.

Average in-cabin levels were little affected by different vehicles or fuels except for an MTBE fuel effect. However, averaging over the fuels and vehicles, the high emitter mode resulted in much higher trailing vehicle in-cabin values than the normal emitter mode, on average 2.2 times higher; except for HCHO which was relatively unchanged from background. Similarly, the season had no strong effect upon the trailing vehicle concentrations.

Trailing vehicle ventilation status also affected in-cabin values. Although mean canister (integrated) in-cabin values were similar under high and low ventilation conditions, the range of concentrations observed by continuous PID and CO monitors was much larger under high ventilation. This may be rationalized as the vehicle moving into and out of the exhaust plume of the leading vehicle with in-cabin values changing rapidly under high ventilation; whereas under low ventilation, in-cabin concentrations trapped as the vents were closed stayed relatively constant during the remainder of low ventilation conditions.

Trailing vehicle tests indicated that the largest impact on in-cabin values came from the emissions mode of the leading vehicle. Emissions observed in Bag 2 of the FTP tests were compared to the observed trailing vehicle levels of benzene, MTBE and 1,3-BD. Benzene and MTBE have both exhaust and evaporative emissions while 1,3-BD is only emitted in exhaust. In-cabin benzene and MTBE levels appear to correlate with FTP emissions, however, 1,3-BD does not but correlates with other in-cabin species.

Appendix A

Exposure Protocol and Study Plan for the Section 211(B) Tier 2 High End Exposure Screening Study of Baseline and Oxygenated Gasoline

APPENDIX A

Exposure Protocol and Study Plan for the Section 211(B) Tier 2 High End Exposure Screening Study of Baseline and Oxygenated Gasoline

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1. INTRODUCTION

The U.S. Environmental Protection Agency (EPA) has recently issued requirements for a test program in accordance with the Alternative Tier 2 provisions of the fuels and fuel additives (F/FA) health effects testing regulations, which are required pursuant to Section 211(b) of the Clean Air Act. In response to these requirements, the American Petroleum Institute (API) contracted with a research team consisting of the Desert Research Institute (DRI), Southwest Research Institute (SwRI), Lovelace Respiratory Research Institute (LRRI), and TRJ Environmental, Inc (TRJ) to conduct a screening study of the high-end distribution of inhalation exposures to evaporative and combustion emissions of baseline- and oxygenated gasoline. This study plan describes the exposure protocols and specifies the measurement methods, sampling & analytical procedures, and quality assurance protocols that will be used in the study.

The goal of this research program is to screen potential high-end inhalation exposure microenvironments dominated by evaporative and exhaust emissions of baseline- and oxygenated-gasoline. The specific objectives are to provide information allowing the Agency to:

- Quantify personal exposures to motor vehicle oxygenated and non-oxygenated gasoline evaporative and exhaust emissions in microenvironments (MEs) representing the upper end of the exposure frequency distribution of such exposures;

- Determine the quantitative relationships between personal exposures in selected MEs with fixed site measurements in these MEs and at nearby air monitoring stations;

- Determine how personal exposures differ in cities and seasons in which methyl tertiary butyl ether (MTBE)-oxygenated, ethanol (EtOH)-oxygenated, and baseline gasolines are in use;

- Extrapolate to other sites and, if possible, other oxygenated fuels;

- Determine the relative contributions of vehicle fuel exhaust and evaporative emissions to personal exposures from oxygenated and non-oxygenated gasoline.

The overall approach for the exposure study is based upon the draft June 29, 2001 S211b Tier 2 Exposure Study Protocol that was developed in May 2001 by the API Section 211(b) Research Group and reviewed by the U.S. Environmental Protection Agency (EPA). The main study protocol has changed significantly from the original version based on the results from the first Reno pilot study (submitted to EPA April 25, 2002) and recommendations made by EPA during the summer Atlanta site visit in August 2002, specifically in relation to the measurement methods approach. These changes were incorporated into the second Reno pilot study in April 2003 (submitted to EPA June 13, 2003). Additional protocol adjustments incorporated into this September 4, 2003 draft have been the result of continuous dialog between EPA and DRI.

The main exposure study consists of gathering data under controlled and field conditions. First, DRI and SwRI will conduct exposure measurements under controlled conditions in order to establish quantitative relationships between vehicle tailpipe and evaporative emissions to exposure levels in two specific microenvironments, a trailing vehicle cabin and an attached residential garage. In the field, DRI and LRRI will monitor microenvironmental and personal exposures in various potential high-end microenvironments in Houston, Chicago, and Atlanta during summer (July to September) and winter (January to March). These cities have ongoing ambient monitoring programs and have MTBE-RFG, EtOH-RFG, and baseline gasoline formulations, respectively. A number of key variables will be measured in ambient air within microenvironments, in subjects' personal breathing zones and in breath. Section 3 specifies the microenvironments and exposure protocols. The results of this study will provide information to quantify the upper-end personal exposure to gasoline and oxygenated gasoline emissions and extrapolations to other cities using oxygenated fuels. The information from this study will permit sensitivity analyses to determine the range of these exposures, especially during heavy traffic, in residential and public parking garages and during refueling.

2. MEASUREMENT METHODS AND PROTOCOLS

The exposure screening study uses three approaches to measure the targeted air toxics in high-end microenvironments: (1) reference method time-integrated samplers to quantify concentrations over 5-60 minute sampling periods; (2) continuous surrogate method monitors to determine short-term concentration variations over 10-60 second sampling periods; and (3) supplementary methods to provide additional short-term surrogate concentration estimates over intermediate time frames of one to several minutes. It should be noted that the supplemental methods are newer methods that, in many cases, utilize instruments that have not been fully adapted for field use. These methods are independent checks on the surrogate approach, providing periodic corroboration under differing conditions and locations encountered during the tests. The supplementary method data are not required to conform to the CAA requirements and therefore should not to be used in regulatory decision making.

1. The reference methods include pumped whole-air canister samplers used for CO, CO2, benzene, toluene, ethylbenzene, xylenes (BTEX), MTBE and 1,3 butadiene (BD), acidified 2,4-diphenylhydrazine (DNPH) cartridges for formaldehyde (HCHO) & acetaldehyde (CH3CHO) and a multi-bed (TenaxTA-Carbotrap-Carbosieve) solid adsorbent tube for EtOH. Canister CO and CO2 are converted to methane for analysis by gas chromatography with flame ionization detection (GC/FID) and BTEX, MTBE, 1,3 BD are quantified by capillary GC/FID, or GC/MS for breath samples, using separate analysis. The aldehyde cartridges are eluted with acetonitrile and analyzed by high performance liquid chromatography with photodiode array UV detection of their hydrazone derivatives. The multi-bed tubes are thermally desorbed into a gas chromatograph and quantified by mass spectrometric detection (GC/MS). In addition, the multi-bed tubes provide the opportunity to compare the values for toluene, ethylbenzene and xylenes obtained by the canister method with those obtained by the tube method. These methods are basically standard TO-15, -11A, and -17 EPA procedures with improvements incorporated by the Desert Research Institute (DRI), as described in Section 2.3.5. .

2. The surrogate methods include both active non-dispersive infrared (NDIR) and passive T-15 Langan electrochemical cell devices for CO and an active photo-ionization detector (PID) for volatile organic compounds with an ionization potential below 10.6 eV (principally olefins and aromatic species). These continuous instruments respond to concentration changes of a few seconds and provide sensitive proportionate measures of the short-term variability of target exhaust and evaporative species quantified by the time-integrated reference methods. These methods are used to generate the short-term time-series of concentrations for BTEX, MTBE, EtOH, 1,3 BD, and the aldehydes quantified by the reference methods.

3. The supplemental methods include both active continuous instruments with one to several minute time responses, respectively, for BTEX and HCHO and a passive sorbent fiber sampling of a flowing analyte stream for BTEX over a 10-minute period. The continuous BTEX monitor quantifies species diffusing through a semi-permeable membrane by ionizing them at 70 eV by electron impact and pulsing them into a time-of-flight (TOF) mass spectrometer. The HCHO instrument bubbles ambient HCHO into a flowing aqueous 2,4-pentanedione reagent to produce a formaldehyde-specific product, 3,5-diacetyl-1, 4-dihydrolutidene that is quantified by ultra-violet fluorescence. The 75 um solid phase (carboxen/polydimethylsiloxane) (SPME- CAR/PDMS) fiber is passively exposed for ten minutes, retracted into its syringe holder, and promptly injected into a GC with PID/FID detection optimized for BTEX quantification.

The surrogate approach is used to generate short-term time-series values for the target species (MTBE, EtOH, 1,3 BD, CH3CHO) for which there are no continuous measures. In microenvironments with running engines exhaust emissions may dominate and either CO or PID surrogates should provide comparable time-series measures of short-term values, as shown in Figure 2-1. In engine-off microenvironments, evaporative species should dominate and the PID surrogate should provide the time-series measure since CO isn't emitted, as shown in Figure 2-2.

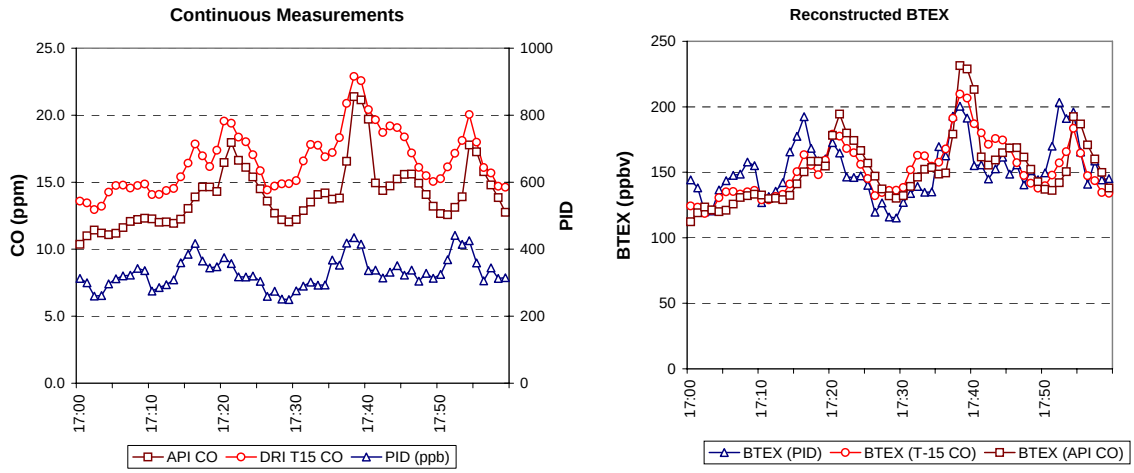

Figure 2-1

Since collocated contemporaneous reference measurements are paired with surrogate measures during each sampling period, each time-series generated is individually calibrated to the specific target compound/CO or target compound/PID relationship determined by the vehicles, fuels, and conditions measured during that period. The area under the continuous surrogate trace is normalized to that of the integrated reference measurement which is assumed to be relatively constant over the 20-40 minute period of measurement.

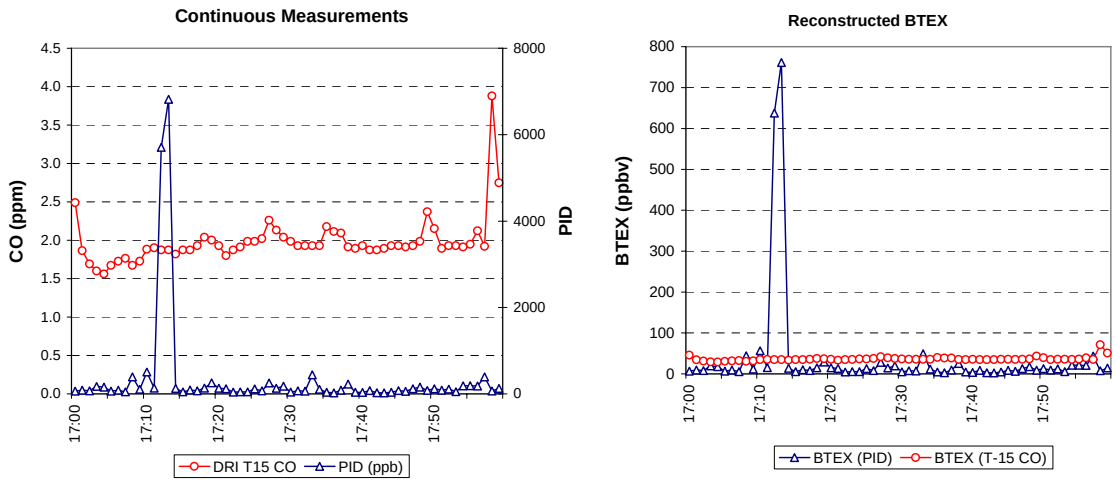

Figure 2-2

A constant compound/surrogate ratio is required during the period of measurement to provide reliable time-series values. However, where continuous monitors are available (although of different time resolutions), such values (e.g., BTEX, HCHO) may be compared to surrogate time series results as backup confirmatory data reducing uncertainties in the measurements, as shown in Figures 2-3 and 2-4.

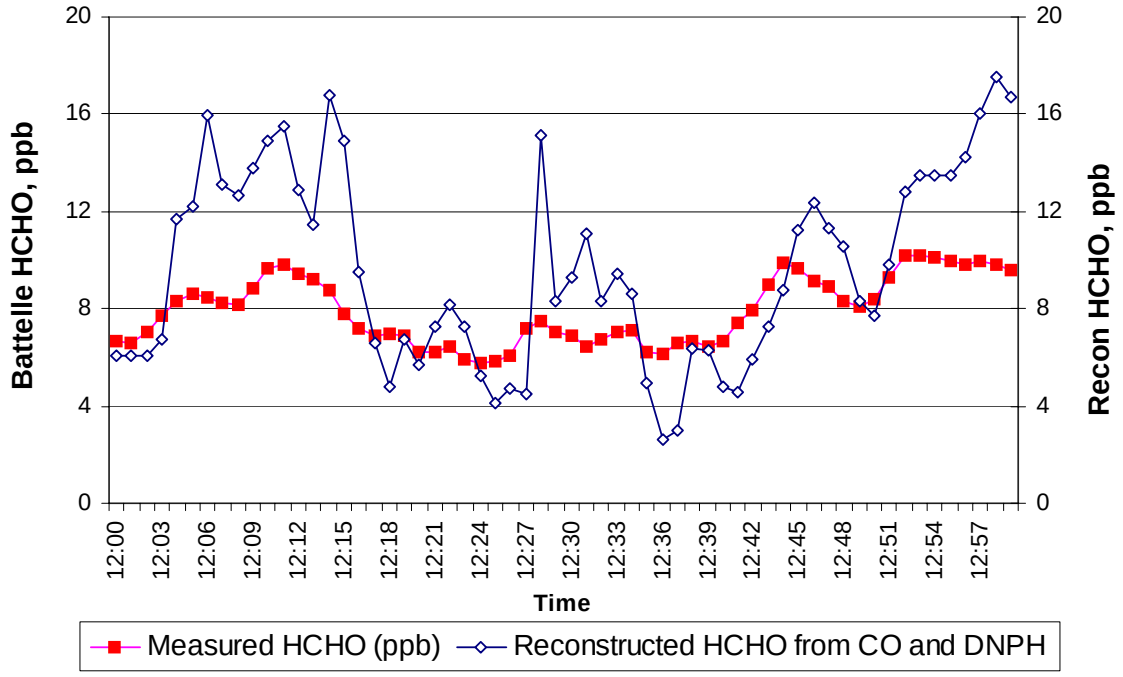

Figure 2-3

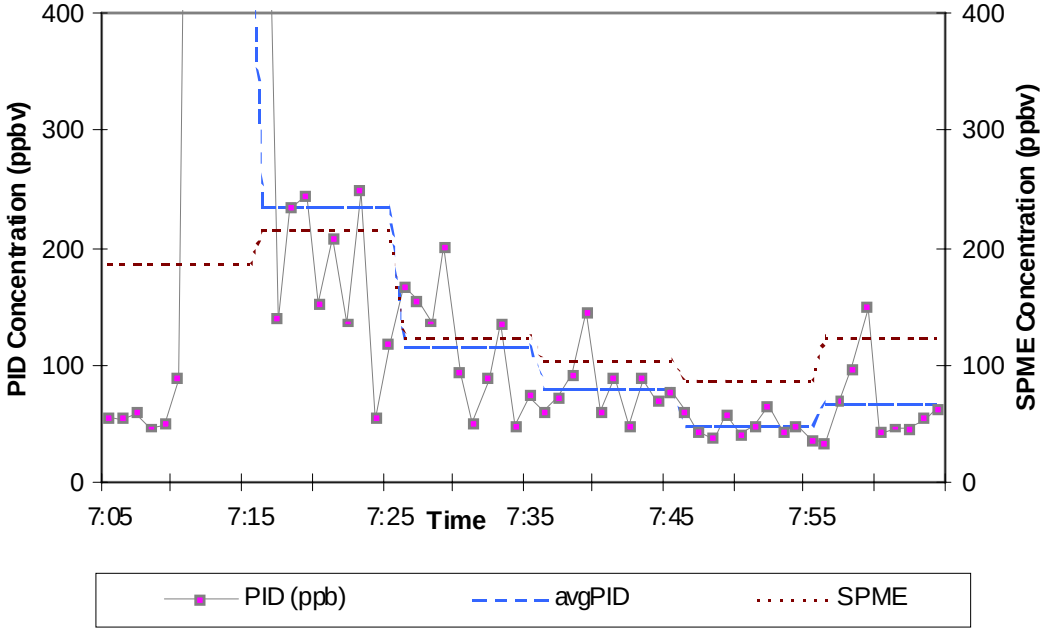

Figure 2-4

Analytical method descriptions and data quality objectives are tabulated below. Note that in the Measurement Data Quality Objectives table, the Time Resolution row reflects the time resolution logged in this study rather than the higher time resolution capabilities typical of specific instruments noted in the Continuous Methods table.

Integrated and Semi-Continuous Methods

Method	Integrated			Semi-Cont.
	Canister	DNPH	Adsorbent	SPME
Applicable Environments	all	all	all	all
Time Resolution	5-60 min	20-60 min	20-60 min	10 min
Detection Limits	0.05 ppbC	0.1 ppbv	0.2 ppbv	0.2 ppbv
Data Application	Reference (R)	Reference (R)	Reference (R)	Confirmatory (C)
CO	R			
PID				
BTEX	R			C
1,3-Butadiene	R			
MTBE	R			C
Formaldehyde		R		
Acetaldehye		R		
Ethanol			R	
NMHC	R			

Continuous Methods

Method	Continuous				
	T15 CO	NDIR CO	ppbRAE	MS200	HCHO
Applicable Environments	outdoor and in-cabin	all	all	higher end	stationary
Time Resolution	seconds	seconds	seconds	1 min	1 min
Detection Limits	0.1 ppm	0.04 ppm	1 ppb	1-3 ppbv	1 ppbv
Data Application	Surrogate (S)	Surrogate (S)	Surrogate (S)	Confirmatory (C)	Confirmatory (C)
CO	Surrogate	Surrogate			
PID			Surrogate		
BTEX	S (a)	S (a)	SC (c)	C	
1,3-Butadiene	S (a)	S (a)	S (c)		
MTBE	S (a)	S (a)	S (c)		
Formaldehyde	S (b)	S (b)	S (d)		C
Acetaldehye	S (b)	S (b)	S (d)		S (g)
Ethanol	S (e)	S (e)	S (f)		
NMHC	S (a)	S (a)	S (c)		

S (a). Time series reconstructed from canister/CO ratio for exhaust-dominated samples.
S (b). Time series reconstructed from DNPH/CO ratio for exhaust-dominated samples except outdoor daytime samples.
S (c). Time series reconstructed from canister/PID ratio for exhaust- or evap-dominated samples in outdoor MEs.
S (d). Time series reconstructed from DNPH/PID ratio for exhaust-dominated samples except outdoor daytime samples.
S (e). Time series reconstructed from solid adsorbent/CO ratio for exhaust-dominated samples.
S (f). Time series reconstructed from solid adsorbent/PID ratio for exhaust and evap-dominated samples.
S (g). Time series reconstructed from $CH3CHO_{DNPH}/HCHO_{Cont}$ ratio for exhaust dominated samples.

Measurement Data Quality Objectives

Instrument	Canister	DNPH	SPME	CO-T15	CO-NDIR	PID	HCHO (1)	MS-200
Accuracy	<5%	<5%	3-50%	+/- 1 ppm (2)	<0.1 ppm or 0.5%	NA	<25%	<8%
Precision	<3%	<3%	2-15%	+/-0.1 ppm	+/-0.1 ppm or 1%	0.1	<25%	<5%
Detection Limit	0.05 ppbC	0.1 ppbv	0.2 ppbv	0.1 ppm	0.05 ppm	1 ppb	1 ppb	1-3 ppbv
Time Resolution (3)	variable	variable	variable	10 sec	10 sec	10 sec	1 min	1 min
Artifacts	None	None	None	H2, very high humidity	$CO2>10^{-4}$ $H2O>4x10^{-5}$	plastics,very high humidity	None	None
Method	GC/FID	HPLC/ Photodiode array	GC/FID & PID	Electro-chemical Detector	NDIR	10.6 eV lamp PID	Hantzch rxn fluorescence	Mass spectrometer
Source	DRI QA/QC Ext Audits Comparisons	DRI QA/QC Ext Audits Comparisons	DRI Use/intercomparisons	Manufacturer literature	Manufacturer literature	Manufacturer literature	DRI Use/intercomparisons	DRI Use/intercomparisons

(1) HCHO performance paramters based on Alpha Omega instrument's performance in the 2nd Reno pilot study.
(2) Based on DRI test
(3) Time resolution for continuous instruments designates data logging resolution used in the study rather than instrument time resolution

The continuous Kore MS200 will be used to monitor BTEX on a one-minute basis, sampling during the initial 10 second portion of each 60 second period. This instrument uses a time-of-flight mass spectrometer to separate compounds of interest. Rather than using a gas chromatograph, this instrument uses a software solution to apportion the contribution of each component of interest to the time-of-flight (TOF) mass spectrum seen by the instrument. The software does not distinguish between specific isomers, thus xylenes and ethylbenzene are reported together. The inlet uses a polydimethylsiloxane membrane preferentially to allow non-polar organic compounds into the analyzer while maintaining the vacuum inside the analyzer chamber. This membrane inlet does limit the types of compounds that can be analyzed, however. Common air constituents and polar organic molecules do not pass the membrane quickly. The instrument performed well during the pilot studies, comparing favorably with the canister measurements for most samples. Although we have attempted to secure the availability of another Kore MS200, which Horiba Instruments, Inc. in Irvine, CA, maintains, repeated shipping damage to this only other MS200 in the US has made its availability problematic. Given the periodic corroborative use proposed for this device, we do not believe the information provided by this instrument, while desirable, is necessary to fulfill the goals of the screening study. In the unlikely event this device goes out of service in the field, we will attempt to access the Horiba backup unit. Due to interferences from the vehicle's ignition system, likely the result of occasional resonances set up between engine electrical radio-frequency noise and MS200 circuits, this instrument may not provide full data capture during the mobile ME. Use of alternative instrument grounding and engine ignition filters will be investigated to remedy this occasional nuisance. Since the MS200 runs directly off isolated 12V AGM battery power, it should also be isolated from battery inverter electrical noise

Carbon monoxide will be monitored continuously by the Langan T15 CO monitor and by the ML 9830 (Monitor Lab) NDIR instrument. Langan T15 is an electrochemical monitor for CO. The response time of this instrument is somewhat slower than the response of the infrared-based instruments.

A Continuous Formaldehyde Monitor was purchased from Alpha-Omega Power Technology, Ltd. (Albuquerque, NM). The Alpha-Omega (AO) instrument utilizes the Hantzch reaction - it absorbs formaldehyde in acidified water, reacting it with 2,4-pentanedione and ammonia to form a cyclized product, 3,5-diacetyl-1, and 4-dihydrolutidene, which is continuously detected by fluorescence. The method is highly specific for formaldehyde and very sensitive. The AO device has been extensively modified by DRI to enhance its field reliability and ruggedness to vibration and shock and is designated as the DRI-formaldehyde instrument in subsequent discussion. However, its use is limited to stationary microenvironments in the present study since sensitivity to motion remains.

2.1 Biomarker Measurements

During the 1st Reno pilot study both urinary and breath concentrations of MTBE and the BTEX compounds were measured in two subjects after three separate scripted exposures. Breath measurements showed an exposure effect (post-exposure concentration in breath higher than pre-exposure concentration) when samples were collected soon after exposure (within ~2-3 minutes). Breath samples collected after longer post-exposure durations showed no increase relative to pre-exposure breath concentrations, most likely due to the short 1-3 minute half lives of these compounds in breath (Lindstrom and Pleil, 1996). The short half-life of absorbed volatile vapors such as BTEX in breath will require fast, precise timing for sample collection.

Urinary measurements from the pilot study showed little exposure effect from most compounds for 2 of the three exposures. In all cases the urinary concentrations of MTBE, toluene, ethyl benzene, and xylene were below detection limits. In most cases the concentrations of benzene (the only observed compound) post-exposure were similar to pre-exposure due to the fact that the exposure concentrations were low in most cases. After the highest exposure in the pilot study (refueling a vehicle - hourly canister average of about 10 ppbv benzene) there was a relatively strong exposure effect observed in one subject and a lesser exposure effect observed in a second subject. There was a time course in the elimination of benzene that showed urinary benzene concentrations increasing with time. This is similar to the results reported by Lee and Weisel (1998) on the behavior of MTBE in urine. Because of an inability to see the decay of urinary benzene 3 hours post exposure, a second scripted refueling exposure was conducted in Reno, NV, to repeat this peak exposure and see if the urinary VOC concentration data can be linked to an exposure effect at these levels and to follow the full time course of elimination. The measurements of urinary MTBE/BTEX from the second refueling experiment were successful, but demonstrated no differences between pre- and post-exposure.

Based on the pilot study results, since it was not possible to discriminate urinary benzene concentrations in post-exposure as compared to pre-exposure, it was decided not to conduct urinary measurements.

Based on results from the 2nd Reno pilot study, breath sampling will be conducted in three microenvironments; outdoor refueling, trailing high emitting vehicles (or roadway tunnel in Chicago and Houston), and underground garages. Three 1 liter breath canister samples will be collected for each experiment: before the exposure in the isolated subject, and 10 seconds (timed with a stopwatch) immediately after active refueling or a measured peak exposure in the other MEs. In addition, a third backup breath sample will be collected immediately after the second sample for these three microenvironments, in case there is a problem with the second sample.

2.1.1 Breath Sample Collection

Breath samples will be collected from technicians who participate in a scripted exposure. Since this study requires the use of human subjects, the final protocol was reviewed by an Institutional Review Board certified with NIH.

Technicians will be instructed to avoid exposure to material that may compromise the exposure assessment prior to and during the scripted exposures. This will include avoiding alcohol ingestion (ethanol) and first-hand or second-hand cigarette smoke for at least 3 days prior to the scripted exposures. Breath samples collected before the exposure will be used to assess background levels in the technician.

The test subject technician will take the three breath samples. One sample is taken before initiating ME sampling; the second, ten seconds (timed with a stopwatch) immediately after completing active refueling task or experiencing a measured peak exposure in another ME, and the third one immediately following the second. The 3rd sample will be analyzed only in case there is a problem with the second sample. The technician takes a 1-liter canister, places the tube in his mouth, and breathes smoothly and regularly through the mouth around the tube until a resting breath pattern is established. At the end of a normal exhalation, the technician closes the mouth, opens the canister valve, and continues to expel the expiratory reserve. The canister vacuum will collect 1 L of the expiratory reserve. When the flow stops, the technician closes the canister valve to capture the sample (Pleil and Lindstrom, 1995; 2002).

2.1.2 VOC Analysis in Breath Samples

The analysis of VOC in breath samples will be conducted as described by Pleil and Lindstrom (1995, 2002) Prior to the commencement of the study, the CO2 level in alveolar breath of all technicians performing breath sample collection will be measured using GC/FID. Since the FID does not respond to CO2, this species is converted to methane by a methanator, positioned after the GC column, but ahead of the FID. Three breath samples will be collected and analyzed, and the mean CO2 value will be used for further comparison. After breath sample collection, the CO2 will be measured using the same method. The target VOC (MTBE, 1,3-butadiene, ethanol, BTEX) will be measured using a GC/MS technique. The GC/MS system includes: Entech 7100 preconcentrator, Varian 3800 gas chromatograph with FID and column switching valve, and Varian Saturn 2000 ion trap mass spectrometer. Breath canister samples are pressurized with laboratory-grade zero air and a dilution factor is calculated based on initial and final pressures. An additional normalization factor could be determined for samples that deviate significantly from the expected CO2 level (subject-specific CO2 level/dilution factor). Approximately 200 to 300 ml of the breath sample is concentrated and injected at the head of a 60 m x 0.32 mm polymethylsiloxane column (CPSil-5, Varian, Inc.) held at 30 °C. This column is connected to the switching valve leading into a 30 m x 0.53 mm GS-GasPro column (J&W Scientific). After approximately 7 min the valve is switched so that the effluent from the first column elute onto a second 15 m x 0.32 mm polymethylsiloxane column connected to the mass spectrometer. The column switch is timed so that the C2 and C3 compounds elute on the FID and all C4 and higher compounds elute on the mass spectrometer.

2.2 Instrument Measurement Protocol

This section describes protocols that will be applied for each method and applicable quality assurance procedures.

2.2.1 Kore MS200

The Kore MS200 will be used to measure BTEX in select MEs. The protocol for use includes the following calibration and operational procedures.

Calibration Procedures:

1. Start instrument and establish zero.
2. Apply span gas and allow 2 minutes to stabilize response.
3. Collect at least 5 spectra
4. Using calibration section in software, confirm calibration response or enter new calibration values as needed.

Daily Startup Procedures:

1. Check Battery Status (or plug in).
2. Inlet valve: Middle position (heater).
3. Inlet pump: On
4. Wait until inlet vacuum is less than $3x10^2$ pa and inlet temperature LED is green
5. Sample pump On
6. TOF MS: On
7. TDC: On (unless you are on battery, then wait as this draws a lot of current.)

Once you are ready to sample:

1. Inlet Valve Down position (confirm that vacuum is ok and heat is still ok)
2. Apply zero air and allow it to flow for at least 1 minute.
3. Collect 5 spectra of background air to assess variability.
4. Begin sampling

If possible, during a run perform a zero check as follows:

Apply zero air for 15 to 30 seconds, allowing the instrument to collect one spectrum.

After a sampling run, perform a zero check as follows:

Apply zero air and immediately collect at least 5 spectra. Allow the zero air to remain on the instrument for 5 minutes and collect another 5 spectra.

During sampling runs, keep track of the main analyzer chamber vacuum. If the vacuum is regularly getting above 20 $x10^{-6}$ Pa, the instrument may need baking out. Follow the written procedures for bakeout.

2.2.2 CO Instruments

Two CO monitoring instruments will be used for the field study: a high sensitivity, fast response gas-correlation unit (Monitor Labs 9830) as a reference device, and a portable, battery-powered passive electrochemical unit (Langan T15). Prior to each period of field measurements both instruments will be calibrated using a zero-air generator and span gas (10.5 ppm) to provide two reference points encompassing the expected range of concentrations anticipated during actual testing. The two-point calibration procedure is as follows:

1. Collocate instruments and warm up for a minimum of 45 minutes. During the study the CO units will be powered 24/7 since the van is on AC power overnight to recharge the batteries and the passive Langan unit draws little power from its long-lasting batteries. Collocated Langans will be tested for calibration stability in high CO MEs and paired during runs if found to be unstable.
2. Record ambient concentration as determined by each instrument.
3. Connect inlet lines from both instruments to a zero-air source (for passive sampler use flooder cap provided by manufacturer) and check for positive flow rate of >1 lpm with rotometer.
4. Let instruments stabilize, record current baseline, then adjust zero.
5. Connect inlet lines to a tank of span gas with appropriate CO concentration for anticipated range and verify flow rate
6. Let instruments stabilize, record current reading, and adjust span to correct value.

7. Re-connect zero-air source, let stabilize and check baseline zero readings.
8. Repeat steps 4-7 if necessary.
9. Check third concentration level with span gas if available.

During field measurement periods the passive sampler will be checked against the reference unit, which has an automatic baseline stabilization and internal zero-air source, at the beginning and end of each sampling day and baseline readings will be recorded. If any significant deviations are observed a re-calibration will be performed.

The electrochemical cell in the Langan instruments exhibits a significant response to temperature variations as shown in Figure 2.2-1. Note that these variations are due to changes in the temperature of the electrolyte in the cell, not in the ambient air temperature. Prior to field use, the temperature response will be characterized at realistic CO levels in the laboratory. If the response appears to be sufficiently reproducible, the resulting concentration data will be adjusted based on the units internal temperature sensor, which has an accuracy of +/- 2 C. If the temperature compensation approach does not appear feasible, the instrument will be thermally isolated and maintained as close to calibration temperature (typically 20 C) as possible during use.

Our initial evaluation indicated that the lead-acid batteries are a source of hydrogen that interferes with the Langan CO monitor. This was confirmed by observing the Langan CO monitor in the presence of the batteries when both were removed from the vehicle. In order to eliminate this source of interference, the wet-cell lead acid batteries were replaced with AGM batteries that are sealed and hence do not outgas. We have currently installed 4 large AGM batteries and two new battery chargers in the van along with two new power inverters providing a total of approximately 3000 Watts of continuous power at 110V AC. The power system will be permanently installed so that we will not need to remove the batteries to charge them, they will simply be plugged in to charge. To handle the additional load, we have installed overload springs on the van. Furthermore, racks have been installed to secure instruments from movement and vibration; instrument & sampler inlet mounts have been installed to collocate inlets further within driver's breathing zone (including one PID inlet with the other PID sampling outside the vehicle on the radio antenna at least six inches above the hood); a remote switch was installed to allow cabin on/off control of the integrated samplers; and a hitch-mounted rack was installed to transport the instrument cart. We will continue to use the other batteries for the cart experiments since the lack of a trapped space means we will not encounter interferences. We will also use the NDIR-based CO instrument, which does not suffer from the same artifact as the Langan, inside the vehicle cabin.

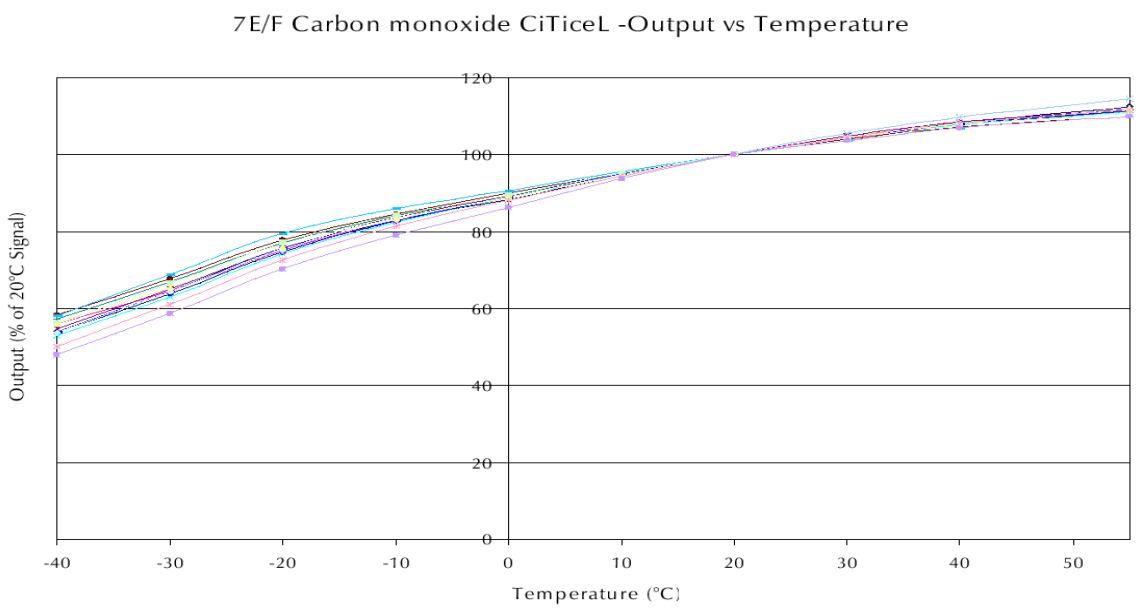

Figure 2-5. Variability of CO Electrochemical Cell Response with Temperature.

2.2.3 Continuous ppbRAE Photoionization Detector (PID)

A RAE Systems Model PGM-7240 (ppbRAE) portable PID monitor is used to continuously monitor ambient VOC levels in the microenvironments. The monitor is equipped with a 10.6 eV photoionization (PID) detector and responds to organic and inorganic gases that have an ionization potential of less than 10.6 eV, which includes most compounds of interest in this study. It does not respond to light hydrocarbons such as methane, ethane, propane or to acetylene, CO, or formaldehyde. .

2.2.4 Continuous Formaldehyde Monitor

The continuous monitor for gaseous formaldehyde was purchased from Alpha-Omega Power Technologies. This instrument uses Hantzsch reaction to produce a fluorescent derivative from HCHO that is monitored with a fluorescent detector. An aqueous calibration standard in the 10^{-7} to 10^{-6} M range made by serial dilution of 37% formalin solution in the 0.1 N H_2SO_4 scrubber solution is used for the daily instrument calibration (Kelly and Fortune, 1994). This daily calibration standard is compared with the gaseous formaldehyde standard, purchased from Apel-Riemer Environmental, Inc. The monitor is zeroed by supplying high-purity air to the inlet. Span and zero samples are provided to the monitor at regular intervals using automated valving. We've completed re-engineering the Alpha Omega HCHO instrument to make it more field-rugged and reliable.

The modified Alpha-Omega HCHO instrument was evaluated during the 2nd Reno Pilot study. One of the most significant limitations of the formaldehyde monitor was an apparent sensitivity to moving environments. It has been observed that when the formaldehyde instrument was warmed up and operated in a stationary environment, such as a parking garage, and then subjected to transport while still operating, response at the detector oscillated and increased overall. Another limitation of this continuous instrument was the long stabilization time required for the fluorescence detector upon instrument start-up. In some cases, response at the detector was still stabilizing when the sampling period began. Thus, the supplemental continuous formaldehyde analyzer will be used for monitoring stationary microenvironments only.

2.2.5 BTEX by Solid Phase Microextraction (SPME)

Carboxen/(poly)dimethylsiloxane (CAR/PDMS) coated (75 μm) quartz fibers are used for 10 min BTEX sampling. All SPME samples are analyzed in a mobile laboratory with a Model 8610C SRI Instruments GC equipped with a heated injection port suitable for SPME desorption and a CP-Sil 5 (Varian, Inc.) capillary column (60m, 0.32mm i.d.) and a PID detector. The heated flash vaporization injector is maintained at 250°C and PID at 150°C. The column temperature program was 60°C for 2 min, 8°C/min to 165°C and held for 1 min, and then 45°C/min to 240°C and held for 2 min. Helium carrier gas flow rate was 3 ml/min.

Blanks and calibration checks are performed daily on the SRI GC in order to determine the performance of the instrument and quality of the data. Fibers are kept in the injector port throughout the sample run to guarantee that the entire sample was desorbed and to begin the conditioning of the fiber. In addition, fibers are cleaned in a fiber conditioner at 300°C for at least one hour. One fiber per batch of 5 is checked for purity after conditioning. The fiber conditioner consisted of a 70 cm x 16 cm stainless steel box with 5 ports machined to fit the needle size and a Watlow heater/temperature controller capable of maintaining the temperature in the 200-300° C range. A helium flow of approximately 10 ml/min is maintained during fiber conditioning. Testing showed that the same fiber can be subsequently reused up to 40 times for collecting additional samples, unless breakage of the fiber or failure of the fiber mounting mechanism occurs.

The SRI GC is calibrated with 1 μl injection of liquid standards prepared in pentane with BTEX at different concentrations (1, 5, 10, 20, 40, 50, and 100 ng/μl). Carboxen/PDMS fibers are calibrated by introducing the SPME for a defined time to a flowing standard gas containing the calibration component, which loads a known mass of standard onto the fiber. The fiber is then introduced to the analytical instrument for calibration. SPME gas calibrations are done initially and throughout the study when necessary. BTEX calibration is performed with certified gas standards at different concentrations (20, 80, 100 and/or 200 ppbv for each compound).

SPME is a passive method, thus the rate of the fiber uptake is controlled by the diffusion rate of the analytes to the fiber. In a stationary environment without any air movement, the gradient of concentration is formed in the boundary layer between the fiber and surrounding environment. This is a situation that occurs during the fiber

calibration in a static system, such as a Tedlar bag. However, in an outdoor environment there is always some air movement, so the air is passing continuously across the surface of the fiber. The sorption rate will be higher in this situation, since the thickness of the boundary layer will be somewhat smaller.

We tested the fiber uptake in the dynamic (flow-through) conditions, in the apparatus shown in Figure 2.3-1, page 2-9 of the 2nd Reno Pilot Study Report (Zielinska et al., 2003) When the BTEX standard mixture was flowing through the system with the rate of 100 ml/min, the fiber uptake was approximately three times higher than in static (no flow) conditions. In addition, the dynamic calibration was more reproducible and more precise. For the summer study we will employ flow-through sampling conditions for the fiber. The calibration of the fiber will be performed in the identical flow-through conditions, using the same flow rate.

Sampling temperature is an important parameter affecting the SPME data. Temperature corrections are obtained in the laboratory with an experimental set up that consists of a 1L glass bulb that has two stopcocks in each side to let the calibration gas flow through and an injection port covered with a sleeve septum to allow a SPME fiber to be introduced. The bulb is temperature controlled with a cooling/heating system. Temperature inside the glass bulb is measured with a thermocouple. For introducing humidity, a heated injection port is added before the glass bulb entrance in order to inject water with a syringe pump (Harvard Apparatus) to produce the desired relative humidity (Tuduri, Ludovic et al., 2001; Nelson, 1992; Martos, P. and J. Pawliszyn, 1997, and Lodge 1984).

SPME Carboxen/PDMS coated (75 μm) fibers are used with portable or manual samplers. When manual samplers are used, the tip of the needle is closed with a septum or Teflon tape (Martos and Pawliszyn, 1997 and Chai and Pawliszyn, 1995). Prior to sampling, the pre-cleaned fibers will be kept at ambient temperature with an activated charcoal protector. This storage method has been tested in the laboratory and we have not seen any increases in the BTEX background up to 48 hours of storage following cleaning (the longest tested period). After sampling, fibers are kept in sealed Mylar bags inside a cooler with dry ice. Samples are analyzed 4-10 hours post-sampling, on average, with a minimum of 1 hour and a maximum of 20 hours between sampling and analysis.

2.2.6 Time-Integrated Air Sample Collection and Analysis

Time-integrated monitoring methods are used primarily for quantification of the responses of continuous surrogate instruments. The methods include canister sampling for VOC (BTEX, 1,3-butadiene, MTBE), solid adsorbent sampling (for ethanol) and DNPH-coated Sep Pak cartridges sampling for carbonyl compounds. The DRI Organic Analytical Laboratory (OAL) routinely uses these methods and DRI standard operating procedures (SOPs) for sampling and analysis are available upon request. Five to sixty minute samples will be collected depending on the ME sampled.

Sampling. The DRI custom built sampler that can sample simultaneously a canister, solid adsorbent cartridges (two in parallel) and DNPH-impregnated Sep-Pac cartridge, is used for this study. The sampler is compact; it can be set-up in a vehicle cabin and run from the battery. Prior to use the sampler is checked for cleanliness by sampling zero air through the canister inlet. If the concentration of any targeted compound exceeds 0.1 ppb, the sampler is thoroughly cleaned and re-tested. As noted earlier, a remote switch was installed to allow cabin on/off control of the sampler (no longer requiring access through the van tailgate) and the protocol was modified to require that the van engine be off during changes of sampler media.

The canister sampler uses a differential pressure flow controller to supply air to the sampler canister. A calibrated mass flow controller will check the flow rate. Since the actual flow rate is less important than the fact that the flow rate remains constant, additional quality assurance checks on the flow controllers is not necessary. For the 5-min canister samples, an additional battery-operated sampler will be used, allowing up to 3 L/min flow rates to pressurize the 3 L canister.

Both the solid adsorbent and DNPH samplers use the same vacuum pump controlled by mass flow controllers. These controllers will be calibrated at the start of the field program by using a primary flow device (e.g. Gillibrator) and then will be periodically checked while in the field to confirm that the flow rates are accurate.

Canister samples. Prior to sampling, the canisters are cleaned by repeated evacuation and pressurization with humidified zero air, as described in the EPA document "Technical Assistance Document for Sampling and Analysis of Ozone Precursors" (October 1991, EPA/600-8-91/215). Six repeatable cycles of evacuation to ~0.5 mm Hg

absolute pressure, followed by pressurization with ultra-high-purity (UHP) humid zero air to ~20 psig are used. The differences between the DRI procedure and the EPA recommended method are that, in the DRI method, canisters are heated to 140°C during the vacuum cycle and more cycles of pressure and vacuum are used. According to our experience and that of others (Rasmussen, 1992), heating is essential to achieve the desired canister cleanliness. Also, the canisters are kept longer under vacuum cycles, about one hour in the DRI method, as opposed to half an hour in the EPA method. At the end of the cleaning procedure, one canister out of 12 in a lot is filled with humidified UHP zero air and analyzed by the gas chromatograph/flame ionization detection (GC/FID) method. The canisters are considered clean if the total non-methane organic compound (NMOC) concentration is less than 20 ppbC. The actual concentrations of blank-check canisters are typically below 10 ppbC.

Canister samples are analyzed for speciated VOC concentrations promptly upon receipt of samples from the field, using gas chromatography with flame ionization detection (GC/FID, Hewlett Packard) according to guidance provided by the EPA Method TO-15. The GC/FID response is calibrated in ppbC, using NIST Standard Reference Materials (SRM) 1805 (254 ppb of benzene in nitrogen). Based on the carbon response of the FID to hydrocarbons, the response factors determined from these calibration standards are used to convert area counts into concentration units (ppbC) for every peak in the chromatogram. Identification of individual compounds in an air sample is based on the comparison of linear retention indices (RI) with those RI values of authentic standard compounds. A DB-1 column (60 m long 0.32 mm i.d., 1 µm film thickness) is used for these analyses. Breath canisters will be quantified for CO2, MTBE, and BTEX by the method of Pleil & Lindstrom using GC/MS.

Blanks are performed once daily, while performance standards are executed three times per week. Our analysis plan and data processing standards call for the replicate analysis of approximately 10% of the samples. For canisters the replicate analysis is conducted at least 24 hours after the initial analysis to allow re-equilibration of the compounds within the canister. The replicate analyses are flagged in our database and the programs we have for data processing extract these replicates and determine a replicate precision. Replicate analysis is important because it provides us with a continuous check on all aspects of each analysis, and indicates problems with the analysis before they become significant. A portion (5%) of the canisters will also be analyzed by a second independent laboratory (negotiations with Battelle-Columbus are currently underway).

Solid adsorbent samples. Ethanol will be quantified using solid adsorbent cartridges, in addition to canister method. Although MTBE is stable in SUMMA canisters and can be quantified with high precision and accuracy, ethanol is relatively unstable and the replicate analyses of canister samples show a high degree of scatter (Goliff and Zielinska, 2001). Thus, the solid adsorbent samples are only necessary for quantification of ethanol, although TEX data may be obtained from the solid adsorbent samples to serve as a comparison with canister data for QA purposes. For sample collection we will use multibed adsorbent cartridges consisting of Tenax TA, Carbotrap (or Carboxen) and Carbosieve (Shire et al., 1996; Tsai and Weisel. 2000; Vayghani et al., 1999). Prior to use, the Tenax-TA solid adsorbent is cleaned by Soxhlet extraction with hexane/acetone mixture (4/1 v/v) overnight, and dried in a vacuum oven at ~80 °C. The dry Tenax is packed into Pyrex glass tubes together with Carbotrap and Carbosieve and thermally conditioned for four hours by heating in an oven at 300 °C under nitrogen purge. Approximately 10% of the precleaned tubes are tested by GC/FID for purity prior to sampling. After cleaning, the tubes are capped tightly using clean Swagelok caps (brass) with graphite/vespel ferrules, placed in metal containers with activated charcoal on the bottom, and kept in a clean environment at room temperature until use.

After sampling at nominal monitored flows of 200-300 ml/minute, tube samples are analyzed by the thermal desorption-cryogenic preconcentration method, followed by high-resolution gas chromatographic separation and mass spectrometric detection (MSD) of individual compounds. The Chrompack Thermal Desorption-Cold Trap Injection (TCT) unit is used for the purpose of sample desorption and cryogenic preconcentration. The compounds are quantified by MS, using the response factors of authentic standards, prepared at five different concentrations with a static dilution bulb.

Carbonyl compounds. Formaldehyde and acetaldehyde will be collected with Sep-Pak cartridges that have been impregnated with an acidified 2,4-dinitrophenylhydrazine (DNPH) reagent (Waters, Inc), according to the EPA Method TO-11A. When ambient air is drawn through the cartridge at nominal flow rates of 1 L/min, carbonyls in the air sample are captured by reacting with DNPH to form hydrazones, which are separated and quantified using HPLC in the laboratory (Fung and Grosjean, 1981). Depending on the type of sorbent (C18 or silica gel) in the cartridge, the ambient measurement results are subject to various artifacts due to interaction with ozone, thus the ozone denuder is recommended for sample collection. We will use a honeycomb denuder coated with sodium

carbonate/sodium nitrite/glycerol mixture (Koutrakis, et al., 1993). After sampling, the cartridges will be eluted with acetonitrile. An aliquot of the eluent will be transferred into a 1-ml septum vial and injected with an autosampler into a high performance liquid chromatograph (Waters Alliance System) for separation and quantization of the hydrazones (Fung and Grosjean 1981). A portion (5%) of these aliquots will also be analyzed by a second independent laboratory (negotiations with Battelle-Columbus are currently underway).Liquid fuel samples. Liquid gasoline samples will be collected for each service station (if more than one is used per city) after ME 3/7 refueling measurements during subsequent off-loading of the van fuel tank at the mobile lab site. Composition of these fuels will be determined by GC/FID for comparison to measured species (benzene & oxygenates) reported in summer and winter gasoline surveys conducted for the three cities being sampled and for determining relative exhaust/evaporative emissions sources in measured MEs. Relative exhaust and evaporative emissions may be estimated from fuel component ratios as noted in Graboski et al., 1998.

3. EXPERIMENTAL PROTOCOL

This section specifies the tasks required to meet the objectives for the S211 (b) Tier 2 Exposure Study and how each element of the proposed testing protocol will be carried out. Details of the methods and procedures and quality assurance program are described in Section 2. The exposure studies have two components. First, Desert Research Institute (DRI) and Southwest Research Institute (SwRI) will conduct exposure measurements in San Antonio under controlled conditions in order to establish quantitative relationships between vehicle tailpipe and evaporative emissions to exposure levels in a trailing vehicle cabin and in a residence with an attached garage. Second, DRI will monitor microenvironmental and personal exposures in 12 high-end exposure microenvironments in Atlanta, Chicago, and Houston during summer and winter conditions. Selection of the high-end microenvironments was made in consultation with EPA and independent peer reviewers. Figures 3-1 and 3-2 show the monitoring requirements for the overall study and for the controlled San Antonio studies, respectively.

3.1 San Antonio Controlled In-Cabin and Residential Garage Exposure Measurements

DRI and SwRI will determine the quantitative relationships between evaporative and tailpipe emission from characterized test vehicles to exposure in (1) a cabin of a trailing vehicle under normal operation and with induced malfunctions and (2) a residence with an attached garage. The exposure measurements were made in San Antonio during June 2002 for summer fuels and will be made during January 2005 for winter fuels according to the following protocol. Part of the measurements made in June 2002 may be repeated in June 2004 after review of the entire San Antonio database by EPA. Table 3-1 shows the exposure matrix and the number of samples and hours of measurements for controlled in-cabin trailing vehicle and residential garage studies.

3.1.1 Procurement of Test Fuels from Houston, Chicago and Atlanta

With API and DRI guidance, SwRI will procure six test fuels (a summer regular grade and winter regular grade fuels in each of the three cities – Houston, Atlanta, and Chicago) for the study. SwRI will procure two 55-gallon drums of each fuel from a major supplier in each city to conduct the work in San Antonio. Three summer fuels were procured and evaluated during May 2002 and the three winter fuels will be procured during December 2004. SwRI will test fuels for bulk properties and DRI will speciate the chemical composition of each of the six blended fuels.

Figure 3-1: Overall Structure of 211(b) Monitoring Requirements

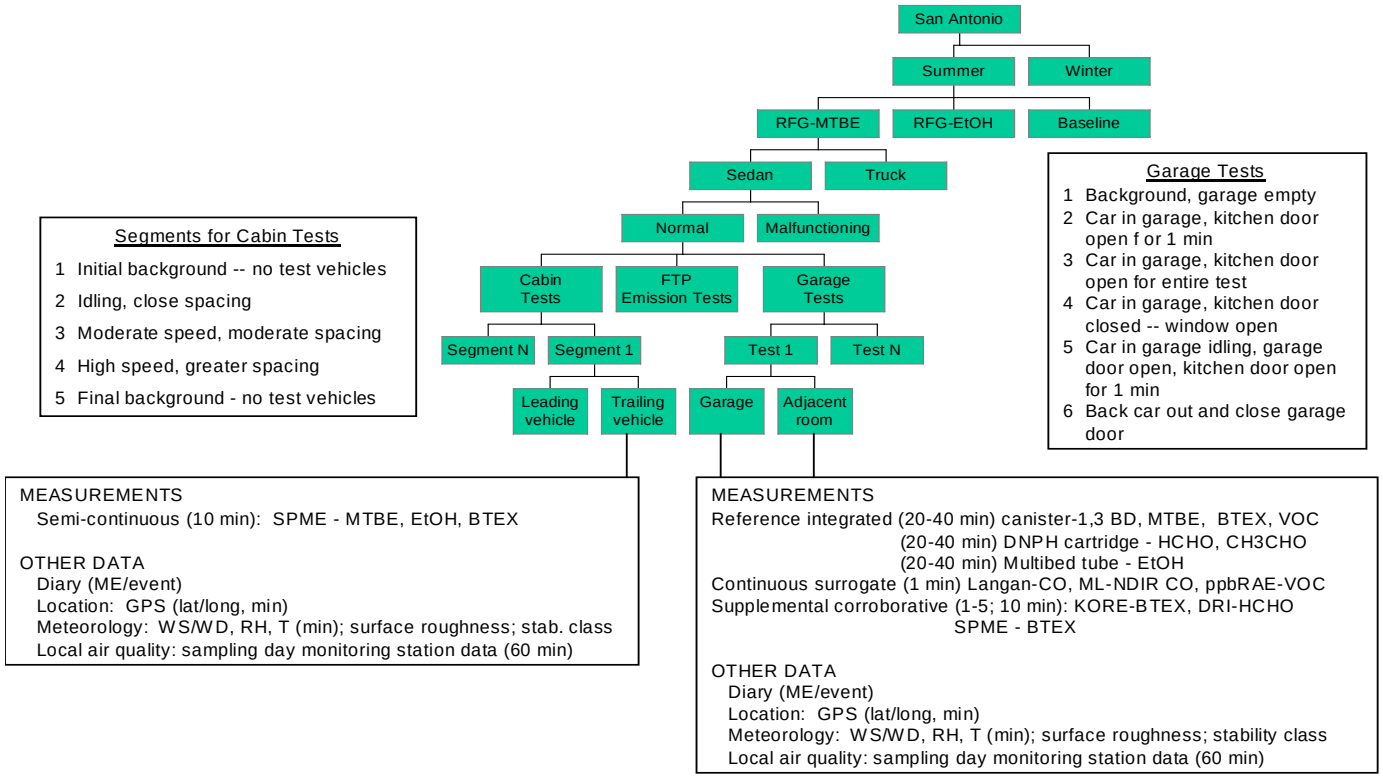

Figure 3-2. Monitoring Requirements for San Antonio Study

Table 3-1. Collection of Time-Integrated Samples for Chemical Analysis – San Antonio

	Test Duration (min)	Sample time SPME (min)	SPME	Cans	DNPH	Solid Adsorb. [a]	No. of Tests	SPME	Cans	DNPH	Solid Adsorb.
San Antonio - Trailing Vehicle											
Initial background	10	10	1	1	1	1	24	24	24	24	4
Exposure Measurements	120	10	12	1	1	1	24	288	24	24	4
Idle	20	10	2	1	1	1	24	48	24	24	4
Subtotal			15	3	3	3		360	72	72	12
San Antonio - Residential Garage Exposure											
In-garage (baseline)	30	30	1	1	1	1	24	24	24	24	4
In-garage (during exposure)	150	30	5	1	1	1	24	120	24	24	4
adjcent room (baseline)	(b)	30	1	1	1	1	24	24	24	24	4
adjcent room (during exposure)	(b)	30	5	1	1	1	24	120	24	24	4
Subtotal		30	12	4	4	4		288	96	72	12

3.1.2 Determination of Tailpipe and Evaporative Emissions of Test Vehicles

SwRI will procure two test vehicles and determine evaporative and tailpipe emissions for the vehicles with and without malfunctions using the six test fuels. The two test vehicles will be 1993 to 1996 model year vehicles with 90 to 110K odometer miles. One vehicle will be a sedan, and the second a full sized pickup truck with a V-8 engine. The SWRI will measure the vehicle's exhaust emissions on a dynamometer according to the Federal Test Procedures (FTP). SwRI will modify these vehicles so that emission control system components (e.g., ECU, O_2 sensor, catalyst) can be reversibly disconnected to represent normal and reasonable high-end approximations (e.g., ≥ 2 gm HC/mile exhaust) of real world exhaust emissions. SwRI will determine exhaust emission rates for the two test vehicles, with and without malfunction, using three regional fuels during each of two seasons (with seasonal fuels). This will result in 12 combinations for each season. SwRI also will measure evaporative emissions using the same test vehicles with and without induced malfunction (e.g., disconnecting fuel line to carbon canister). Hydrocarbon samples will be collected in canisters and analyzed by DRI for complete hydrocarbon speciation. The data will be used to apportion the relative contributions of exhaust and evaporative emissions by applying these source composition profiles to the microenvironmental measurements from the three cities using Chemical Mass Balance (CMB) receptor modeling.

The emission tests will be coordinated with the trailing vehicle tests described in Section 3.1.3 and the residential garage exposure tests describes in Section 3.1.4. SwRI will install the reversible malfunction on the two test vehicles and perform all emission testing prior to start of the exposure measurements. Two days will be required for the trailing vehicle and residential garage exposure measurements described in Tasks 2c and 2d for each of six combinations of vehicle and test fuel per season. The trailing vehicle exposure measurements will be scheduled in the morning, followed by garage exposure measurements in the afternoon. Measurements will be made on the first day with normal emissions and on the second day with induced malfunctions. During the exposure tests of one vehicle, SwRI will switch the fuel in the other vehicle and condition the vehicles with the new fuel prior to the exposure measurements.

For the dynamometer FTP exhaust emissions testing, regulated exhaust emissions (total hydrocarbons, THC; non-methane hydrocarbons, NMHC; carbon monoxide, CO; and oxides of nitrogen, NOx, carbon dioxide, CO_2; and speciated VOC emissions (to include MTBE, ethanol, benzene, toluene, ethyl benzene, xylene, 1,3-butadiene, formaldehyde, and acetaldehyde) will be determined for each test. During hot soak SHED tests, total hydrocarbon and VOC emissions (as above except without aldehyde/ketone measurements) will be determined. Table 3-2 presents a suggested test plan for the emissions testing at SwRI.

The exhaust emission portion of the FTP utilizes the Urban Dynamometer Driving Schedule (UDDS), which is 1372 seconds in duration. The UDDS is divided into two segments; the first consisting of 505 seconds, and the second consisting of 867 seconds. An FTP is composed of a 505-second cold transient (bag 1) portion and an 867-second cold stabilized (bag 2) portion, followed by a ten-minute soak and then a 505-second hot transient (bag 3) portion. A summary of the cycle duration, driving distance, and average speed is given in Table 3-3. The FTP driving schedule with the cold- and hot-transient test segments identified is given in Figure 3-1.

The evaporative emission portion of the FTP will consist of a one-hour Diurnal Heat Build (DHB) and a one-hour Hot Soak Loss Test (HSL). Total hydrocarbons and VOC emissions will be recorded only during the HSL segment of the test. Prior to the cold-start exhaust portion of the FTP, the DHB evaporative segment of the FTP will be conducted by fueling the test vehicle to 40 percent of tank capacity with test fuel at a temperature below 55°F. A heating blanket will be attached to the outside of the fuel tank, and a thermocouple placed in the fuel inside the fuel tank will be connected to the computer controller. The fuel inside the tank will be raised to a nominal temperature of 60°F, at which point the DHB segment of the test will begin. The fuel temperature will be raised at a linear rate of 0.4°F per minute for the 60-minute test. The final nominal temperature will be 84°F.

The HSL segment of the evaporative emission test will be conducted immediately following exhaust emission testing. For the HSL segment, the vehicle will be driven into the evaporative emission enclosure immediately after the exhaust emission portion of the FTP has been completed. The vehicle will be allowed to "soak" in the enclosure

for one hour. Total hydrocarbon and VOC emissions will be measured at the beginning and end of the one-hour segment to permit calculation of hot soak evaporative emissions.

Table 3-2. Test Plan for Each Vehicle

STEP	DESCRIPTION
1	Obtain test vehicle. Verify proper mechanical operation.
2	Determine malfunction condition to achieve 2 or more grams/mile total hydrocarbons.
3	Equip vehicle to allow switching between normal and malfunction conditions. Return vehicle to normal operating condition.
4	Remove canister from test vehicle.
5	Purge canister with 300°F zero nitrogen at 20L/min for five hours, reattach canister.
6	Drain fuel tank and fill to 40 percent capacity with test fuel.
7	Perform a 2-hour diurnal heat build from 70 to 120°F at a ramp rate of 0.4°F/min.
8	Operate vehicle on chassis dynamometer over one UDDS cycle.
9	Turn engine off for five minutes.
10	Start engine and idle for one minute.
11	Turn engine off for one minute.
12	Start engine and idle for one minute.
13	Remove canister from vehicle and purge canister with zero air for 60 minutes.
14	Reattach canister, drain fuel from tank, and fill to 40 percent capacity with chilled test fuel.
15	Conduct one hour DHB (no emission measurements).
16	Operate vehicle on chassis dynamometer over one UDDS.
17	Soak vehicle overnight.
18	Next day prior to the cold-start exhaust portion of the FTP, conduct one-hour Diurnal Heat Build (DHB). No emission measurements.
19	Conduct 3-bag FTP exhaust emission test. Measure regulated gaseous emissions and VOC emissions.
20	Conduct the Hot Soak segment of the SHED test immediately following the exhaust emissions testing. Measure total hydrocarbons and VOC emissions (same as with exhaust except no aldehyde emissions).
21	Switch vehicle to malfunction per Step 2, and disconnect evaporative canister.
22	Repeat Steps 8 through 12 and Steps 16 through 20.
23	Repeat Steps 3 through 22 for each of the remaining five test fuels.

Table 3-3. Summary of the FTP Driving Cycle

Segment	Duration, Seconds	Distance, Miles	Average Speed, Miles/Hr.
Transient Phase	505	3.6	25.7
Stabilized Phase	867	3.9	16.2
UDDS	**1372**	**7.5**	**19.7**

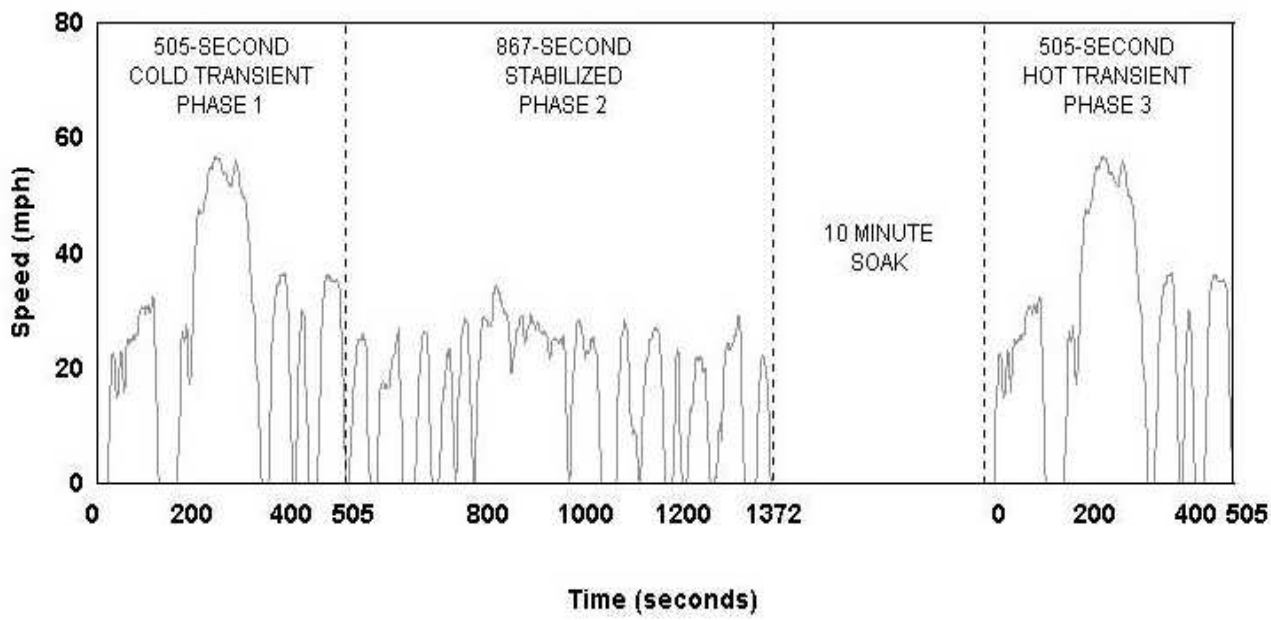

Figure 3-3. FTP Driving Cycle.

3.1.3 Relationship Between Exhaust Emission Rates and In-Cabin Exposure

DRI and SwRI will use the two test vehicles in normal operation and with induced malfunction to determine exposure in a cabin of a third vehicle that is trailing the test vehicles. In addition to the two test vehicles, SwRI will procure a third vehicle that will be used as the trailing vehicle. DRI will install the instrument and sampling systems on board the trailing vehicle. This trailing vehicle will be towed to the three cities and used to conduct the exposure measurements described in Tasks Section 3.2. The trailing vehicle tests will be conducted on a remote road upwind of San Antonio, Texas. The test matrix will mirror the dynamometer tests - two test vehicles with and without malfunction, three regional fuels, and two seasonal fuels for 12 combinations per season. Tests using summer and winter fuels will be conducted in June and January, respectively.

During each test, the trailing vehicle will be driven behind the test vehicle over a travel loop of several miles for a period of up to 3 hours. Measurements will be made during the first 10 minutes without the test vehicles in order to establish background exposure levels. The trailing vehicle study will implement three scenarios (far, near, and passing) for each low or high speed (30 and 60 mph) as scheduled in the table below. During each 'far' scenario, the trailing vehicle will follow continuously at the conventional 'safe' following distance for the indicated speed, defined as one car length (about 10 feet) for each 10 mph. During the 'near' scenario, the vehicle will 'tailgate' the leading vehicle continuously following at a closer distance deemed 'safe' for professional drivers under low-traffic density and prevailing meteorological conditions by SwRI and DRI staff. During the “passing” scenario, the trailing vehicle will spend 10 min at “tailgating” distance, i.e., as close as safety permits, and 10 min at “passing” distance at an adjacent lane position that maximizes potential cabin penetration (based on maximal hood TVOC).

Table 3-4 details the trailing vehicle protocol. We are continuously monitoring total VOC (with ppbRAE PID) inside the cabin and outside the cabin, with the inlet mounted on the radio antenna 6 inches above the hood of the vehicle. In addition, we measure TNMHC from time-integrated canister samples.

Table 3-4. Protocol for trailing vehicle tests

Time Min.	Speed Mph	Ventilation Setting	Distance	Notes	Continuous Instruments	SPME	Time Integrated
10	high	high		background	Y	1	1
10	low	high	far	Vehicles: Toyota Camry and Pick-up truck, in normal and malfunction mode. Fuels: baseline, MTBE, ethanol	Y	1	1
10	low	high	near		Y	1	
10	low	high	passing		Y	1	
10	high	high	far		Y	1	
10	high	high	near		Y	1	
10	high	high	passing		Y	1	
10	low	low	far		Y	1	
10	low	low	near		Y	1	
10	low	low	passing		Y	1	
10	high	low	far		Y	1	
10	high	low	near		Y	1	
10	high	low	passing		Y	1	
10	idle	low	adjacent		Y	1	1
10	idle	high	adjacent		Y	1	

3.1.4 Relationship Between Evaporative Emission Rates and Exposure in a Residence With an Attached Garage

The two test vehicles (with and without malfunctions) will be used to determine indoor exposures in homes with attached residential garages. The same test vehicles will be used to measure indoor exposures in a residence with an attached garage using the following testing matrix. The vehicles will be parked in a closed residential garage also containing a gasoline powered lawnmower and gas container with in-garage and adjacent room monitoring conducted before, during and after the vehicle cool-down period. Door openings between the garage and adjacent room and room window openings will be monitored. The vehicle will also be ‘warmed up’, idling in the garage (with the garage door open) during a period of the 3-hour monitoring process. The measurements will be made in

San Antonio at the residence of a SWRI employee who has agreed to provide access to the house during the study. The test procedure will be similar to those described by Tsai and Weisel (2000). We propose to collect two time-integrated samples of each kind per test (one in the garage and one in the adjacent room). A set of continuous and semi-continuous methods will be operated during the vehicle exposure period of approximately two hours.

The attached garage study will implement six scenarios as described in the Table 3-5. Measurements will be taken over 30-minute periods with the collocated sampling inlets located at breathing height (1.5 m) at least three feet away from nearby walls in both the unvented garage and adjacent indoor room (kitchen). The two PID instruments will sample continuously both before (background) and during the tests with one unit each having its collocated inlet in the garage and adjacent room. Langan CO and/or NDIR CO instruments will sample continuously in the garage and adjacent room. The MS200 BTEX and DRI aldehyde monitors will sample continuously from collocated inlets in the adjacent room for corroborative purposes. A half-filled two gallon standard plastic gasoline storage container with vent open will be placed with a lawnmower with gas tank half filled against the center of the garage wall common to the adjacent room. The appropriate fuel (i.e. from Houston, Atlanta or Chicago) will be placed in the garage one day before the series of tests for this fuel and left there over the duration of these tests. Scenario conditions will be changed every 30 minutes over the 3-hour protocol as described in the table.

The ambient garage temperature will be recorded every 30 min during each experiment and the tests will be conducted every day (excluding weekends) over the period of two weeks.

Table 3-5.Protocol for attached garage experiments. The same vehicles and fuels as for trailing vehicle experiment are used.

Condition	Time (min)	Garage Door	Kitchen Door	Kitchen Window	Inlet Location	Continuous	SPME	Integrated Samples
Back-ground	30	closed	closed	closed	garage	Langan CO PID1	2	2
					kitchen	MS200 DRI PID2 NDIR CO		
Hot soak	30	closed	open 1min & closed	closed	garage	Langan CO PID1	2	2
					kitchen	MS200 AO PID2 NDIR CO		
Maximal AER to indoors	30	closed	closed	closed	garage	Langan CO PID1	2	
					kitchen	MS200 DRI PID2 NDIR CO		
Maximal AER to outdoors	30	closed	closed	open	garage	Langan CO PID1	2	
					kitchen	MS200 DRI PID2 NDIR CO		
Cold start	30	open	open 1 min & closed	closed	garage	Langan CO PID1	2	
					kitchen	MS200 DRI PID2 NDIR CO		

3.2 Microenvironmental Exposure Measurements in Atlanta, Chicago, and Houston

One of the overall goals of the project is to sample high-end microenvironments (MEs), plausibly characterized in the upper 90th centiles of exposure that result from the impacts of exhaust/evaporative emissions from gasoline-fueled vehicles. Selection of high-end microenvironments was made in consultation with EPA and independent peer reviewers.

DRI will determine in-cabin exposure in urban roadway and other high-end exposure microenvironments in Houston, Chicago, and Atlanta over several weeks in each city and season during July-September (summer test) and January-March (winter test). Exposure measurements will be made for thirteen different microenvironments with three replicate measurements for microenvironments with low variability and five replicate measures for highly variable MEs including trailing high emitting vehicles (ME 13), underground garages (ME 11), and outdoor refueling (ME 7). Measurements in each of the microenvironments will be taken over a period of 20-60 minutes and completed within the hour where possible to facilitate comparisons with local ambient monitoring values. Sampling durations will depend on the event and may range from 20 to 60 minutes in the discretion of DRI as necessary to obtain a typical sample. For example, refueling events and clearing of parking garages after sporting events usually occur over periods substantially less than an hour and do not start at the top of the hour. Continuous measurements of carbon monoxide, benzene, toluene, ethyl benzene, xylenes, photoionizable (10.6 eV) VOC, and formaldehyde will be taken during the entire sampling period. Time-integrated canister, DNPH cartridge, and solid adsorbent (in Chicago) samples will also be collected over the full sampling period unless the next sample will be collected during a consecutive hour. In such cases, 60-minute samples will be collected during the first 50 minutes to allow time for replacement of sampling media. In addition, four SPME samples (for BTEX) will be collected during consecutive 10 -minute periods during each sampling period. Liquid fuel samples will be collected after ME3/7 measurements (during off-loading of the van fuel tank) for each service station (if more than one is used per city) sampled for this ME. Video tapes of ME sampling will be conducted as advisable considering local privacy and security concerns; at least one videotape will be provided to EPA for each ME sampled in each city.

Table 3-6. Microenvironment Listing.

ME #	ME Description	Replicates	Biomarker	5 min Canister	Sampling Time (min)
1	In-Cabin Congested Freeway	5			40
2	In-Cabin Urban Canyon	3			40
3	In-Cabin Refueling	5			20
4	In-Cabin Underground Garage	5			40
5	In-Cabin Toll Plaza	3			40
6*	Roadway Tunnel	5	yes	yes	40
7	Outdoor Refueling	5	yes	yes	20
8	Sidewalk	3			40
8/9	Sidewalk/Bus Stop	3			40
10	Outdoor Surface Parking	3			40
11	Outdoor Underground Garage	5	yes	yes	40
12	Outdoor Toll Plaza	3			40
13*	In-cabin Trailing High-Emitting Vehicles	5	yes	yes	40

*ME6 will be sampled in Houston & Chicago and ME13 in Atlanta..

Table 3.6 displays the planned exposure matrix with the number of replicates, and the location of biomarker and 5-minute canister peak sampling. Table 3.7 lists the number of samples for each microenvironment.

Table 3-7. The Number of Samples for Each Microenvironment for Three Cities and Two Seasons

	Total No. of Samples Per Site							Total No. of Samples for Three Cities and Two Seasons				
	Replicates	Test Duration (min)	Sample time SPME (min)	SPME	Cans	DNPH	Solid Adsorb. A&B[3]	Total No. of Tests	Total No. SPME	Total No. Cans	Total No. DNPH	Total No. Solid Adsorb.[3]
Urban Exposures in Vehicle Cabin												
1. In-Cabin Congested Freeway	5	40	10	20	5	5	10	30	120	30	30	20
2. In-Cabin Urban Canyons	3	40	10	20	3	3	6	18	120	18	18	12
3. In-Cabin Refueling	5	20	10	10	5	5	10	30	60	30	30	20
4. In-Cabin Underground Garage	5	40	10	20	5	5	10	30	120	30	30	20
5. In-Cabin Toll plaza	3	40	10	20	3	3	6	18	120	18	18	12
6. Roadway Tunnel[1,4]	5	40	10	20	10	5	10	20	80	40	20	20
13. In-cabin Trailing High-Emitting Vehicles[2,4]	5	40	10	20	10	5	0	10	40	20	10	0
Subtotal[5]	26			110	31	26	52	156	660	186	156	104
Urban Exposures in Other Microenvironments												
7. Outdoor Refueling[4]	5	20	10	10	10	5	10	30	60	60	30	20
8. Sidewalk	3	40	10	20	3	3	6	18	120	18	18	12
8/9. Sidewalkl/Bus Stop	3	40	10	20	3	3	6	18	120	18	18	12
10. Outdoor Surface Parking	3	40	10	20	3	3	6	18	120	18	18	12
11. Outdoor Underground Garage[4]	5	40	10	20	10	5	10	30	120	60	30	20
12. Outdoor Toll Plaza	3	40	10	20	3	3	6	18	120	18	18	12
Subtotal	22			110	32	22	44	132	660	192	132	88
Biomarker Breath Samples												
6. Roadway Tunnel [1]	5	40			15			20	0	60	0	0
7. Outdoor Refueling	5	20			15			30	0	90	0	0
11. Outdoor Underground Garage	5	40			15			30	0	90	0	0
13. In-cabin Trailing High-Emitting Vehicles[2]	5	40			15			10	0	30	0	0
Subtotal[5]	15				45			90	0	270	0	0
Total	63			220	108	48	96	378	1320	648	288	192

[1]ME6 will be done in Houston and Chicago.

[2]ME13 will be done in Atlanta only.

[3]Chicago only.

[4]Includes 5 minute canister.

[5]Only one ME counted for ME6 and ME13 for Total No. of Samples Per Site.

3.2.1 Exposure Diary and Script Development

Scripted activities will be used during the exposure measurements. This methodology, referred to as the indirect approach, has the advantage of providing estimates of exposure over a range of scenarios based on a limited sample size (Klepeis, 1999). This approach involves the following steps: (1) micro environmental identification, (2) quantification of time spent performing activities in a given microenvironment, and (3) measurements of pollutant concentrations during a specified activity. By multiplying the total time spent during each activity by the pollutant concentrations, activity-specific exposure can be estimated. Using EPA human activity patterns, exposure from these activities can be estimated for the total population (EPA, 1996).

One of the key aspects of the indirect approach is an accurate measure of the time spent performing a specified activity. In order to define exposure time in a reproducible manner, scripted activities are developed for this study by Ted Johnson of TRJ Environmental Inc. for various high-end exposure microenvironments. In this manner, different subjects can reproduce the total time required for a specified activity and an accurate estimate of exposure time can be determined. Scripted activity diaries are developed and completed by field personnel during the exposure measurements to document more detailed information about the sampling location and activities during each monitoring period. Examples of a diary pages are included in Appendix D.

We also will compare personal exposures with ambient measurements from nearby local and state monitoring sites. This can be facilitated by scheduling activities to begin on the hour and end on the hour, enabling a direct comparison with ambient network data. However, many high-end microenvironmental activities take less than an hour (e.g., refueling, transiting a tunnel, leaving a parking garage) so scheduling of start and stop times within the same clock hour will be attempted as an alternative to increase correlation with ambient monitor sampling periods. Ambient monitor locations are provided to allow estimates of distance and directional relationships to ME measures.

3.2.2 In-cabin Exposures in Urban Microenvironments

The trailing vehicle from the controlled exposure tests in San Antonio will be transported to each of the three cities and used for the in-cabin exposure measurements in each of the three cities in both summer and winter. A driving route will be developed for each city, which includes the urban roadway microenvironments and trailing high emitting vehicles encountered in these roadways.

ME#1 – Freeway traffic under stop-and-go conditions (40 minutes)

ME#2 – Downtown surface street loop characterized by an urban canyon effect (40 minutes)

ME#3 – Refueling (20 minutes)

ME#4 – Parking garage (40 minutes)

ME#5 – Toll plaza (40 minutes)

ME#6 – Tunnel or covered roadway (40 minutes)

ME#13 – Trailing high-emitting vehicles (40 minutes)

In addition to continuous measurements, one integrated sample will be collected during each 20-40 minute exposure. Table 3-6 shows the proposed exposure matrix. We will use GPS on board the vehicle to record the location and time during the entire test. Testing over the driving route will be made three – five times for each city and season on rush-hour weekdays with both high ventilation (e.g., window and vent open during the summer) and lower ventilation (i.e., windows and vent closed with AC or heater on during the summer/winter).

We will use scripted technicians and measure breathing zone and ME air levels in the following outdoor and indoor microenvironments: self-service refueling stations, sidewalks near high-density traffic, underground parking garage, bus stop, toll booth, and an above ground parking garage. Technicians will follow the activity scripts developed and will use diaries and/or GPS monitors to document actual exposure locations and conditions.

The exposures in each microenvironment will be monitored for 20-40 minutes. We propose to repeat the measurements in each microenvironment three to five times and collect time-integrated canister, DNPH and solid adsorbent (for Chicago only) samples during each exposure period (see Table 3-7). For all tests the inlet for portable and time-integrated instruments will be collocated at breathing zone height (i.e. 1.5 m above the ground) and in the breathing zone of the technician as appropriate.

3.2.3 Technician Biomarker Analysis

Breath measurement will be used as the biomarker of choice. Since we were not able to distinguish background benzene concentrations from low-level exposures (e.g. walking down street), we propose only to conduct bio-monitoring experiments for projected "high-end" exposures such as outdoor refueling, trailing high emitters on congested roadways, and exiting an underground parking garage. Breath sampling will be conducted similar to the 2nd pilot study, with pre- and post-exposure collections (plus a backup sample) of the subject's breath. Samples will be collected and analyzed according to the protocols described in detail in Section 2.

3.2.4 Criteria for Selecting High End Microenvironments

General selection criteria for the 13 high-end MEs are listed below. These selection criteria were developed to bias selection towards sampling ME locations and conditions with higher levels of accumulated emissions. Survey technicians will also use pollutant sniffers (e.g., Langan CO and ppbRAE VOC monitors) to sense relative peak pollutant levels within and among these candidate locations, choosing the ME locations with the highest levels in each category for inclusion in the city-specific sampling scripts. Detailed descriptions of the Houston, Atlanta and Chicago microenvironments are presented in the city plans appended to the protocol.

1. Congested (stop-and-go) freeway (vehicle cabin)
    - Rush hour sampling on roadway parallel to wind direction
    - Locally known choke points & signaled intersections on high density routes
    - Locations most shielded from air dispersion by local topography
    - Lane reductions due to ongoing construction or breakdowns/accidents
    - Downwind direction from traffic density centroid
    - Trailing high emitting vehicles encountered

    Protocol: Prior to test, identify roadway segment that best satisfies above conditions and confirm high potential concentrations using sniffer. Drive back and forth on the segment continuously during the 40-minute rush-hour test period. Drive in most congested (slowest) lane. Maintain a safe following distance, about one car length (10 feet) per 10 mph speed, closing to within 3 feet during stopped conditions. Sample alternative 20-minute periods under high- and low-ventilation (vehicle windows & vents open and windows & vents closed). Trail high emitting vehicles where encountered.

2. Urban canyon (vehicle cabin)
    - Rush hour sampling on roadway perpendicular to wind direction
    - Greatest contiguous length & height of high-rise buildings
    - Narrowest canyon width
    - Highest traffic density
    - Mid-block sampling most shielded from air dispersion

    Protocol: Urban canyons are streets edged by tall buildings that were selected to be deep as possible generally with height/width ratios > 1. Prior to test, identify roadway segment that best satisfies above conditions and confirm high potential concentrations using sniffer. Drive back and forth on the segment

continuously during the 40-minute rush-hour test period (an around-the-block downtown loop may be used if entire loop is associated with high canyon concentrations). Drive in most congested (slowest) lane. Maintain a safe following distance, about one car length (10 feet) per 10 mph speed, closing to within 3 feet during stopped conditions. Sample alternative 20-minute periods under high- and low-ventilation (vehicle windows & vents open and windows & vents closed). Trail high emitting vehicles where encountered. Note that GPS data are often unavailable or unreliable in tall urban canyons as the satellite signals are blocked.

3. Refueling (vehicle cabin)

    - Peak refueling period for station
    - Largest number of pumps
    - Downwind direction from centroid of pump locations
    - Location most shielded from air dispersion by topography
    - Period with the lowest achievable wind speeds

- Protocol: Prior to test, identify service station that best satisfies above conditions and use sniffer to locate refueling stations associated with highest concentrations. Drive van sufficiently to elevate measured fuel tank temperature prior to the refueling test. Park car at refueling location and sample alternative 10-minute periods under high- and low-ventilation (vehicle windows & vents open and windows & vents closed). Refuel car over a 1 to 2-minute active refueling period at mid-point of high-ventilation sampling period, spilling a few drops of fuel (whose volume is estimated by spot diameter) as the nozzle is withdrawn from the fuel tank inlet. The number of gallons dispensed will be recorded along with number and diameters of spill spots; the start and stop times of active fueling will be recorded on monitor charts. Endeavor to sample the same service station at the same time of day on different days as is possible.

4. Parking garage (vehicle cabin) underground
    - Rush hour exit sampling
    - High capacity & usage
    - Near internal entrance/exit lanes
    - Location with smallest external openings & most shielded from air dispersion by topography
    - Downwind direction from centroid on most occupied parking level

Protocol: Prior to test, identify aboveground parking lot that best satisfies above conditions and use sniffer to locate parking area within lot associated with highest concentrations. Park car at the location and sample alternative 40-minute periods under high- and low-ventilation (vehicle windows & vents open and windows & vents closed), during most active period of vehicles exiting.

5. Toll plaza apron (vehicle cabin)
    - Rush hour sampling
    - General location of idling traffic queue (e.g., at road toll, parking garage entrance/exit, emissions testing facility, controlled on-ramp, multi-road signal-controlled intersection)
    - Location most shielded from air dispersion by topography
    - High use location
    - Downwind direction from centroid of traffic mass

Protocol: Prior to test, identify toll plaza apron that best satisfies above conditions and use sniffer to locate parking area within plaza associated with highest concentrations. Park car at the location, if feasible, and sample alternative 20-minute periods under high- and low-ventilation (vehicle windows & vents open and windows & vents closed). If not, repeatedly traverse the plaza queue during the 40-minute test period, sampling as above, trailing any high emitting vehicles encountered.

6. Tunnel/Covered Roadway (vehicle cabin)
    - Rush hour sampling

- Stop-n-go traffic flow
- Highest traffic density
- Lack of mechanical ventilation, if available
- Smallest enclosed volume

Protocol: Prior to test, identify tunnel or covered roadway that best satisfies above conditions and use sniffer to confirm high concentrations. Drive back and forth on enclosed roadway during the 40-minute test period maximizing time spent in the enclosed environment. Drive in slowest, most congested lane. Maintain a safe following distance, about one car length (10 feet) per 10 mph speed, closing to within 3 feet during stopped conditions. Note that GPS data are unavailable inside the tunnel as the satellite signals are blocked. Sample alternative 20-minute periods under high- and low-ventilation (vehicle windows & vents open and windows & vents closed). Trail high emitting vehicles where encountered. Collect 5-minute canister sample during tunnel transit of peak concentration. Biomarker samples (breath) will be collected from the technician, who will be isolated from further exposure before performing this task.

7. Outdoor Refueling (self-service)
    - Peak refueling period for station
    - Largest number of pumps
    - Downwind direction from centroid of pump locations
    - Location most shielded from air dispersion by topography
    - Period with lowest achievable wind speeds

- Protocol: Prior to test, identify service station that best satisfies above conditions and use sniffer to locate refueling area associated with highest concentrations. After driving car sufficiently to elevate measured temperature of fuel tank, park car at refueling location and sample alternative 10-minute background (at pump) and refueling periods. With collocated sampling inlets in the breathing zone, refuel the vehicle over a 1 to 2-minute active refueling period at the mid-point of the second 10 min sampling period. A 5-minute canister sample is taken to include the active refueling period. Return to the vehicle cabin for the rest of the 10-minute sampling period. During active refueling, maintain manual control of the nozzle (i.e., use an unlatched nozzle) and stand downwind of the vehicle fuel tank inlet, spilling a few drops of fuel (whose volume is estimated by spot diameter) as the nozzle is removed from the fuel tank inlet. The number of gallons dispensed will be recorded along with number and diameters of spill spots; the start and stop times of active fueling will be recorded on monitor charts. Endeavor to sample the same service station at the same time of day on different days as is possible. Liquid fuel samples will be collected after ME7 measurements (during off-loading of the van fuel tank) for each service station (if more than one is used per city) sampled for this ME.

Biomarker samples (breath) will be collected from the technician, who will be isolated from further exposure before and after performing this task.

8. Sidewalk/crosswalk near high density traffic
    - Rush hour sampling on roadway parallel to wind direction
    - Downwind direction from traffic mass centroid
    - Location most shielded from air dispersion by topography
    - Highest traffic density
    - In urban canyon

Protocol: Prior to test, identify roadway segment with sidewalks that best satisfies above conditions and identify the highest concentration area using sniffer. With cart sampler inlet in breathing zone, walk along loop route on both sides of roadway using crosswalks to cross roadway during the 40-minute sampling period. Walk within three feet of curb.

9. Bus stop
    - Rush hour sampling on roadway parallel to wind direction
    - High traffic density route
    - Located on traffic island/median strip

- Downwind direction near high density traffic intersection
- In urban canyon

Protocol: Prior to test, identify bus stop (or cab stand) satisfies above conditions and confirm high concentrations using sniffer. With cart inlet in breathing zone, stand/sit at this location (within three feet of curb) for the entire 40-minute test.

10. Outdoor Surface Parking
    - Rush hour/maximal usage sampling
    - High capacity & usage location
    - Near internal entrance/exit lanes
    - Downwind direction from centroid of traffic mass
    - Location most shielded from air dispersion by topography

    Protocol: Prior to test, identify stadium parking lot that best satisfies above conditions and locate parking area within lot where vehicles will queue as they attempt to exit. Identify approximate time that the game/event ends. Sample during 40-minute test, approximately dividing the time to see the peak number of vehicles leaving the lot. Sample with front windows down, sliding doors open and vents open, as appropriate.

11. Outdoor Underground Parking Garage
    - Rush hour sampling
    - High capacity & usage
    - Near internal entrance/exit lanes
    - Lowest level with high capacity usage
    - Lack of mechanical ventilation, or away from fans & vents if present

    Protocol: Prior to test, identify underground parking lot that best satisfies above conditions and use sniffer to locate parking area within garage associated with highest concentrations. Park car at location during 40-minute rush-hour test with front windows down and vents open. Maximize number of vehicles passing the sampling point as they exit the garage. Collect a 5-minute canister sample during a period of peak concentration. Biomarker samples (breath) will be collected from the technician, who will be isolated from further exposure before performing this task.

12. Outdoor Toll booth
    - Rush hour/maximal usage sampling
    - Lack of mechanical ventilation, if available
    - Enclosed queues (e.g., from parking garages, tunnels, testing facilities)
    - Central booth & location most shielded from air dispersion by topography
    - Downwind direction from centroid of traffic mass

    Protocol: Prior to test, identify tollbooth area that best satisfies above conditions and confirm highest concentrations using sniffer. With cart inlet in the breathing zone, sample a location representative of the tollbooth operator's exposure during the 40-minute test.

13. Trailing High Emitters
    - Rush hour sampling on roadway perpendicular to wind direction
    - Greatest contiguous length & height of high-rise buildings
    - Narrowest canyon widths
    - Highest traffic density

    Protocol: Prior to test, identify roadways which have the most high emitters using sniffers. Acquire candidate high emitters from PID/CO sensors and follow as closely as is prudent. Maintain a safe following distance, about one car length per 10 mph speed, closing to within 3 feet during stopped conditions. Sample alternative 20-minute periods under high- and low-ventilation (vehicle windows &

vents open and windows & vents closed). Trail high emitting vehicles as long as possible or until a higher emitter is encountered. Collect a 5-minute canister sample during a peak concentrations period. Biomarker samples (breath) will be collected from the technician, who will be isolated from further exposure before performing this task.

Appendices A, B and C contain the specific city plans for sampling in Houston, Atlanta, and Chicago, respectively.

3.3 Meteorology

For portions of the sampling periods involving stationary activities, local meteorological variables such as wind speed and direction, temperature and relative humidity will be taken periodically with a handheld monitoring station. During both these and mobile sampling periods, additional information representing regional conditions will be obtained from nearby NOAA/FAA sites, or other agencies if available. Stability information requires upper air data. The closest locations to the selected cities of San Antonio, Houston, Atlanta, and Chicago, that take routine radiosonde measurements, are at Corpus Christi TX, Lake Charles LA, Peachtree City GA, and Davenport IA or Lincoln IL. Sections of two of the cities, Houston and Chicago, can also be affected by land/ocean breezes. Although in situ surface-based observations are preferable, diagnostic output from operational numerical models can also be analyzed.

Field participants in the experiment will make the local on-site measurements using a portable meteorological station. Dr. Kelly Redmond, Regional Climatologist, of the Western Regional Climate Center (WRCC), will undertake remaining phases. A principal role of this NOAA-funded facility, housed within DRI's Division of Atmospheric Sciences, is to acquire, store, summarize, distribute, and interpret atmospheric data. The Climate Center has excellent access to past data nationwide through its own considerable in-house capabilities, as well as strong programmatic ties to the other five Regional Climate Centers and to the National Climate Data Center. (The entire national program is funded through DRI.) Each day WRCC processes approximately 100-200 MB of weather and climate data from the national distribution circuits, and saves indefinitely the entire feed containing observations from all NOAA/FAA sites in North America. The Climate Center has a wide variety of software for producing climatological summaries of differing degrees of sophistication, depending on the need.

3.4 Data Analysis

Compile summary statistics of the data, perform consistency checks, and identify outliers.

The data validation process consists of procedures that identify deviations from measurement assumptions and procedures. We will apply the following tests to evaluate the internal, spatial, temporal, and physical consistency of each data set and identify invalid data and outliers. DRI will compile and validate the data from Tasks 2 through 4 and prepare statistical summaries of the data and perform the following validation checks.

- Compare averages derived from continuous and semi-continuous measurements with data from time-integrated samples. Determine systematic biases.

- Derive summary statistics (mean, maximum, standard deviation) for all species, sort the concentrations and note any unusually high or low concentrations.

- Determine variations in fractions of benzene, toluene, ethyl benzene, xylenes, MTBE, and ethanol, formaldehyde, acetaldehyde to TNMHC and significant differences in the ratios among microenvironments.

- Prepare scatter plots of mean CO and PID with BTEX from canister and MS200), 1,3-butadiene and MTBE from canisters, ethanol from adsorbent cartridges, formaldehyde and acetaldehyde from DNPH cartridges, and formaldehyde from continuous measurements.

- Determine ratios of the sum of formaldehyde and acetaldehyde to CO, and relate variations in the ratios with MEs and time of day with expectations in the relative contributions of direct emissions versus photochemical formation.

Evaluate the suitability of candidate measurement methods for use in the main exposure study.

- Summarize results of laboratory evaluations of continuous and semi-continuous methods.

- Compare time-averaged continuous data from the pilot study with corresponding semi-continuous and time-integrated measurements over the same time intervals. Determine significant biases among methods and determine whether continuous measurements will be suitable for determining time-integrated exposure or for documenting peak exposures only.

- For continuous and semi-continuous measurement methods, characterize the effect of time resolution on measurement of peak exposures.

Determine quantitative relationships between tailpipe emission rates and variations in fuel formulations with exposures in the cabin of a trailing vehicle.

- Quantify the variations in the background values for BTEX, MTBE, 1,3-butadiene, HCHO, CH_3CHO, EtOH, TVOC and CO during the initial and final loops without the test vehicle.

- Subtract the average time-integrated background values from the corresponding time integrated exposure levels for the default driving condition for each of the 24 test combinations (i.e., two test vehicles, two emission conditions, three fuels, and two season) and four replicates.

- Quantify separately for each of the two vehicles, the specific differences due to emission condition, fuel and season. Quantify absolute differences for each designated species and differences normalized to concurrent CO data.

- Variations in MTBE/benzene and EtOH/benzene ratios (or other HC species) will be related to extent of the potential contribution of tailpipe and evaporative emissions.

- Determine the effect on cabin exposure of varying speed, spacing between test and trailing vehicle, and degree of ventilation.

- Determine variations of the in-cabin exposures within the test and trailing vehicle due to variation in normal/malfunction test vehicle emission rates under idle.

Determine quantitative relationships between evaporative emission rates and variations in fuel formulations with exposures in a residence with an attached garage.

- Subtract the time-integrated background values of BTEX, MTBE, and TVOC from the corresponding time integrated exposure levels in the garage and in the adjacent room and determine the increased exposure due to hot-soak evaporative emissions for the vehicle and fuel combinations that were tested.

- Determine the time-evolution in the levels of the BTEX, MTBE, and TVOC above background levels and determine the penetration of evaporative emissions from the garage to the adjacent room for the vehicle and fuel combinations that were tested.

Quantify exposures to conventional and oxygenated evaporative and exhaust emission in microenvironments.

- Process GPS data and develop a log of exposure measurements with respect time, location, and speed.

- Compare time-integrated exposure levels measured in the microenvironments that were investigated among the three cities by season. Develop correlations of individual toxic species from time-integrated measurements with CO or PID measurements as appropriate for microenvironments dominated by vehicle exhaust or fuel evaporative emissions.

- Evaluate the consistency in time-series among continuous CO, PID, MS200, and HCHO measurements in each microenvironment by city and season.

- Reconstruct the time-series of individual air toxics using the surrogate CO and PID measurements and their correlations to time-integrated measurements.

- Determine the differences in mean and peak exposures by city and season for each microenvironment and characterize the variability of replicate tests for each microenvironment.

- Characterize the extremes in exposure levels for each microenvironment using the reconstructed 1-minute data.

- Determine the effect of varying cabin ventilation conditions on exposure levels using the ratios of in cabin CO concentrations to ambient CO (measured in the mobile laboratory).

- Compare CO/BTEX/HCHO/NMHC levels that were measured during the exposure study with nearby values from the local ambient air monitoring station.

- Estimate the relative importance of tailpipe and evaporative emissions on exposure using the ratio of MTBE to benzene as described in the RFP.

- Determine the levels of the designated species in the urine and breath of technicians carrying out the scripted behaviors and determine significant differences due to varying fuel formulation.

3.5 Reporting

This task will require completion of the following:

- Report after completion of the 1st Reno Pilot Study (complete)
- Detailed preliminary protocol (peer-reviewed by API and submitted for EPA approval prior to initiating the main exposure measurements) (complete)
- Interim Data Report after 2002 summer field study (complete)
- Atlanta Summer Field Study report (complete)
- Report after completion of the 2nd Reno Pilot Study (complete)
- Final protocol (after incorporating protocol changes) (this document)
- Comprehensive draft report (including the hypotheses, descriptions of statistical analyses, and interpretations of the findings)Final report incorporating reviewers' comments (submitted to EPA for review and approval together with the reviewers' comments and a statement of the disposition of the reviewers' comment)

4. PROJECT SCHEDULE AND DELIVERABLES

- 10/03 Final protocol submitted to EPA for formal approval
- 11/03 Send summer 2002 San Antonio & Houston data report to EPA
- 12/03 Send summer 2003 Chicago & Atlanta data report to EPA
- 1/04 EPA approves San Antonio and/or Houston re-sampling plan
- 2/04 DRI begins winter Atlanta sampling
- 3/04 DRI completes winter Chicago sampling
- 7/04 DRI begins summer re-sampling in San Antonio (if required)
- 8/04 DRI completes summer re-sampling in Houston
- 1/05 DRI begins winter San Antonio sampling
- 2/05 DRI completes winter Houston sampling
- 5/05 Send draft report to EPA & peer reviewers
- 6/05 Revise draft report incorporating peer reviewer comments
- 7/05 Send draft final report to EPA
- 9//05 Receive EPA comments
- 1/06 Address EPA comments, send final report to EPA, & archive results

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6. APPENDICIES

APPENDIX A

Exposure Protocol and Study Plan for the Section 211(B) Tier 2 High End Exposure Screening Study of Baseline and Oxygenated Gasoline - Summer/Winter Sampling Plan for Houston

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October 1, 2003

INTRODUCTION

This sampling plan specifies the details for the field measurement program that will be carried out in Houston, Texas during the summer of 2004 and winter of 2005 as part of a screening study of the high-end exposures to baseline and oxygenated gasoline. It specifies example dates, times and measurement locations for the twelve categories of microenvironments and explains the selections with respect to the objective of capturing the upper-end of the distribution of exposures for each microenvironment. This document is an addendum to the Exposure Protocol and Study Plan, which describes the proposed measurement methods and rationale for their selection.

Exposure levels are directly related to the activity and emission rates of sources in the microenvironment and inversely related to the distances between sources of emissions and the measurement location and the extent of dilution of emissions, which is a function of meteorological conditions and the presence of physical obstruction that inhibit dispersion. The API and EPA have prescribed a goal to capture the 99th percentile exposure levels within each type of microenvironment. Due to the scope of this study, it will not be possible to fully characterize (by measurements) the range of exposures that include the 99th percentile. However, we considered available surrogate parameters for emission levels and dispersion to select sampling times and locations with the greatest potential for higher exposures. These emission surrogates include traffic counts, and diurnal variations in average highway speeds, length of queues at toll plazas, number of cars refueling or entering and exiting parking garages. Surrogates for dispersion include wind roses and diurnal variations in temperature. Measurements in microenvironments with unrestricted dispersion will be made in the early morning or evening during calm conditions and minimal vertical mixing. In moderate wind conditions, we will drive parallel to the prevailing wind to reduce the impact of cross winds. Our sampling strategy also recognizes that vehicle exhaust emission levels are significantly higher for high emitters and are higher for all vehicles during cold starts and accelerations. All of these factors are important in understanding the large temporal and spatial variations that are likely to exist within each of the microenvironments. We plan to examine available hourly CO data and PAMS BTEX and 1,3-butadiene data for June through September 2003 to place the field measurement data in context with seasonal variations.

Desert Research Institute personnel, accompanied by the API project officer, surveyed potential microenvironments in Houston on June 20-22, 2002 (Thursday to Saturday). The objectives of the survey were to ascertain the suitability of sampling locations with respect to access and potential for higher-end exposures, and to determine the variations in air pollutant levels in several of the microenvironments with a portable gas analyzer. We visited the following locations: I-10 during the morning commute period, urban canyons in downtown Houston, Washburn Tunnel, various toll plazas on the Sam Houston Tollway and Hardy Toll Road, toll plaza at the Ship Channel Bridge, covered terminals at the Bush International and Hobby Airports, parking garages in downtown Houston and the Texas Medical Center, underground parking garages at the City Hall Annex and Greenway Plaza (Compaq Center), and parking lots at Minute Maid Park after a Houston Astros baseball game. A RAE Systems Model PGM-7240 (ppbRAE) portable PID monitor was used to continuously monitor ambient VOC levels in several of the microenvironments. The monitor is equipped with a 10.6 eV photoionization (PID) detector and responds to certain organic and inorganic gases that have an ionization potential of less than 10.6 eV, which includes most compounds of interest in this study. It does not respond to light hydrocarbons such as methane, ethane, and propane or to acetylene, formaldehyde or methanol. For the purposes of the survey of microenvironments in Houston, the PID detector was used to measure variations rather than absolute VOC levels.

SURVEY RESULTS

Figures 1 through 5 show the time-series plots of the PID response in several microenvironments. Data are plotted for the 10-second average and maximum PID response during each 10-second interval. Because we inspected many sampling locations within a short time, many of the PID measurements do not coincide with periods of highest emissions. Coupled with expected variations in emission activity levels, these measurements may be used to assess the potential for the highest exposures. Figure 6 shows the historic mean wind speed and direction in Houston for July.

Figure 1 shows the PID response for a one-hour trip during the morning commute period on eastbound I-10 from Barker-Cypress Rd. to downtown Houston via southbound I-45. The trip ended south of the downtown area at the Fannin St. exit off westbound SR-59. The trip was made on Thursday, June 20, 2002 from 7:27 to 8:27 a.m. The

first 40 minutes of the trip was in congested traffic (average speed of 20-25 mph). For most of this period, the maximum PID response hovered around 100 ppb with occasional excursions to up to 200 ppb. The maximum PID response increased to between 400 and 600 ppb during a three-minute period in the first ten minutes of the trip. These high values were associated with a suspected high emitter. The vehicle was a landscape service truck, which was towing a trailer containing lawn and garden equipment. Three spikes in the PID response coincided with slow downs in traffic followed by accelerations. Without concurrent CO data, we cannot rule out evaporative emissions from the lawn and garden equipment. However, we followed one other landscape service truck with no increase in the PID response. From the I-610 loop to I-45, the traffic moved near the speed limit and the PID response was consistently at or below 100 ppb. VOC concentrations were higher during the last ten minutes of the trip when we encountered congested traffic in downtown Houston and substantial backup at the junction of southbound I-45 and westbound SR-59. This trip demonstrates what we have observed with similar measurements. A great majority of the on-road vehicle fleet are relatively low emitters that have little impact on in-cabin exposure levels at highway speed. Congested stop-and-go conditions result in some increase in exposure levels due to shorter gap between vehicles and due to intermittent accelerations. Higher exposures are anticipated when following high emitters.

Figure 2 shows the time-series of the PID response during a 1.3-hour tour through downtown Houston. The first half of the tour covered the west side of downtown with potential urban canyons. The PID response varied with traffic in the area, which was relatively light during this period. We sampled in an above-ground parking garage at about 9:00 a.m. for about five minutes. The VOC levels measured in the garage were not significantly above the surrounding urban background. The second half of the tour covered the eastside of downtown near Minute Maid Park (Houston Astros baseball stadium). The large parking lot east of the stadium is a potential sampling site during ballgames (see Figure 4).

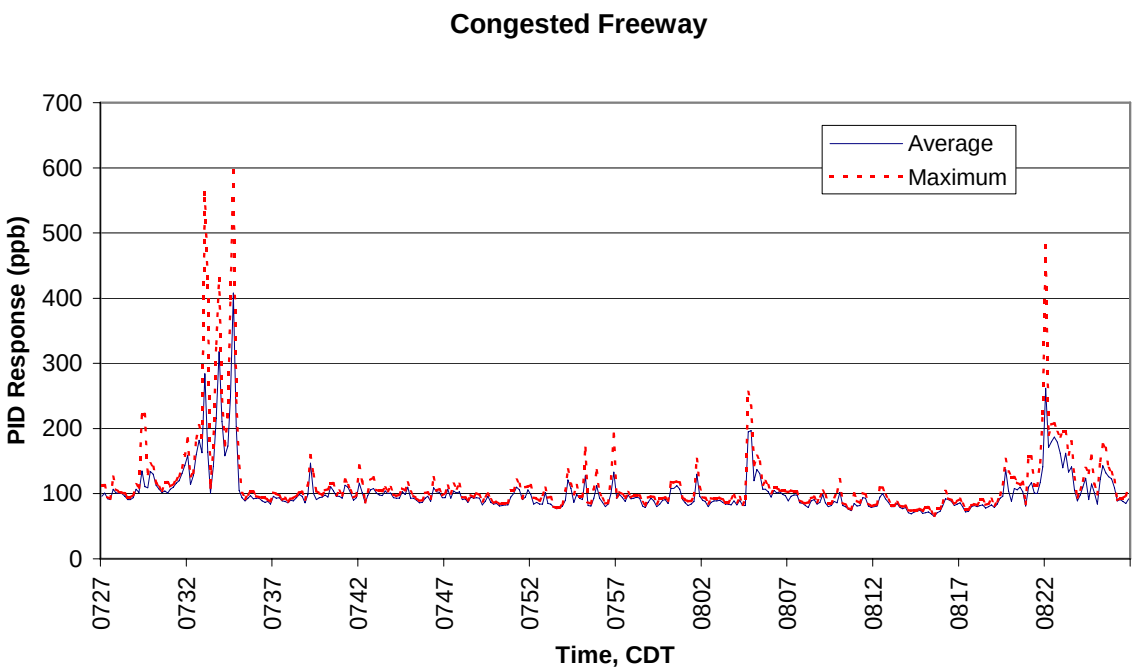

Figure 1. Eastbound I-10 from Barker-Cypress Rd. through downtown Houston via southbound I-45 and westbound SR-59 and ending at Fannin exit.

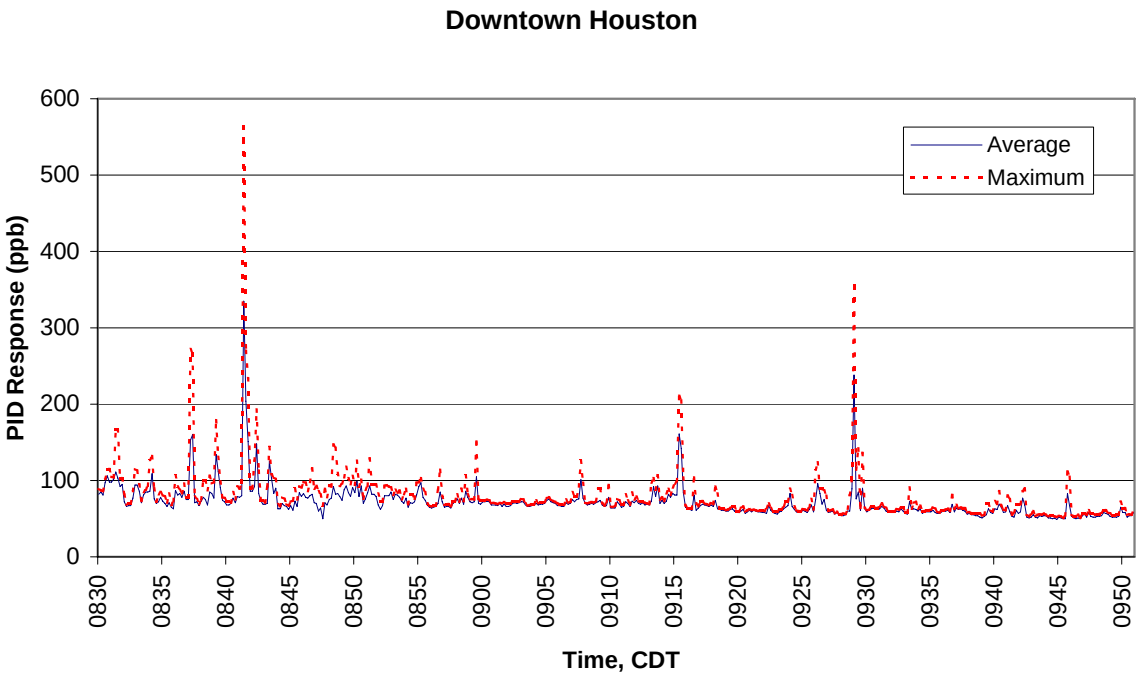

Figure 2. Tour of downtown Houston.

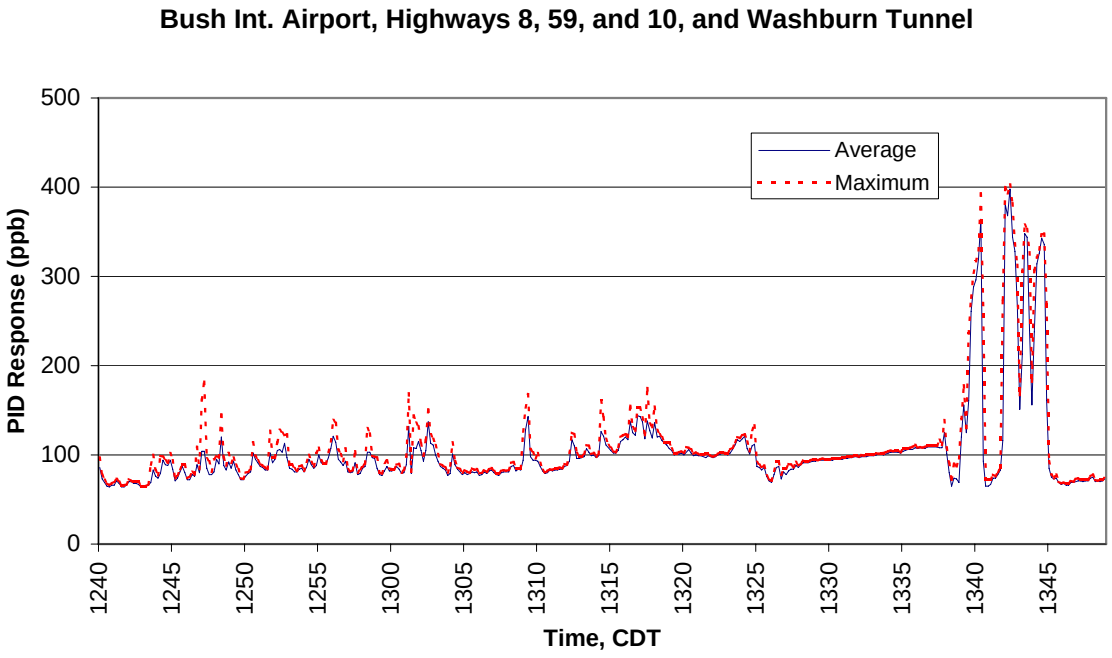

Figure 3. George Bush International Airport and drive to Washburn Tunnel.

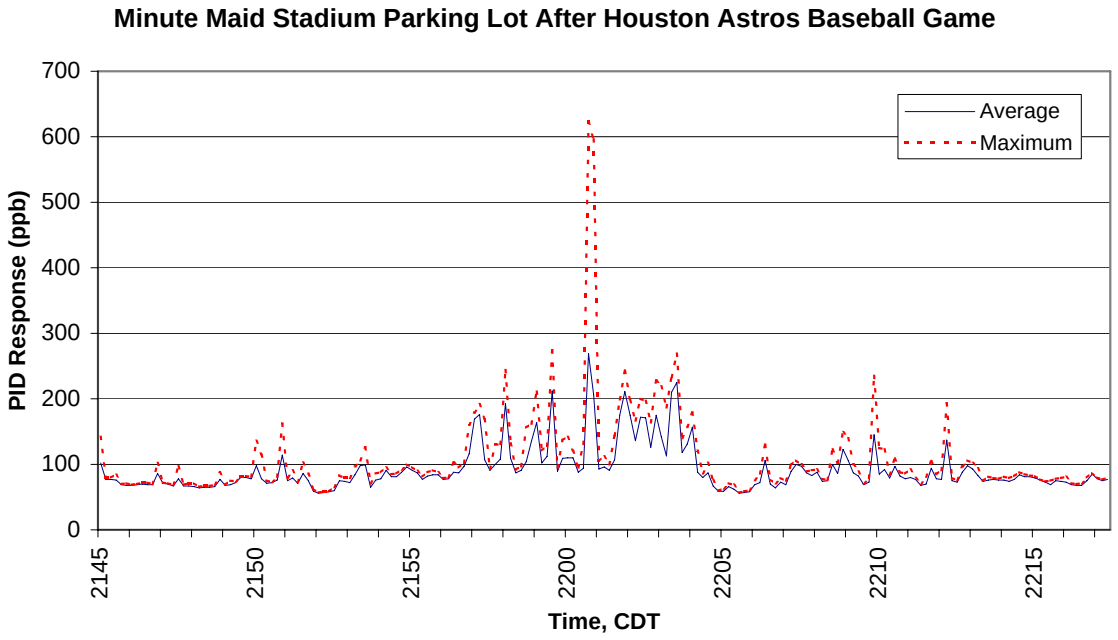

Figure 4. Minute Maid Park at the end of a ballgame on evening of June 21, 2002.

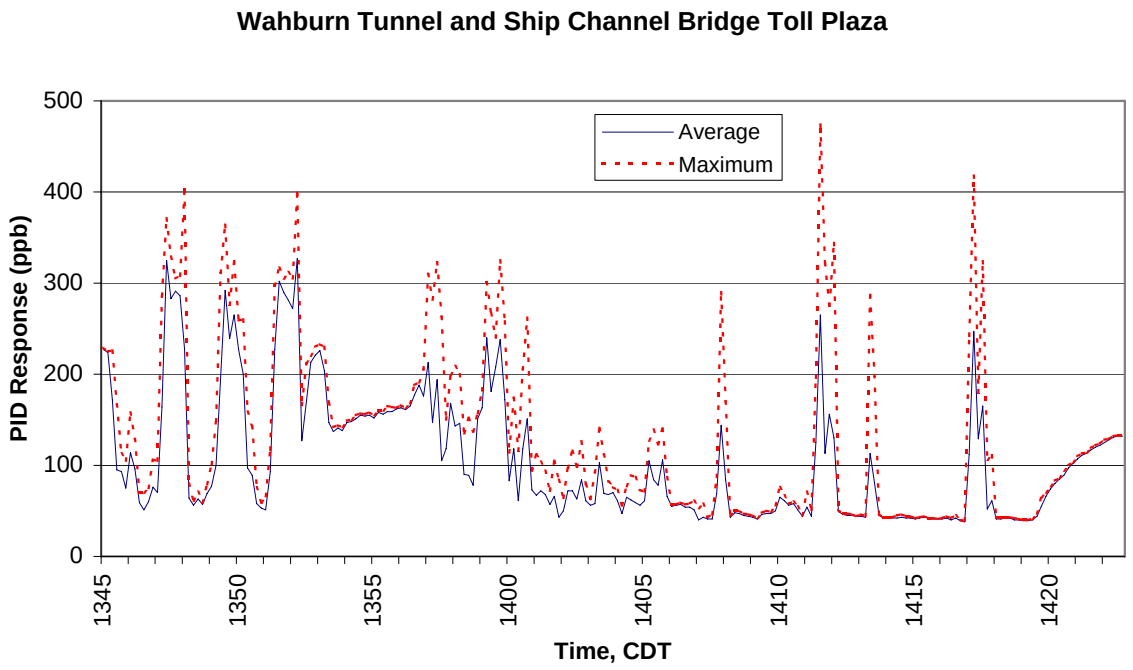

Figure 5. Tour of Washburn Tunnel and the Ship Channel Toll Plaza on the Sam Houston Tollway.

The first 20 minutes in Figure 3 show the variations in PID response at the George Bush International Airport. The road through the airport is split into two levels at each of the four terminals with passenger pick-up being the lower, covered level. Terminal C appeared to have the greatest length of covered roadway in front of the terminal. Traffic was light during this time and we observed about a 50 to 100 percent increase in PID response while driving past Terminal C. We expect significantly higher VOC levels during peak periods. We also visited the Hobby Airport (data not shown), which also has a two-level road at the terminal. The length of covered roadway is greater at Hobby and adjacent parking garage is larger. We propose to sample in-cabin exposure at the Hobby Airport terminal during peak periods.

Figure 3 also shows the variations in PID response during three trips through the Washburn Tunnel. The first three spikes in Figure 5 correspond to trips through the tunnel on another day. Travel time through the tunnel is 52 seconds at 35 mph from portal to portal. The tunnel is book ended on each side by a rotary. Passage through the tunnel is controlled during peak periods to avoid congestion within the tunnel. A queue of vehicles develops during these controlled periods. We propose to sample during peak periods in order to measure exposure while in the queue as well as in the tunnel.

Figure 4 shows the time-series of the PID response at Minute Maid Park at the end of a ballgame on the evening of June 21, 2002. We were parked in the middle of Lot C and made

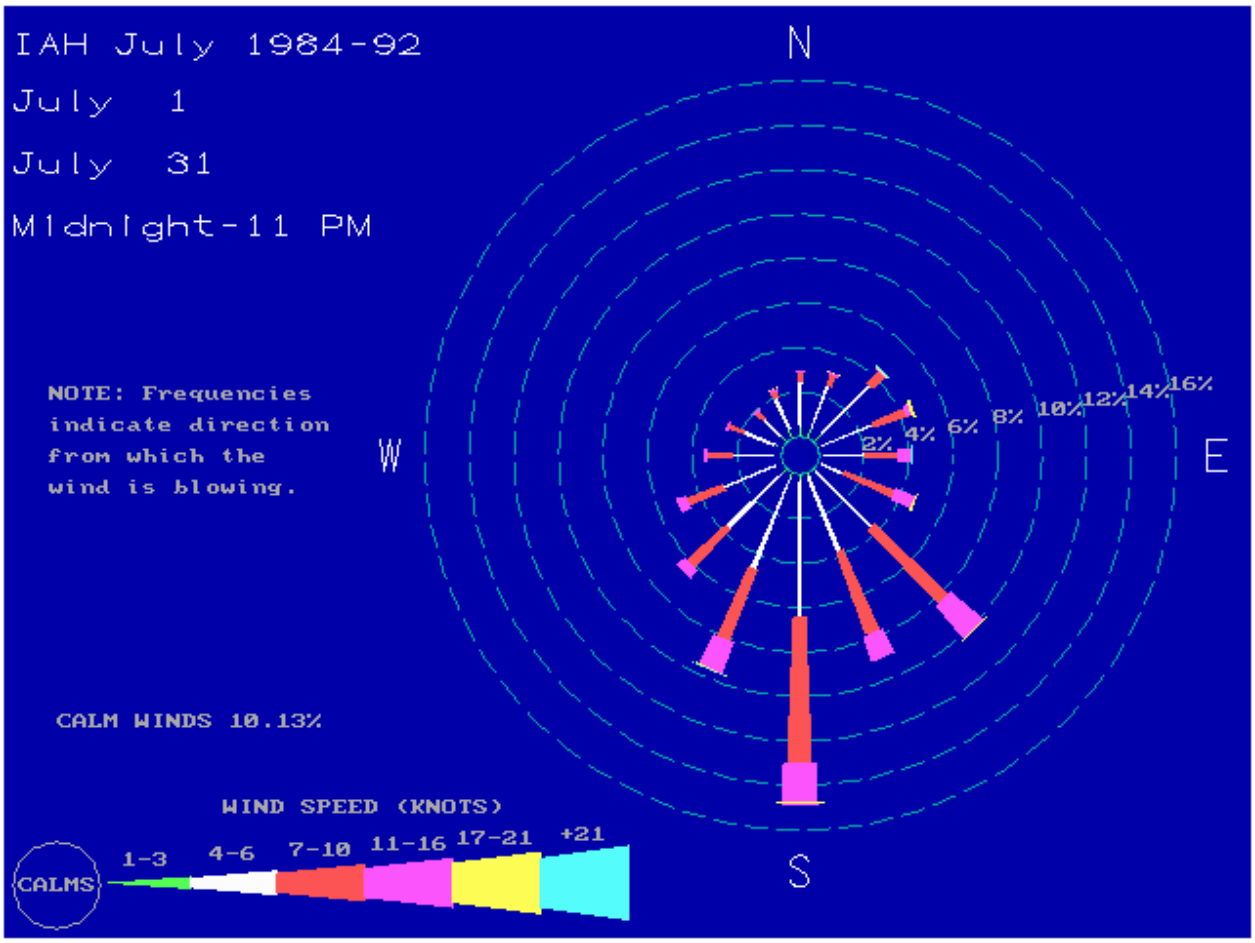

Figure 6. Frequencies of wind speed and direction in Houston during July.

measurements at this location for about ten minutes while vehicles began to leave the lot. The PID response was nearly constant during this period. We then walked to the parking lot exit and made measurements there. The spikes in the PID coincide with the passage of vehicles accelerating out the parking lot, while presumably still in cold-start mode. We then walked along the sidewalk towards the park. These measurements were lower than at the parking lot exit but higher and more variable than at the center of the parking lot. Based upon these results, we propose to sample with a sampling cart for a one-hour period at the end of the game with 15-minute sampling times alternating between a fixed location at the exit of the parking lot and a walk along the sidewalk.

The second half of the time-series in Figure 5 shows the variations in the PID response at the toll plaza at the Sam Houston Tollway Ship Channel Bridge. The speed limit on the Tollway is 70 mph. As the vehicles leave the toll plaza, they accelerate rapidly leaving a puff of higher emissions at the tollbooth. The emissions of vehicles are typically much higher under hard accelerations. The spikes in PID response in Figure 5 coincide with vehicles accelerating rapidly from the tollbooth. Based on these results, we propose to sample with a sampling cart as close to a tollbooth as allowed by the Harris County Tollway Authority. Prior to setup, we will make one pass through the toll plaza to measure in-cabin exposure with continuous instruments only. We will endeavor to use the same ME locations during both the winter and summer studies.

DESCRIPTIONS OF MICROENVIRONMENTS (ME) AND SAMPLING PROTOCOL

1. In vehicle: commuter rush hour in stop-and-go traffic (ME1)

   Make one to two 20-minute roundtrips (depending on traffic conditions) on a segment of freeway during peak weekday morning commuter traffic (Option A or B depending upon wind speed and direction) from 7:00 to 8:00 a.m. Use high ventilation conditions (window and vent open, AC on during summer and heater on during winter) during the first half and low ventilation (windows and vent closed, AC on during summer and heater on during winter) during the second half of the ME. Maintain a safe following distance, about one car length (15 feet) per 10 mph speed, closing to within 3 feet during stopped conditions. Use the middle lane and do not follow the same vehicle for more than two minutes. Attempt to get behind at least one high-emitter.

   Sample in-cabin air at driver's breathing zone continuously with Langan T15 CO monitor, NDIR CO instrument, and ppbRAE, r and collect one set of canister and DNPH samples integrated over the entire sample. Collect four SPME samples, one every 10 minutes. Sample the outside air with the second portable PID monitor during the entire period without compromising the ventilation condition in the cabin. Monitor and record the van's position (GPS), and in-cabin temperature and relative humidity. A forward facing camcorder will record roadway activities and locations for this and other in-cabin MEs during the sampling run. Other relevant data collected by the City of Houston include CO and meteorological data at the Lang (C408) monitoring station in west Houston at 4401 ½ Lang. Check wind speed and direction at the mobile laboratory and traffic conditions (radio reports of any accidents on sampling routes) prior to sampling run and select the appropriate sampling route from the following options. If accidents, other hazards, or local conditions change, substitute other, equivalent routes with similar distances and speeds as needed.

   a. Option A (use for calm wind conditions or winds from west or east). A six-mile segment of I-10 between Dairy Ashford Rd. (2 mile west of the Sam Houston Tollway) and Voss Rd. (4 miles east of the SH Tollway). Start with the inbound (east) direction at Dairy Ashford Rd. Average speeds in the inbound and outbound directions are 20-25 mph and 50-60 mph, respectively.

   b. Option B (use for moderate winds from south-southeast or north-northwest). An eight-mile segment of US-290 between N. Eldridge Parkway (3 miles northwest of SH Tollway) to Bingle Rd (5 miles southeast of SH Tollway). Start with inbound (southeast) direction from N. Eldridge Parkway. Average speeds in the inbound and outbound directions are about 30 mph and 65-70 mph, respectively.

2. In vehicle: urban street canyons (ME2)

   The greatest volume of traffic in the downtown Houston occurs during the morning and afternoon commute periods and to a lesser extent during the noon hour. We propose the weekday afternoon commute period from 4:00 to 5:00 p.m. because the vehicles exiting the parking garages may still be in cold-start mode and because ME1 precludes ME2 during the morning commute period.

Make multiple trips during a 40-minute period along a four by one block surface street loop in downtown Houston. The loop consists of four one-way streets and four left turns. Starting from the intersection of Louisiana and Clay, go northeast on Louisiana for four blocks, turn left on Walker, left on Smith, left on Clay, and left on Louisiana to complete the loop. Use high ventilation conditions (window and vent open, AC on during summer and heater on during winter) during first 20 minutes and low ventilation (windows and vent closed, AC on during summer and heater on during winter) during second 20 minutes. Drive at or near the end of a pack of vehicles as much as possible.

Sample in-cabin air at driver's breathing zone continuously with the Langan T15 CO, NDIR CO, and ppbRAE analyzer and collect one set of canister and DNPH samples integrated over the entire period. Collect four SPME samples, one every 10 minutes Sample the outside air with the second portable PID monitor during the entire period without compromising the ventilation condition in the cabin. Monitor and record the van's position (GPS), and in-cabin temperature and relative humidity. Note that GPS data is often unavailable or unreliable during this ME as the tall buildings block satellite signals. A forward-facing camcorder will record roadway activities and locations during the run. Other relevant data collected by the City of Houston include CO and meteorological data at the Houston Texas Avenue (C411) monitoring station in downtown Houston at 2311 Texas Avenue.

3. In vehicle: refueling (ME3)

Select appropriate refueling location(s) and sampling times based on the following guidance. The fuel pump islands should be located on the lee side of the service station building or other large obstruction such as the raised section of highway. Given the prevailing southerly to southeasterly winds, the turnarounds at the north sides of I-10, South I-610 loop, or SR 59 are potential areas for the search. Conduct sampling during the peak or near-peak refueling periods for the station as indicated by service station personnel.

After driving to elevate measured fuel tank temperatures, park sampling van at refueling location and sample alternate 10-minute periods under background (parked at pump) and refueling conditions Park the van downwind from the centroid of the pump locations. Sample in-cabin air at driver's breathing zone continuously with a KORE MS 200, Langan T15 CO, NDIR CO, and ppbRAE PID, and collect one set of canister and DNPH samples integrated over the sampling period. Collect two SPME samples, one 10-minute sample during the background sampling period and one 10-minute sample during the refueling period. Sample both the outside and in-cabin air with the two portable PID monitors during the entire sampling period. Monitor and record the outside wind speed, and direction, as well as the sampling location temperature and relative humidity. A camcorder will be positioned to record the sampling scene from outside the van; a pan of the sampling site will also be provided to record details of the location. Van windows are to be down and doors open as appropriate during this ME

4. In vehicle: parking garage (ME4)

Drive within a parking garage for 40 minutes. Use high ventilation conditions (window and vent open, AC on during summer and heater on during winter) during first 20 minutes and low ventilation (windows and vent closed, AC on during summer and heater on during winter) during second 20 minutes. Potential garages include the Houston City Hall Annex, Greenway Plaza, and Hobby Airport (covered road in front of terminal and adjacent parking structure).

Sample in-cabin air at driver's breathing zone continuously with a KORE MS 200, Langan T15 CO, NDIR CO, ppbRAE, and DRI HCHO analyzer and collect one set of canister and DNPH samples integrated over the entire hour. Collect six SPME samples, one every 10 minutes. Sample both the outside and in-cabin air with the two portable PID monitors during the entire hour without compromising the ventilation condition in the cabin. Monitor outside wind speed and direction (if any) and record the in-cabin temperature and relative humidity. A camcorder will be positioned to record the sampling scene from outside the van; a pan of the sampling site will also be provided to record details of the location.

5. In vehicle: toll plaza (ME5)

Measurements for this microenvironment are combined with the tunnel and tollbooth microenvironments. See ME6 and ME12.

6. In vehicle: tunnel (ME6)

Make several trips though the Washburn Tunnel for one hour during peak periods when traffic through the tunnel is controlled. Use high ventilation conditions (window and vent open, AC on during summer and heater on during winter) during first 20 minutes and low ventilation (windows and vent closed, AC on during summer and heater on during winter) during second 20 minutes.

Sample in-cabin air at driver's breathing zone continuously with a Langan T15 CO, NDIR CO, and ppbRAE, and collect one set of canister and DNPH samples integrated over the entire period. Collect a 5-minute canister sample during a peak concentration period. Collect four SPME samples, one every 10 minutes. Biomarker samples (breath) will be collected from the technician, who will be isolated from further exposure before performing this task. Sample the outside and in-cabin air with the two portable PID monitors during the entire hour without compromising the ventilation condition in the cabin. Monitor and record the van's position (GPS), and in-cabin temperature and relative humidity. Note that the GPS data will be unavailable for the period the van is inside the tunnel as the tunnel blocks the satellite signals. A front-facing camcorder will record the roadway activities and also, when stopped, provide a pan of the sampling site location.

7. Outdoor: refueling vehicle (ME7)

Select appropriate refueling location(s) and sampling times based on the following guidance. The fuel pump islands should be located on the lee side of the service station building or other large obstruction such as the raised section of highway. Given the prevailing southerly to southeasterly winds, the turnarounds at the north sides of I-10, South I-610 loop, or SR 59 are potential areas for the search. Conduct sampling during the peak or near-peak refueling periods for the station as indicated by service station personnel if possible and strive for as low wind speed (< 5 mph) as possible. Conduct sampling in the morning to accommodate the collection of biomarker samples and presence of low wind speeds.

Park the van downwind from the centroid of the pump locations after driving it sufficiently to elevate measured fuel tank temperatures. With sampling inlets in the breathing zone, refuel the vehicle over a 1 to 2 minute active refueling interval within the second 10-minute sampling period. During refueling, maintain manual control of the nozzle and stand downwind of the vehicle fuel tank inlet, spilling a few drops of fuel after removing the nozzle from the fuel tank. Sample the breathing zone continuously with a KORE MS 200, NDIR CO, and ppbRAE and collect one set of canister and DNPH samples integrated over the entire 20-minute period. Collect a 5-minute canister sample that includes the active refueling period. Biomarker samples (breath) will be collected from the technician, who will be isolated from further exposure before performing this task. Collect two SPME (background and refueling) samples during the initial background and final refueling periods. Record the ambient temperature and relative humidity. A camcorder will be positioned to record the sampling scene from outside the van; a pan of the sampling site will also be provided to record details of the location. Local wind speed, direction, temperature and humidity will be collected with the hand held meteorological monitor. A liquid fuel samples will be collected after ME7 measurements (during off-loading of the van fuel tank) for each service station (if more than one is used per city) sampled for this ME.

8. Outdoor: sidewalk near high-density traffic (ME8)

Conduct sidewalk sampling by cart in downtown Houston along the city block bordered by Polk, Louisiana, Clay and Smith. A portion of Polk St. is covered and several eating establishment are located there with outdoor seating. After the first trip around the block, remain in the covered section of Polk Street for at least 10 minutes, and then continue the walk around the block. Sampling should be conducted during the morning and afternoon commute periods and during the noon hour. A camcorder will be positioned to record the sampling scene from the cart; a pan of the sampling site will also be provided to record details of the location.

Sample the breathing zone continuously with Langan T15 CO, and ppbRAE portable PID monitor and collect one set of canister and DNPH samples integrated over the entire 40 minute period. Collect four SPME samples,

one every 10 minutes. Record the local wind speed, direction, ambient temperature and relative humidity with the hand held meteorological device.

9. Outdoor: bus stop (ME9)

Sample the ambient air at a bus stop by cart in downtown Houston during the morning and/or afternoon commute periods. Conduct as described in ME8 above.

10 Outdoor: stadium parking lot (ME10)

Sample for 40 minutes at the end of Houston Astros baseball games. Attempt to determine the end of the game time by listening to the radio to determine the progress of the game. Park the van near the exit of the parking lot where vehicles will queue up as they exit, down wind of the exhaust. Sample the breathing zone continuously with a KORE MS 200, Langan T15 CO, DRI HCHO analyzer, and portable PID monitor and collect one set of canister and DNPH samples integrated over the entire period. Collect four SPME samples one every 10 minutes. A camcorder will be positioned to record the sampling scene outside the van; a pan of the sampling site will also be provided to record details of the location.

11. Outside underground parking garage (ME11)

Sample the ambient air in an underground parking garage for one hour. Potential garages include the Houston City Hall Annex and the Greenway Plaza. The Greenway Plaza is preferable for several reasons. The Greenway Plaza is a business complex of ten office towers, the Renaissance Hotel and the Compaq center, home to the NBA Houston Rockets and the WNBA Comets. The complex includes 13,000 parking spaces. A large fraction of the parking is underground. During our study period in Houston, the Comets are scheduled to play. We propose three separate 40-minute sampling periods. The first will start about 4:00 p.m. when the office workers leave the complex (cold start emissions). The second starts about 7:00 p.m. when the basketball fans arrive for the game (hot stabilized exhaust and hot soak emissions) and the final sampling period will be after the game (cold start emissions).

Sample the breathing zone continuously with a KORE MS 200, Langan T15, DRI HCHO analyzer, and portable PID monitor and collect one set of canister and DNPH samples integrated over the entire period. Collect a 5-minute canister sample that includes a peak period during the crowd exit after the game. Biomarker samples (breath) will be collected from the technician, who will be isolated from further exposure before performing this task Collect four SPME samples, one every 10 minutes. Collect breath biomarker samples after a peak period encountered early during the sampling event. Record the local ambient wind speed, direction (if any), temperature and relative humidity with the hand held meteorological instrument. A camcorder will be positioned to record the sampling scene outside the van; a pan of the sampling site will also be provided to record details of the location.

12, Outdoors: toll booth (ME12)

Sample the ambient air at the Ship Channel Bridge toll plaza for 40 minutes. Locate the sampling cart behind the concrete barrier on the west end of the plaza as close to the tollbooth as possible. Notify Patricia Watson of the Harris County Tollway Authority (281/875-1400) of the Harris County Tollway Authority at least 24 hours prior to sampling.

Sample the breathing zone continuously with a KORE MS 200, Langan T15 CO, and portable PID monitor and collect one set of canister and DNPH samples integrated over the entire hour. Collect six SPME samples with each sampling period lasting 10 minutes. Record the ambient wind speed, direction, temperature and relative humidity with the hand held meteorological instrument. A camcorder will be positioned to record the sampling scene from the cart; a pan of the sampling site will also be provided to record details of the location.

If time permits before or after the sampling period and sufficient traffic exist, conduct measurement of in-cabin exposure during one pass through the toll plaza. Collect one SPME sample during this sampling period.

DAILY SAMPLING SCHEDULE

The daily schedules for the Houston summer and winter sampling program will be finalized prior to summer 2004 and winter 2005 studies. In order to stay on project schedule as much as possible, sampling will be conducted on Saturdays in case we encounter unsuitable meteorological conditions on scheduled sampling days.

APPENDIX B

Exposure Protocol and Study Plan for the Section 211(B) Tier 2 High End Exposure Screening Study of Baseline and Oxygenated Gasoline
Addendum B – Summer/Winter Sampling Plan for Atlanta

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October 1, 2003

INTRODUCTION

This sampling plan specifies the details for the field measurement program that will be carried out in Atlanta, GA during the summer as part of a screening study of the high-end exposures to baseline and oxygenated gasoline. It specifies example dates, times and measurement locations for the twelve categories of microenvironments and explains the selections with respect to the objective of capturing the upper-end of the distribution of exposures for each microenvironment. This document is an addendum to the Exposure Protocol and Study Plan, which describes the proposed measurement methods and rationale for their selection. We will endeavor to use the same ME locations during both the winter and summer studies.

Desert Research Institute personnel, accompanied by the API project officer, surveyed potential microenvironments in Atlanta on July 24-26, 2002. The objectives of the survey were to ascertain the suitability of sampling locations with respect to access and potential for higher-end exposures, and to determine the variations in air pollutant levels in several of the microenvironments with a portable gas analyzer. We visited the following locations: I-20 W and I-75 NW during the morning commute period, urban canyons in downtown Atlanta, Justus C. Martin Jr. Tunnel, GA400 toll road plaza, parking garages in downtown and midtown Atlanta and in Buckhead, service stations, parking garage at the Georgia Dome and parking lots at Turner Field. A RAE Systems Model PGM-7240 (ppbRAE) portable PID monitor was used to continuously monitor ambient VOC levels in several of the microenvironments. The monitor is equipped with a 10.6 eV photoionization (PID) detector and responds to certain organic and inorganic gases that have an ionization potential of less than 10.6 eV, which includes most compounds of interest in this study. It does not respond to light hydrocarbons such as methane, ethane, and propane or to acetylene, formaldehyde or methanol. For the purposes of the survey of microenvironments in Atlanta, the PID detector was used to measure relative variations rather than absolute VOC levels.

Information for the survey were obtained from the following Atlanta web sites:

Air Quality Agencies

http://www.dnr.state.ga.us/environ/ Georgia Environmental Protection Division
http://www.air.dnr.state.ga.us/amp/index.html Current air quality
http://www.cleanairforce.com/ Vehicle inspection program
http://www.atlreg.com/ Atlanta Regional Commission

http://www.atlanta-airport.com/ Atlanta Airport
http://www.dot.state.ga.us/ Georgia Dept. of Transportation
http://www.accessatlanta.com/autos/special/roadwords.html Road works

http://www.georgia-navigator.com/traffic/ Real-time traffic map
http://www2.georgianavigator.com/links.html Atlanta Visitor Links
http://www.itsmarta.com/ Metro Atlanta Rapid Transit Authority
http://www.metrogirl.com/dna/links.htm Downtown Atlanta Links
http://www.atlantadowntown.com/downtownlivedirectory.htm Downtown Events
http://www.gadome.com/ Georgia Dome/World Congress Center, Falcons
http://braves.mlb.com/NASApp/mlb/atl/ballpark/atl_ballpark_history.jsp Turner Field, Braves
http://www.atlantaarena.com/st0300/main/main.shtml Phillips Arena, Hawks
http://www.aaaparking.com/property2.htm parking garages
http://www.accessatlanta.com/shopping/guides/mallguide.html Mall Guide

DESCRIPTIONS OF MICROENVIRONMENTS (ME) AND SAMPLING PROTOCOL

1. In vehicle: commuter rush hour in stop-and-go traffic (ME1)

Drive for 40 minutes in congested freeway traffic during weekday morning rush hour from 0700 to 0800, local time or evening rush hour from 1700 to 1800. During the morning, drive southbound on I-75 beginning at S.

Marietta Parkway to downtown Atlanta. Drive the opposite direction during the evening rush hour. A forward facing camcorder will record roadway activities and locations for this and other in-cabin MEs during the sampling run. Use high ventilation conditions (window and vent open, AC on during summer and heater on during winter) during the first 20 minutes and low ventilation (windows and vent closed, AC on during summer and heater on during winter) during the second 20 minutes. Maintain a safe following distance, about one car length (15 feet) per 10 mph speed, closing to within 3 feet during stopped conditions. Use the middle lane and do not follow the same vehicle for more than two minutes. Attempt to get behind at least one high-emitter during each of the two ventilation conditions. If accidents, other hazards, or local conditions change, substitute other, equivalent routes with similar distances and speeds as needed.

Sample in-cabin air at driver's breathing zone continuously with a Langan T15 CO, NDIR CO, and ppbRAE PID analyzer and collect one set of canister and DNPH samples integrated over the entire hour. Collect four SPME samples, one every 10 minutes. Sample the outside air with a second portable PID monitor during the entire hour without compromising the ventilation condition in the cabin. Monitor and record the van's position (GPS), and sampling point temperature and relative humidity. Other relevant data collected by the City of Atlanta include CO and meteorological data at the Roswell monitoring station at 4434 Roswell Rd. and the PM Super site at 829 Jefferson St. NW.

2. In vehicle: urban street canyons (ME2)

Make multiple trips during a 40-minute period along a surface-street loop in downtown Atlanta bordered by Peachtree Street NW, Forsyth/Carnegie, Spring Street NW, and Harris Street (four right turns). Make the measurements during either the morning commute period from 0700 to 0800 or evening commute period from 1700 to 1800. Use high ventilation conditions (window and vent open, AC on during summer and heater on during winter) during first half and low ventilation (windows and vent closed, AC on during summer and heater on during winter) during second half. Drive at or near the end of a pack of vehicles at stoplights as much as possible and attempt to get behind at least one high-emitter during each of the two ventilation conditions.

Sample in-cabin air at driver's breathing zone continuously with a Langan T15 CO, NDIR CO, ppbRAE PID analyzer and collect one set of canister and DNPH samples integrated over the entire hour. Collect four SPME samples, one every 10 minutes. Sample the outside air with a second portable PID monitor during the entire hour without compromising the ventilation condition in the cabin. Monitor and record the van's position (GPS), and sampling point temperature and relative humidity. Note that GPS data are often unavailable or unreliable in urban canyons as the tall buildings block satellite signals.

3. In vehicle: refueling (ME3)

Sample for 20 minutes at the Racetrak or Quicktrip (QT) service station located north of the Thornton Rd exit off I-20. Conduct sampling during the peak or near-peak refueling periods for the station as indicated by service station personnel.

After driving to elevate measured fuel tank temperatures, park sampling van at refueling location and sample alternate 10-minute periods under background (parked at pump) and refueling conditions Park the van downwind from the centroid of the pump locations. Sample in-cabin air at driver's breathing zone continuously with a KORE MS 200, Langan T15 CO, NDIR CO, and ppbRAE PID, and collect one set of canister and DNPH samples integrated over the sampling period. Collect two SPME samples, one 10-minute sample during the background sampling period and one 10-minute sample during the refueling period. Sample both the outside and in-cabin air with the two portable PID monitors during the entire sampling period. Monitor and record the outside wind speed, and direction as well as the sampling location temperature and relative humidity. A camcorder will be positioned to record the sampling scene from outside the van; a pan of the sampling site will also be provided to record details of the location. Van windows are to be down and doors open as appropriate during this ME.

4. In vehicle: parking garage (ME4)

Drive within a parking garage for 40 minutes. Use high ventilation conditions (window and vent open, AC on during summer and heater on during winter) during the first half and low ventilation (windows and vent closed, AC on during summer and heater on during winter) during the second half. Potential garages include Colony Square parking garage at Peachtree Street and 14th Street in Midtown Atlanta during the morning and evening commute period and prior to and after the Atlanta Falcons' pre-season football games if possible

Sample in-cabin air at driver's breathing zone continuously with a Langan T15 CO, NDIR CO, ppbRAE, and DRI HCHO analyzer and collect one set of canister and DNPH samples integrated over the entire period Collect four SPME samples, one every 10 minutes. Sample both the outside and in-cabin air with the two portable PID monitors during the entire period without compromising the ventilation condition in the cabin. Monitor outside wind speed and direction (if any) and record the in-cabin temperature and relative humidity. A camcorder will be positioned to record the sampling scene from outside the van; a pan of the sampling site will also be provided to record details of the location.

5. In vehicle: toll plaza (ME5)

Sample during the morning commute period for 40 minutes at the toll plaza between exit 2 and 3 on the GA 400 toll road.

Sample in-cabin air at driver's breathing zone continuously with a Langan T15 CO, NDIR CO and ppbRAE PID analyzer and collect one set of canister and DNPH samples integrated over the entire period Collect four SPME samples, one every 10 minutes. Sample the outside air with a second portable PID monitor during the entire period without compromising the ventilation condition in the cabin. Monitor and record the van's position (GPS), and sampling point temperature and relative humidity.

6. In vehicle: tunnel (ME6)

The Justus C. Martin Jr. Tunnel is the only roadway tunnel in Atlanta. It is located less than two miles south of the toll plaza on GA 400. The tunnel consists of separate bores for the northbound and southbound direction consisting of four lanes each. The tunnel is very short and is unlikely to restrict dilution of emissions to any significant degree. Traffic in both directions remains uncongested during the evening commute period. No sampling is planned for this microenvironment in Atlanta.

7. Outdoor: refueling vehicle (ME7)

Sample at the Racetrak or Quicktrip (QT) service station located north of the Thornton Rd exit off I-20. Conduct sampling during the peak or near-peak refueling periods for the station as indicated by service station personnel.

Park the van downwind from the centroid of the pump locations after driving it sufficiently to elevate measured fuel tank temperatures. Collect biomarker samples during refueling periods with low (< 5 mph) local wind speed. Breath samples are taken before and 10 seconds immediately after active refueling. A backup breath samples is taken immediately after the second breath sample. With sampling inlets in the breathing zone, refuel the vehicle over a 1 to 2 minute active refueling interval within the second 10-minute sampling period. During refueling, maintain manual control of the nozzle and stand downwind of the vehicle fuel tank inlet, spilling a few drops of fuel after removing the nozzle from the fuel tank. Sample the breathing zone continuously with a KORE MS 200, NDIR CO, and ppbRAE and collect one set of canister and DNPH samples integrated over the entire 20-minute period. Collect a 5-minute canister sample that includes the active refueling period. Collect two SPME (background and refueling) samples during the initial background and final refueling periods. Record the ambient temperature and relative humidity. A camcorder will be positioned to record the sampling scene from outside the van; a pan of the sampling site will also be provided to record details of the location. Local wind speed, direction, temperature and humidity will be collected with the hand held meteorological monitor. A liquid fuel samples will be collected after ME7 measurements (during off-loading of the van fuel tank) for each service station (if more than one is used per city) sampled for this ME.

8. Outdoor: sidewalk near high-density traffic (ME8)

Conduct sidewalk sampling in downtown Atlanta along the city block bordered by Peachtree Street NE, Andrew Young International, Spring Street NW, and Harris Street NW. Sampling should be conducted during the morning and afternoon commute periods and during the noon hour.

Sample the breathing zone continuously with a Langan T15 CO, and portable PID monitor and collect one set of canister and DNPH samples integrated over the entire 40 minute period. Collect four SPME samples, one every 10 minutes. Record the ambient temperature and relative humidity.

9. Outdoor: bus stop (ME9)

Combined with ME8.

10. Outdoor: stadium parking lot (ME10)

Sample for 40 minutes at the end of an Atlanta Braves baseball game. Because the atmosphere is more stable in the evening, night games are preferable to day games. Attempt to determine the end of the game time by listening to the radio to determine the progress of the game. Park the van near the exit of the parking lot where vehicles will queue up as they exit, down wind of the exhaust.

Sample the breathing zone continuously with a KORE MS 200, Langan T15 CO, DRI HCHO analyzer, and portable PID monitor and collect one set of canister and DNPH samples integrated over the entire period. Collect six SPME samples one every 10 minutes. A camcorder will be positioned to record the sampling scene outside the van; a pan of the sampling site will also be provided to record details of the location.

11. Underground parking garage (ME11)

Sample the ambient air in the Colony Square underground parking garage (Peachtree and 14th Streets) for 40 minutes starting about 5:00 p.m. when office workers leave the complex (cold start emissions). Sample at exit queues and ramps.

Sample the breathing zone continuously with a KORE MS 200, Langan T15, DRI HCHO analyzer, and portable PID monitor and collect one set of canister and DNPH samples integrated over the entire period. Collect a 5-minute canister sample after a peak exposure encountered during the sampling period. Breath biomarker samples are collected before and within 10 seconds after a similar peak exposure and followed immediately by backup breath canister sample. Collect four SPME samples, one every 10 minutes. Record the local ambient wind speed, direction (if any), temperature and relative humidity with the hand held meteorological instrument. A camcorder will be positioned to record the sampling scene; a pan of the sampling site will also be provided to record details of the location.

12. Outdoors: toll booth (ME12)

Make the measurement on the northbound side of the toll plaza. Access to the toll plaza is from the northbound direction. This is an employee parking lot on the eastside of the plaza. An underground tunnel accesses the southbound lanes. There is an elevator down to the tunnel. Contact the John Leonard, deputy director at the Georgia Department of Transportation, 24 hours prior to sampling (404/463-8766). On-site supervisor at the toll plaza is Robert Smith. Clarice Boone is another on-site contact (404/760-5893).

Sample the breathing zone continuously with a KORE MS 200, Langan T15, DRI HCHO analyzer, and portable PID monitor and collect one set of canister and DNPH samples integrated over the entire 40 minute period. . Collect four SPME samples, one every 10 minutes. Record the ambient temperature and relative humidity.

If time permits before or after the sampling period and sufficient traffic exist, conduct measurement of in-cabin exposure during one pass through the toll plaza. Collect one SPME sample during this sampling period.

13. Trailing high emitters (ME13)

Attempt to trail high emitters in Atlanta locations with higher fractions of high emitters. Protocol will follow ME2 except there will be no limits placed on what streets may be driven. Collect a 5-minute canister sample after a peak exposure encountered during the sampling period. Breath biomarker samples are collected before and within 10 seconds after a similar peak exposure and followed immediately by backup breath canister sample.

DAILY SAMPLING SCHEDULE

The prospective summer 2003 schedule for the Atlanta summer sampling program is summarized in Table 1. The sampling schedule is subject to change due to field conditions encountered. Actual summer and winter schedules will appear in the draft/final reports. In order to stay on project schedule as much as possible, sampling will be conducted on Saturdays in case we encounter unsuitable meteorological conditions on scheduled sampling days. However, this daily schedule doesn't take into consideration the potential for prolonged weather delays. The winter daily sampling schedule for Atlanta will be finalized prior to the 2004 winter study.

Table 1
Prospective Summer 2003 Daily Sampling Schedule for Atlanta

		August/September 2003				
Sunday	**Monday**	**Tuesday**	**Wednesday**	**Thursday**	**Friday**	**Saturday**
24	**25**	**26**	**27**	**28**	**29**	**30**
Arrival/ Setup	7am ME1	7am ME1	7am ME1	7am ME1	7am ME1	10am ME3/ME7
	8am ME13	8am ME13	8am ME13	8am ME13	8am ME13	
	5pm ME11	5pm ME11	5pm ME11	5pm ME11	5pm ME11	
31	**1**	**2**	**3**	**4**	**5**	**6**
	8am ME3/7	8am ME3/7	8am ME3/7	8am ME3/7		
	5pm ME4	5pm ME4	5pm ME4	5pm ME4	5pm ME4	
7	**8**	**9**	**10**	**11**	**12**	**13**
	Packing	Leave				
		for Reno				

APPENDIX C

Exposure Protocol and Study Plan for the Section 211(B) Tier 2 High End Exposure Screening Study of Baseline and Oxygenated Gasoline
Addendum C – Summer/Winter Sampling Plan for Chicago

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October 1, 2003

INTRODUCTION

This sampling plan specifies the details for the field measurement program that will be carried out in Chicago, IL during the summer of 2003 and winter 2004 as part of a screening study of the high-end exposures to baseline and oxygenated gasoline. It specifies the measurement locations for the twelve categories of microenvironments and explains the selections with respect to the objective of capturing the upper-end of the distribution of exposures for each microenvironment. This document is an addendum to the Exposure Protocol and Study Plan, which describes the proposed measurement methods and rationale for their selection. We will endeavor to use the same ME locations during both the winter and summer studies.

Desert Research Institute personnel surveyed potential microenvironments in Chicago on August 14-16, 2002. The objectives of the survey were to ascertain the suitability of sampling locations with respect to access and potential for higher-end exposures, and to determine the variations in air pollutant levels in several of the microenvironments with a portable gas analyzer. We visited the following locations: I-57 and I-94 during the morning commute period, urban canyons in downtown Chicago (particularly under the elevated trains), Tri-State Tollway ((I-294) toll plazas, parking garages in downtown Chicago (Millennium, Monroe St and Grant Park underground garages), service stations (Gas City in Tinley Park), parking lots at United Center (Chicago Bulls and Blackhawks) and Comiskey Park (White Sox), and three centralized vehicle inspection stations (#14, 27 and 28). A RAE Systems Model PGM-7240 (ppbRAE) portable PID monitor and Langan Products Inc. T15 were used to continuously monitor ambient VOC and CO levels, respectively, in several of the microenvironments. For purposes of the survey of microenvironments in Chicago, the PID was used to measure relative variations rather than absolute VOC levels.

The location of the mobile laboratory is a significant logistical consideration in the selection of some of the microenvironments. Accordingly, selecting a base of operations for the mobile laboratory was the initial task during the survey trip. A suitable RV park is located in Tinley Park (Windy City Campground at 18701 South 80th Avenue), which is about 20 miles southeast of Downtown Chicago. Our search for some microenvironments such as service stations, vehicle inspection stations, and congested freeway was focused in this general area.

DESCRIPTIONS OF MICROENVIRONMENTS (ME) AND PROPOSED SAMPLING PROTOCOL

1. In vehicle: commuter rush hour in stop-and-go traffic (ME1)

Begin the run at 0700 in South Chicago near the I-57 and I-94 interchange and drive north on I-94 towards Downtown Chicago. The ten miles to the I-290 (Eisenhower Expressway) and I-94 interchange will take roughly 20 minutes. Use high ventilation conditions (window and vent open, AC on during summer and heater on during winter) during the first half of the run. Continue north on I-94 and turn around about 5 miles north of the I-290 and I-94 interchange. Reenter the I-94 going south and exit the freeway after the second 20 minutes. This stretch of freeway includes a series of overpasses, with the longest about a quarter of a mile. Use low ventilation (windows and vent closed, AC on during summer and heater on during winter) during the second half. Maintain a safe following distance, about one car length (15 feet) per 10 mph speed, closing to within 3 feet during stopped conditions. Use the middle lane and do not follow the same vehicle for more than two minutes. Attempt to get behind at least one high-emitter during each of the two ventilation conditions. If accidents, other hazards, or local conditions change, substitute other, equivalent routes with similar distances and speeds as needed.

Sample in-cabin air at driver's breathing zone continuously with: Langan T15 CO monitor, NDIR CO instrument, and ppbRAE, and collect one set of canister and DNPH samples integrated over the entire sample. Collect four SPME samples, one every 10 minutes. Sample the outside air with the second portable PID during the entire period without compromising the cabin ventilation condition. Monitor and record the van's position (GPS), and in-cabin temperature and relative humidity. A forward facing camcorder will record roadway activities and locations for this and other in-cabin MEs during the sampling run. Relevant data collected by the Illinois EPA include CO and meteorological data at the CTA Building monitoring station at 320 S. Franklin.

2. In vehicle: urban street canyons (ME2)

Make multiple trips during a 40-minute period along a surface-street loop in downtown Chicago bordered by Lake Street, Wabash Avenue, Van Buren Street, and State Street (four right turns). The elevated train covers three sides of this loop. Make the measurements during either the morning commute period from 0700 to 0800 or evening commute period from 1700 to 1800. Use high ventilation conditions (window and vent open, AC on during summer and heater on during winter) during first 20 minutes and low ventilation (windows and vent closed, AC on during summer and heater on during winter) during second 20 minutes. Drive at or near the end of a pack of vehicles at stoplights as much as possible and attempt to get behind at least one high-emitter during each of the two ventilation conditions.

Sample in-cabin air at driver's breathing zone continuously with the Langan T15 CO, NDIR CO, and ppbRAE analyzer and collect one set of canister and DNPH samples integrated over the entire period. Collect four SPME samples, one every 10 minutes. Sample the outside air with the second portable PID monitor during the entire period without compromising the ventilation condition in the cabin. Monitor and record the van's position (GPS), and in-cabin temperature and relative humidity. Note that GPS data is often unavailable or unreliable during this ME as the tall buildings block satellite signals. A forward-facing camcorder will record roadway activities and locations during the run.

3. In vehicle: refueling (ME3)

Sample at the Gas City (80th Avenue just north of I-80) or Speedway (Harlem Avenue just north of I-80) service stations in Tinley Park. Conduct sampling during the peak or near-peak refueling periods for the station as indicated by service station personnel.

After driving to elevate measured fuel tank temperatures, park sampling van at refueling location and sample alternate 10-minute periods under background (parked at pump) and refueling conditions Park the van downwind from the centroid of the pump locations. Sample in-cabin air at driver's breathing zone continuously with a KORE MS 200, Langan T15 CO, NDIR CO, and ppbRAE PID, and collect one set of canister and DNPH samples integrated over the sampling period. Collect two SPME samples, one 10-minute sample during the background sampling period and one 10-minute sample during the refueling period. Sample both the outside and in-cabin air with the two portable PID monitors during the entire sampling period. Monitor and record the outside wind speed, and direction, as well as the sampling location temperature and relative humidity. A camcorder will be positioned to record the sampling scene from outside the van; a pan of the sampling site will also be provided to record details of the location. Van windows are to be down and doors open as appropriate during this ME. A liquid fuel sample will be collected after ME3 measurements (during off-loading of the van fuel tank) for each service station (if more than one is used per city) sampled for this ME.

In vehicle: parking garage (ME4)

Drive within a parking garage. Use high ventilation conditions (window and vent open, AC on during summer and heater on during winter) during the first half and low ventilation (windows and vent closed, AC on during summer and heater on during winter) during the second half. Potential garages include Millennium, Monroe Street, or Grant Park underground parking garages in Downtown Chicago. Millennium and Monroe Street garages use the same access. Millennium is to the left after entering the underground garage complex, and the Monroe Street garage is to the right. Millennium is closer to the downtown office building and has many more parked cars than the Monroe St garage, which is located closer to the Michigan Lake shoreline. Monroe St. garage was mostly empty during the weekday, but may see for use during the weekends. Grant Park garage was nearly full and appears to have high fraction of commuters. Park adjacent to the northbound pay station. We observed 150 to 500 ppbC on PID and 8 to 26 ppm CO at this location during the 1700 to 1800 period.

Sample in-cabin air at driver's breathing zone continuously with a Langan T15 CO, NDIR CO, ppbRAE, and DRI HCHO analyzer and collect one set of canister and DNPH samples integrated over the entire 40 minute period. Collect four SPME samples, one every 10 minutes. Sample both the outside and in-cabin air with the two portable PID monitors during the entire period without compromising the ventilation condition in the cabin. Monitor outside wind speed and direction (if any) and record the in-cabin temperature and relative humidity. A

camcorder will be positioned to record the sampling scene from outside the van; a pan of the sampling site will also be provided to record details of the location.

5. In vehicle: toll plaza (ME5)

Sample during the morning commute period 0700-0800 on tollways with high traffic volume with higher fraction of time spent at toll plazas (e.g., exit on ramps in both directions within short distances before and after the toll plaza). Potential plazas include 82nd Street (southbound)/83rd Street (northbound) and Cermak Road (all traffic) on the Tri-State Tollway (I-294) and the York Road (all traffic) on the East-West Tollway (I-88).

Sample in-cabin air at driver's breathing zone continuously with a Langan T15 CO, NDIR CO and ppbRAE PID analyzer and collect one set of canister and DNPH samples integrated over the entire 40 minute period. Collect four SPME samples, one every 10 minutes. Sample the outside air with a second portable PID monitor during the entire period without compromising the ventilation condition in the cabin. Monitor and record the van's position (GPS), and sampling point temperature and relative humidity.

6. In vehicle: tunnel (ME6)

The tunnel in Chicago is a covered roadway with no mechanical ventilation and very limited opportunity for natural ventilation. The route is from West Congress Parkway (Eisenhower Freeway) eastbound, enter Lower Wacker Drive via the off ramp from Congress parkway. Begin sampling anytime after entering the underground portion of the roadway. Proceed north on Lower Wacker Drive; immediately after Lower Wacker Drive turns east, use Orleans Street to turn around and proceed back south on Lower Wacker Drive. Just before exiting Lower Wacker Drive at the south end of the street, there is a turn-around through the center divider that allows you to return northbound again.

Make several trips though the Lower Wacker Drive route for 40 minutes during peak traffic periods. Use high ventilation conditions (window and vent open, AC on during summer and heater on during winter) during first 20 minutes and low ventilation (windows and vent closed, AC on during summer and heater on during winter) during second 20 minutes. Sample in-cabin air at driver's breathing zone continuously with a Langan T15 CO, NDIR CO, and ppbRAE, and collect one set of canister and DNPH samples integrated over the entire period. Collect a 5-minute canister sample during a peak concentration period. Collect four SPME samples, one every 10 minutes. Biomarker samples (breath) will be collected from the technician, who will be isolated from further exposure before performing this task. Sample the outside and in-cabin air with the two portable PID monitors during the entire hour without compromising the ventilation condition in the cabin. Monitor and record the van's position (GPS), and in-cabin temperature and relative humidity. Note that the GPS data will be unavailable for the period the van is inside the tunnel as the tunnel blocks the satellite signals. A front-facing camcorder will record the roadway activities and provide a stopped pan of the sampling site location.

7. Outdoor: refueling vehicle (ME7)

Sample at the Gas City (80th Avenue just north of I-80) or Speedway (Harlem Avenue just north of I-80) service stations in Tinley Park. Conduct sampling during the peak or near-peak refueling periods for the station as indicated by service station personnel.

Park the van downwind from the centroid of the pump locations after driving it sufficiently to elevate measured fuel tank temperatures. Refueling sampling will be conducted during periods with local wind speed below 5 mph. With sampling inlets in the breathing zone, refuel the vehicle over a 1 to 2 minute active refueling interval within the second 10-minute sampling period. During refueling, maintain manual control of the nozzle and stand downwind of the vehicle fuel tank inlet, spilling a few drops of fuel after removing the nozzle from the fuel tank. Sample the breathing zone continuously with a KORE MS 200, NDIR CO, and ppbRAE and collect one set of canister and DNPH samples integrated over the entire 20-minute period. Collect a 5-minute canister that includes the active refueling period. Collect breath biomarker samples, including breath pre-refueling and immediately after refueling (10 second) samples and a backup breath sample immediately after the second breath sample. Collect two SPME (background and refueling) samples during the initial background

and final refueling periods. Record the ambient temperature and relative humidity. A camcorder will be positioned to record the sampling scene from outside the van; a pan of the sampling site will also be provided to record details of the location. Local wind speed, direction, temperature and humidity will be collected with the hand held meteorological monitor. A liquid fuel sample will be collected after ME7 measurements (during off-loading of the van fuel tank) for each service station (if more than one is used per city) sampled for this ME.

8. Outdoor: sidewalk near high-density traffic (ME8)

Conduct sidewalk sampling in downtown Chicago along the city block bordered by Monroe Street, Wabash Avenue, Adams Street, and State Street. Sampling is conducted during the morning periods and at noon.

Sample the breathing zone continuously with Langan T15 CO, and ppbRAE portable PID monitor and collect one set of canister and DNPH samples integrated over the entire 40 minute period. Collect four SPME samples, one every 10 minutes. Record the local wind speed, direction, ambient temperature and relative humidity with the hand held meteorological device.

9. Outdoor: bus stop (ME9)

Combined with ME8.

10. Outdoor: stadium parking lot (ME10)

Sample at the end of a Chicago White Sox baseball game at Comiskey Park during the summer and after a Chicago Bulls or Blackhawks game at the United Center. Because the atmosphere is more stable in the evening, night games are preferable to day games.

Attempt to determine the end of the game time by listening to the radio to determine the progress of the game. Park the van near the exit of the parking lot where vehicles will queue up as they exit, down wind of the exhaust. Sample the breathing zone continuously with a KORE MS 200, Langan T15 CO, DRI HCHO analyzer, and portable PID monitor and collect one set of canister and DNPH samples integrated over the entire 40 minute period. Collect four SPME samples one every 10 minutes. A camcorder will be positioned to record the sampling scene from the cart outside the van; a pan of the sampling site will record details of the location.

11. Underground parking garage (ME11)

Sample underground parking garage starting about 5:00 p.m. when office workers leave the complex (cold start emissions). Sample at exit queue and ramps. Measure temperature, humidity and ventilation velocities. Potential garages include Millennium, Monroe Street, or Grant Park underground parking garages in Downtown Chicago.

Sample the breathing zone continuously with a KORE MS 200, Langan T15, DRI HCHO analyzer, and portable PID monitor and collect one set of canister and DNPH samples integrated over the entire 40 minute period. Collect a 5-minute canister that includes an exposure peak encountered during the sampling period. Collect biomarker samples with breath samples taken before and immediately after (10-seconds) a peak exposure; a backup breath sample will be taken immediately after this second sample. Collect four SPME samples, one every 10 minutes. Record the local ambient wind speed, direction (if any), temperature and relative humidity with the hand held meteorological instrument. A camcorder will be positioned to record the sampling scene; a pan of the sampling site will also be provided to record details of the location.

12. Outdoors: toll booth (ME12)

Two possible locations for this microenvironment are tollbooths on tollways or one of the centralize vehicle inspection stations. The vehicle inspection station at 3824 159th Place is reasonably close to the RV Park and has good access. Sampling at the toll plaza would be conducted behind the tollbooth similar to arrangement in Atlanta. For the vehicle inspection station, we would sample near the dynamometers. We will need to obtain permission from the Illinois EPA to conduct sampling at the inspection station.

Sample the breathing zone continuously with a KORE MS 200, Langan T15, and portable PID monitor and collect one set of canister and DNPH samples integrated over the entire 40 minute period. Collect four SPME samples, one every 10 minutes. Record the ambient temperature and relative humidity. If time permits before or after the sampling period and sufficient traffic exist, conduct measurement of in-cabin exposure during one pass through the toll plaza. Collect one SPME sample during this sampling period.

13. Trailing high emitters (ME12)

Since we'll be sampling the Wacker Drive 'tunnel' (ME6), there are no plans to sample ME13 in Chicago.

DAILY SAMPLING SCHEDULE

The prospective daily schedule for the Summer 2003 Chicago sampling program is summarized in Table 1. The sampling schedule is subject to change due to field conditions encountered. Actual summer and winter schedules will appear in the draft/final reports. In order to stay on project schedule as much as possible, sampling will be conducted on Saturdays in case we encounter unsuitable meteorological conditions on scheduled sampling days. However, this daily schedule doesn't take into consideration the potential for prolonged weather delays. The winter daily sampling schedule for Chicago will be finalized prior to the 2004 winter study.

Table 1

Prospective Summer 2003 Daily Sampling Schedule for Atlanta

		July/August 2003				
Sunday	**Monday**	**Tuesday**	**Wednesday**	**Thursday**	**Friday**	**Saturday**
				31 **Leave Reno**	**1**	**2**
3	**4**	**5**	**6**	**7**	**8**	**9**
Arrival/ Setup	Setup	Final preparations	7am ME1	7am ME1	7am ME1	10am ME3, ME7
	Calibrate		8am ME13	12/1pm ME3/7	8am ME13	
	Familiarize				5pm ME4	
		5pm ME4	5pm ME4	5pm ME4	10 pm ME10	10 pm ME10
10	**11**	**12**	**13**	**14**	**15**	**16**
	7am ME1	7am ME1	7 am ME8/9	7 am ME5	7am ME5	10am ME3, ME7
	8am ME13	8am ME13		8am ME2	8am ME2	
			12pm ME8/9	12pm ME3/7		
	5pm ME11	5pm ME11	5pm ME8/9	5pm ME11	5pm ME11	
17	**18**	**19**	**20**	**21**	**22**	**23**
	7am ME5	7am ME12	7am ME12		Leave for	Arrive
	8am ME2	8am ME3/7		Packing	Atlanta	Atlanta
			5pm ME4			
	5pm ME11	5pm ME12	10pm ME10			
24	**25**	**26**	**27**	**28**	**29**	**30**

APPENDIX D

Example of a Diary Page

P027 API ME Diary Page
(Not for Refueling)

Circle One: **ME1** In-Cabin Freeway; **ME2** In-Cabin Urban Canyon; **ME4** In-Cabin Under-Ground Garage; **ME5** In-Cabin Toll Plaza; **ME6** In-Cabin Tunnel; **ME8** Outdoor Sidewalk; **ME9** Outdoor Bus-Stop; **ME10** Outdoor Surface Parking; **ME11** Outdoor Under-Ground Garage; **ME12** Outdoor Toll Plaza; **ME13** Following Hi-Emitter.

Date:_____Start Time:_____Location:_____

Any Possible Pre-Exposure by Breath Technician?_____

Weather Description: _____

First 10 min: SPME 1. PMI:

Time	Traffic Level	Windspeed Direction	Unusual Events?	Vent
	High Med Low			HI LO Outside

Second 10 min: SPME 2. PMI:

Time	Traffic Level	Windspeed Direction	Unusual Events?	Vent
	High Med Low			HI LO Outside

Third 10 min: SPME 3. PMI:

Time	Traffic Level	Windspeed Direction	Unusual Events?	Vent
	High Med Low			HI LO Outside

Fourth 10 min: SPME 4. PMI:

Time	Traffic Level	Windspeed Direction	Unusual Events?	Vent
	High Med Low			HI LO Outside

Notes:

P027 API ME Diary Page

(Refueling)

Circle One: ME3 In-Cabin Refueling ME7 Outdoor Self-Serve Refueling

Date:_____Start Time:_____Location:_____

Any Possible Pre-Exposure by Breath Technician?_____

Station Description: Total # of Pumps:_____ Van at Pump #?_____

Draw sketch of station with location of van (North is up).

Weather Description: _____

First 10 min: SPME 1. PMI:

Time	# Cars in Station	Windspeed Direction	Unusual Events?	Vent
				HI LO Outside

Second: SPME 2 PMI:

Time	# Cars in Station	Windspeed Direction	Unusual Events?	Vent
				HI LO Outside

Refueling: Time: Start:_____Stop: _____
Gallons:_____# Drops (diameters) spilled:_____

Notes:

APPENDIX E

Quality Assurance

APPENDIX E

1.0 Quality Assurance

The Desert Research Institute maintains a very complete quality assurance and quality control program that is detailed in this section. This section addresses all the required components from the RFP. These include:

a. Daily calibration. All instruments to be used in this study have calibration checks run each day. These checks will confirm both response factors and retention times for both continuous and time-integrated instruments.

b. Daily instrument blank. An appropriate blank will be run daily for each instrument. Generally this is run after the calibration check and before any samples are analyzed. This confirms that there is no carryover from the calibration check as well as confirming the blank or zero level of the instrument.

c. Duplicate analysis for every 10 samples. Our protocols generally call for 10% replicate analyses. These are an important part of our QA/QC program since these are applied to determine replicate precision that allows us to calculate sample uncertainty.

d. Control samples. DRI labs analyze a variety of control samples for QA/QC purposes. These include calibration, replicate, collocated and blind QA samples.

e. Recovery tests for selected analytes. For DNPH analyses internal standards are also added. Recovery for NMHC samples in internally determined by calibration standards.

f. Determine and report minimum trapping efficiency. For solid adsorbent samples, the backup traps are used for approximately 5 % of samples to confirm that no quantifiable levels of compounds are getting through the first trap.

Every measurement consists of four attributes: a value, a precision, an accuracy, and a validity (e.g., Hidy, 1985). The measurement methods described in the previous section are used to obtain the value. Quality assurance is the complementary part of the measurement process which provides the precision, accuracy, and validity estimates and guarantees that these attributes are within acceptable limits.

Quality assurance for the project is the joint responsibility of the laboratory manager and the quality assurance manager. The QA manager must ensure that the program design contains adequate quality control procedures and adequate external checks to assure that the data obtained will be adequate for their intended purposes. It is the responsibility of the laboratory manager to monitor the quality assurance activities during the project and to make certain that problems are rapidly identified and solved.

The quality assurance program includes two types of activities: quality control (QC), and quality assurance (QA). The QC activities are on-going activities of measurement and data processing personnel. QC activities consist of written standard operating procedures to be followed during sample collection, sample analysis, and data processing. These procedures define schedules for periodic calibrations and performance tests (including blank and replicate analyses). They specify pre-defined tolerances that are not to be exceeded by performance tests and the actions to be taken when they are exceeded. The QC activities also include equipment maintenance and acceptance testing, and operator training, supervision, and support.

Quality assurance is a project management responsibility that integrates quality control, quality auditing, measurement method validation, and sample validation into the measurement process. Quality auditing is an external function performed by personnel who are not involved in normal operations An independent auditor will be contracted by API to conduct a quality audit during a one week period in a single city. The purpose of quality

audits is to determine whether the QC procedures are adequate and are being followed and whether the tolerances for accuracy and precision are being achieved in practice. The quality auditing function consists of two components: systems audits and performance audits. Systems audits include review of the operational and QC procedures to assess whether they are adequate to assure valid data that meet the specified levels of accuracy and precision. All phases of the measurement and data processing activities are examined during the systems audit to determine whether the procedures are being followed and the operating personnel are properly trained. Performance audits establish whether the predetermined specifications for accuracy are being achieved in practice. For measurements, the performance audit involves challenging the measurement/analysis system with a known standard sample that is traceable to a primary standard. Performance audits of data processing involve independent processing of raw data and comparing the results with reports generated by routine data processing.

1.1 Quality Assurance Objectives

The objectives of our quality assurance measures are:

1. To maintain a continuing assessment of the quality of data generated by analysts working in the laboratory.
2. To provide a permanent record of instrument performance as a basis for validating data and projecting repairs and replacement needs.
3. To ensure sample integrity.
4. To improve record keeping.
5. To produce analytical results that can withstand scientific and legal scrutiny.

2.0 Organization and Responsibility

The general structure of the organization of the Desert Research Institute, Division of Atmospheric Sciences (DAS), Organic Analytical Laboratory is indicated on the Figure 2-2. For an effective quality assurance program, all individuals must take personal responsibility for monitoring, recording, and reporting all measures that relate to the quality assurance program. Specific responsibilities include the following:

Organizational Structure of OAL

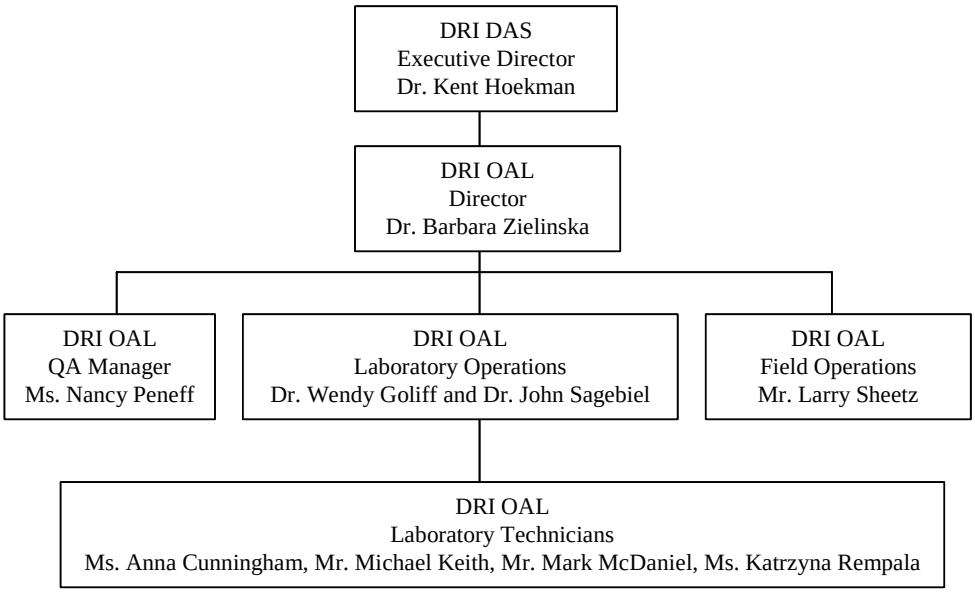

Figure 2-2. Organization of the Desert Research Institute – Division of Atmospheric Sciences, Organic Analytical Laboratory.

DAS Director (Dr. S. Kent Hoekman): Overall management and supervision of the Division of Atmospheric Sciences.

QA Manger (Ms. Nancy Peneff): Responsible for internal audits and checks of laboratory QA program, operations, and procedures. Requests performance audits, and reviews procedures and protocols. Reviews data reduction and handling procedures.

Laboratory Director (Dr. Barbara Zielinska): Responsible for direct supervision of laboratory and field operations. Supervises QA program at the operational level. Approves analytical and sampling methods, and practices. Reviews and approves all SOPs. Reviews and approves sampling media and sampling equipment certification procedures. Reviews and approves all laboratory-generated data. Reviews and ensures continued calibration of instruments.

Laboratory Operations (Dr. John Sagebiel and Dr. Wendy Goliff): Responsible for Laboratory Information Management System (LIMS), data management software and operations. Reviews and approves data. Under general supervision from Laboratory Manager, reviews laboratory practices and corrects as needed. Performs general maintenance on analytical instruments and LIMS computers. Performs Level I validation of data and participates in general review of all laboratory-generated data. Performs general maintenance on laboratory analytical instruments.

Field Operations (Mr. Larry Sheetz): Responsible for assembly, cleaning, maintenance, and certification of all sampling equipment. Maintains records of use of each sampler, including any modifications made. Certifies proper operation of samplers including leak checks, and calibration of flow controlling equipment. Orders certification of flow controllers as needed. Orders certification of cleanliness of sampling equipment as needed. Maintains records of sampler maintenance and cleaning. Responsible for training of field personnel in proper operation, record keeping and maintenance of sampling equipment. Performs general maintenance on laboratory analytical instruments.

Laboratory Technicians (Mr. Michael Keith and Mark McDaniel, Mrs. Anna Cunningham, Ms. Katarzyna Rempala). Perform calibration of analytical instruments. Perform regular calibration checks and recalibrate if calibration does not meet specified parameters. Log in samples in project logbooks upon receipt. Properly store samples in possession. Perform analysis of samples. Perform analysis of media, canisters, and sampling equipment to ensure cleanliness. Responsible for record keeping. Participate in internal and external audits and checks of methodology. Perform other tasks as directed by Laboratory Operations, Field Operations, Laboratory Management, Laboratory QA or Center Director. Performs general maintenance on laboratory analytical instruments.

3.0 Sample Custody

For our quality assurance plan, a sample is considered in custody when it is received by the DRI-DAS receiving department from an official package courier. At this time it is logged into the general receiving department's logbook and the Organic Analytical Laboratory is notified of the package's arrival. A representative of the laboratory signs for the package and returns with it to the laboratory room, where he opens it. The samples are logged into the Organic Analytical Laboratory's LIMS system in lieu of updating the chain-of-custody form (if supplied), and the samples are stored appropriately for the sample type. At this time any unusual situations (damaged shipping container, evidence of damage and/or tampering, etc.) are brought to the attention of the laboratory manager. If necessary, a review will be initiated to determine if the damage compromised the integrity and/or quality of the sample.

Samples are stored in the Organic Analytical Laboratory, inside the DRI Northern Nevada Science Center (2215 Raggio Parkway, Reno, NV). All condensed phase samples and sample extracts are stored in the freezers. The rooms are locked when not in use and the building has limited access (i.e., it is locked from 1730 to 0730 weekdays and all weekend to ensure access only to authorized personnel).

When a sample is analyzed, its identification number (sample number) is recorded both in the written logbook for each instrument and in the LIMS file created for that analysis. The sample number serves as a tracking number, as does the LIMS file itself. Canisters will not be cleaned until each sample has passed initial validation.

Condensed phase samples and sample extracts will be maintained for at least one year following the completion of the project. Samples will be stored in refrigerators or freezers.

4.0 Laboratory Records

Several forms of laboratory records are routinely maintained. Written records include receiving logbooks, shipping log books, chain-of-custody forms, project log books, instrument log books, instrument service logbooks, calibration records which include a calibration standard logbook and graphs of response factors vs. time, a canister cleaning logbook, and sampler maintenance and cleaning logbooks. Computerized records include method files, calibration files, raw data files, processed data files, and combined data files.

Written records are maintained in the appropriate location in the laboratory. Written records are always maintained in non-erasable ink so that any alteration is easily noted. Project logbooks record sample arrival and other information about the sample. Instrument logbooks record each sample run, including all pertinent information. All calibration runs are also recorded here. Other calibration records include the calibration logbook where all standard solutions made in the laboratory are logged, a graph of all calibration checks, and the computerized calibration files. Service logbooks show services and/or modifications done to the instruments. The canister cleaning logbook records each canister number, the project the canister was used for, date of last cleaning, and certification information.

Computerized records are maintained on a central computer (the LIMS file server). Our data collection system includes a history record that maintains lists of files created or modified and the name of the person creating or modifying the file. Each sample has an original report printed at the time the sample run is completed and this report indicates which method and calibration file are used, including the last modification date of the file. Backups of computerized records, including but not limited to removable media (floppy disks) and tapes are stored in the LIMS manager's office as an off-site storage area.

5.0 Standard Operating Procedures

Standard operating procedures (SOPs) codify the actions taken to implement a measurement process over a specified time period. State-of-the-art scientific information is incorporated into the SOP with each revision. SOPs include the following elements:

1. A brief summary of the measurement method, its principles of operation, its expected accuracy and precision, and the assumptions which must be met for it to be valid.
2. A list of materials, equipment, reagents and suppliers. Specifications are given for each expendable item and its storage location.
3. A general traceability path, the designation of primary standards or reference materials, tolerances for transfer standards, and a schedule for transfer standard verification.
4. Start-up, routine, and shutdown operating procedures and an abbreviated checklist.
5. Copies of data forms with examples of filled out forms.
6. Routine maintenance schedules, maintenance procedures, and troubleshooting tips.
7. Internal calibration and performance testing procedures and schedules.
8. External performance auditing schedules.
9. References to relevant literature and related standard operating procedures.

The standard operating procedures for all analyses will be provided upon request.

5.1 Sampling Media Preparation and Certification

For commercial cartridges, e.g. Waters Si-DNPH, DRI shall analyze 5% of the purchase initially to ascertain the blank variability. Another 5% will be analyzed if the initial data show that the blank variability is marginally acceptable (at or slightly higher than 1/3 of the desired lower quantifiable limits (LQL)). This is necessary because, unless cartridges are prepared in-house, there is no other indication of the quality of the product, such as how pure the reagent or the blank cartridges are. In carbonyl measurement, the blank variability is the single most important factor in determining the lower quantifiable limit of the measurement. The other factors, such as flow rate and analytical variability are secondary in importance.

Tenax-TA solid adsorbent is cleaned by Soxhlet extraction with hexane/acetone mixture (4/1 v/v) overnight, and dried in a vacuum oven at ~80 °C. The dry Tenax is packed into Pyrex glass tubes (4 mm i.d. x 15 cm long, each tube containing 0.2 g of Tenax) and thermally conditioned for four hours by heating in an oven at 300 °C under nitrogen purge (25 ml/min nitrogen flow). Approximately 10% of the precleaned Tenax cartridges are tested by GC/FID for purity prior to sampling. If Carbotrab, Carboxen and/or Carbosieve are used, the amount of Tenax is reduced as necessary. After cleaning, the Tenax cartridges are capped tightly using clean Swagelok caps (brass) with graphite/vespel ferrules, placed in metal containers with activated charcoal on the bottom, and kept in a clean environment at room temperature until use.

5.2 Analytical Systems

Prior to analysis all analytical systems (i.e., GC/ECD/FID, HPLC, GC/MS, and GC/IRD/MSD) are checked for purity and are certified clean (less than 0.1 ppbv of targeted compound). Quality control in the laboratory includes instrument calibration for each batch of samples analyzed, replicates of standards, and reanalysis of approximately 10% of the samples for estimation of analytical precision, which historically has been less than 6%. In past programs, field blanks were at the 0.5-1 ppb levels, based on the air volume of the samples. Coefficients of variation (CV) calculated from observed differences between duplicate sample pairs were under 10%. The data quality in this program is likely to be similar.

5.3 Standards and Materials

Primary reference standards are traceable to an NIST Standard Reference Material (SRM). For canister hydrocarbon speciation by GC/FID, we use NIST SRM 1805, which consists of 254 ppb of benzene in nitrogen. In addition, NIST SRM 2764 (245 ppb of propane in N2), is used for calibrating the light hydrocarbon analytical system. For halogenated compound measurements, an NIST-traceable standard mixture of 39 compounds is purchased from Scott Specialty Gases and diluted by DRI scientists for calibration. For VOC measurements by GC/MS system, 74 compound mixture in low ppb level (Air Environmental, Inc., Denver, CO), traceable to the NIST SRM 1805, is used for calibration. For PAH measurements NIST SRM 1647, with the addition of other compounds not present in the mixture, is used.

Gas cylinders of helium, nitrogen, hydrogen and ultra zero air (all UHP grade) — from the best sources available — are used for the GC/FID, GC/MS and GC/IRD/MSD. From a single analysis, the GC/IRD/MSD system gives three dimensions of data for positive compound identification: retention times, infrared spectra, and mass spectra. Identification of individual compounds is based upon matching corresponding data for authentic samples. The current inventory of reference samples at DRI's Organic Analytical Laboratory consists of over 250 single- and multi-component reference samples, and includes most of the compounds of interest in this project.

5.4 Calibrations

The GC/FID, HPLC, GC/MS and GC/IRD/MSD systems are calibrated initially by multipoint calibration (i.e., three levels plus humid zero air), and regularly checked by a one-point calibration, using appropriate NIST SRM or other standard. The day-to-day reproducibility of ±10% is acceptable for either standard. Control charts are used for assessing analytical system performance.

Samples that fall outside the calibration range are diluted until bracketed by the calibration curve. Instrument responses to calibration standards for each parameter are analyzed using a least squares linear regression. The calibration must generate a correlation co-efficient (R2) of 0.99 to be acceptable.

During the course of analysis, calibration standards are routinely analyzed to ensure that the instrument response has not changed. The criterion of 10% of expected response is used by the analyst to determine whether the instrument must be recalibrated.
Retention time windows for each analyte will be established prior to analysis and re-established continuously throughout the course of the analytical period.

5.5 Relative Accuracy and Precision of Sampling and Analysis

Accuracy involves the closeness of a measurement to a reference value and reflects elements of both bias and precision. Percent relative accuracy is calculated:

$$\% \text{ Relative Accuracy} = (X - Y)/X \times 100$$

where: Y = concentration of the targeted compound, as determined by the analytical instrument,

and

X = concentration of the targeted compound in the NIST standard.

If the relative accuracy does not fall within the ± 10% range, the instrument is recalibrated.

Precision is a measure of the repeatability of the results. The overall precision of sampling and analysis is determined by the analysis of collocated or equivalent samples. These precision tests will depend upon available resources, and we will develop the protocol in consultation with the project officer.

5.6 Internal Quality Control Checks

Our entire quality assurance program is organized around providing continuing internal quality control checks. This begins with proper training of the laboratory technicians so that they can identify problems with analyses and point these out to the Laboratory Operations Manager or Laboratory Manager for resolution. Other internal quality control checks include our blank checks, certification of sampling media, and our data analysis system. The ability of our data analysis system to merge multiple samples into a single database allows for rapid and accurate cross-comparisons among the samples.

Other internal quality control checks consist of those ordered by the QA officer and required by our standard operations. Standard operation quality control checks include the calibration procedures, the regular calibration checks, and the duplicate analyses. Duplicate analyses are essential for determining precision of analyses and give us information about the stability of the system over time. The QA officer may, at his discretion, order performance checks at any time. These may include verification of response factors, blank checks of sampling media, and participation in interlaboratory comparisons (see below).

5.7 Preventative Maintenance

All of our equipment is on a preventative maintenance schedule. We have found that the most important preventative maintenance tool is our systematic performance checks. When an instrument is not performing up to standards, we investigate and in this way find most problems before they become significant.

All of our major equipment (the GC/MS:s and HPLC) is on a service contract with the original manufacturer (Hewlett-Packard and Varian). This contract calls for biannual routine service by a Hewlett-Packard or Varian service technician, and immediate response to any service call. Our contract specifically states that any problem will be corrected within 48 hours of notification of the manufacturer.

Several laboratory personnel have extensive experience working with all the major laboratory equipment and DRI has extensive support facilities (electronics and machine shops, QA lab with standard reference materials, etc.). These personnel and facilities ensure the continued smooth operation of all analytical instruments in the Organic Analytical Laboratory.

5.8 Corrective Action

A need for corrective action can be triggered by a number of activities, including the assessments of precision, accuracy, and completeness listed above. The most important corrective action trigger is the response factor chart mentioned above. This is the graph of our daily response factor check and it requires a full multi-point recalibration if the response factor differs by more than ±10% from the original calibration. Other triggers can include an instrument not meeting basic performance criteria, observations by any laboratory personnel of unusual performance by an instrument, or error messages displayed by the controlling computers or the LIMS system.

Once a need for corrective action has been identified, two basic steps follow: identification of the problem, and correction of the problem. Exactly what action is taken depends on what is determined to be wrong. Actions can include replacement of a defective part, correction of an incorrect flow, resetting or adjusting of tuning parameters, and contacting manufacturer service personnel for corrective action through our service contract.

5.9 Laboratory Data Processing

The goal of our data processing is to provide accurate data combined into a single database for each analysis type and to include calculations of replicate precision, mean blank values, and blank variability, and blank-corrected concentrations and standard errors for each reported value based on combined volume (for carbonyl and semi-volatile compounds), replicate (for hydrocarbon, SVOC and carbonyl data), and blank uncertainties (for carbonyl and SVOC data only; substitute minimum detection limits for hydrocarbon data). The uncertainty analysis allows us to present our data with absolute uncertainties associated with each number in the report.

5.10 Laboratory Data Management

The primary functions of laboratory data management are to have data stored in a consistent fashion that is both secure and available. To serve this need we have established a file server system that provides a central storage area for all laboratory and field data. The databases have defined structures that are maintained in one area so that all field names will be consistent, which permits easy merging and comparison of the various databases. Locating all data on a central file server prevents the problems associated with having multiple copies of the same data set, and allows the individuals charged with data processing, security, validation, and QA access to the same database.

5.11 External Quality Assurance

The DRI Organic Analytical Laboratory (OAL) participated in the International Hydrocarbon Intercomparison Experiment, organized by National Center for Atmospheric Research (NCAR). The results of Tasks I, II, and III of this intercomparison have been published (Apel et al., 1994; 1999). The first task involved the circulation of a two-component hydrocarbon mixture of known composition and unknown concentration, prepared by NIST. The DRI values were within the acceptable range of 5% of the nominal values provided by NIST. In task II the participating laboratories were asked to identify and quantify 16 components present, in the ppb range, in a mixture prepared by NIST. The agreement between the DRI values and the NCAR values, as well as with nominal values provided by NIST, were within acceptable ranges (15%). Task III was more complex - it involved the analysis of 60 commonly observed hydrocarbons in low ppbv concentrations in a mixture prepared and analyzed by Scott-Marrin, Inc., NCAR and U.S. EPA laboratory. The next tasks, IV and V, which were carried out in 1996 -1997, involved the analysis of ambient air samples in the ppbv and pptv concentration ranges, respectively. The DRI has successfully completed these tasks — the agreement between the DRI values and the NCAR values were within acceptable ranges (10%).

In the summers of 1995 and 1996 the DRI OAL participated in the NARSTO-Northeast hydrocarbon intercomparison study, involving the analysis of two ambient air samples by participating laboratories. Participants included Biospheric Research Corporation (BRC), State University of New York at Albany (SUNYA), EPA Region I, DRI, and 8 of the PAMS networks in the northeastern U.S. The DRI laboratory performed the best in comparison with all other participants (Fujita et al., 1997). In the summer of 1997, the DRI OAL participated in the SCOS97-NARSTO performance audit and laboratory comparisons involving speciated non-methane hydrocarbons (NMHC), carbonyl compounds, halogenated compounds and biogenic hydrocarbons (Fujita et al., 2003).

During the last six years, the DRI laboratory participated in non-methane hydrocarbon laboratory performance audits, organized by the Quality Assurance Section, Monitoring and Laboratory Division, CARB. The last intercomparison studies, organized in 1999-2002, involved the analysis of ambient air samples by California district laboratories and the DRI laboratory.

6.0 REFERENCES

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Appendix B

Sampling and Analysis Methods

Appendix B. Sampling and Analysis Methods

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1.1 Time-Integrated Air Sample Collection and Analysis

Time-integrated monitoring methods are used for quantification of the responses of continuous surrogate instruments. The methods include canister sampling for VOC (BTEX, 1,3-butadiene, MTBE), solid adsorbent sampling (for ethanol) and DNPH-coated Sep Pak cartridges sampling for carbonyl compounds. The DRI Organic Analytical Laboratory (OAL) routinely uses these methods and DRI standard operating procedures (SOPs) for sampling and analysis are available upon request. Five to forty minute samples are collected depending on the ME sampled.

Sampling. The DRI custom built sampler used for this study can sample simultaneously a canister, solid adsorbent cartridges (two in parallel), and a DNPH-impregnated Sep-Pac cartridge. The sampler is compact and can be set-up in a vehicle cabin and run from a battery. Prior to use, the sampler is checked for cleanliness by sampling zero air. If the concentration of any targeted compound exceeds 0.1 ppb, the sampler is thoroughly cleaned and re-tested. As noted earlier, a remote switch is installed to allow cabin on/off control of the sampler, no longer requiring access through the van tailgate. The protocol requires that the van engine be off during changes of sampler media.

The canister sampler uses a differential pressure flow controller to supply air to the sampler canister and a calibrated mass flow controller to check the flow rate. Since the actual flow rate is less important than that the flow rate remain constant, additional quality assurance checks on the flow controllers is not necessary. For the 5-minute canister samples an additional battery-operated sampler is used that allows flows up to 3 L/minute to pressurize the 3 L canister.

Both the solid adsorbent and DNPH samplers use a common vacuum pump controlled by mass flow controllers. These controllers are calibrated at the start of the field program by using a primary flow device (e.g. Gillibrator) and then periodically checked in the field to confirm that the flow rates are accurate.

Canister samples. Prior to sampling, the canisters are cleaned by repeated evacuation and pressurization with humidified zero air, as described in the EPA document "Technical Assistance Document for Sampling and Analysis of Ozone Precursors" (October 1991, EPA/600-8-91/215). Six sequential cycles of evacuation to ~ 0.5 torr absolute pressure, followed by pressurization with ultra-high-purity (UHP) humid zero air to ~ 20 psig are used. The differences between the DRI procedure and the EPA recommended method are that the canisters are heated in the DRI method to 140°C during the vacuum cycle and that more cycles of pressure and vacuum are used. According to our experience and that of others (Rasmussen, 1992), heating is essential to achieve the desired canister cleanliness. Also, the canisters are kept longer under vacuum cycles, about one hour in the DRI method, as opposed to half an hour in the EPA method. At the end of the cleaning procedure, one canister out of 12 in a batch is filled with humidified UHP zero air and analyzed by the gas chromatograph/flame ionization detection (GC/FID) method. The canisters are considered clean if the total non-methane organic compound (NMOC) concentration is less than 20 ppbC. The actual concentrations of blank-check canisters are typically below 10 ppbC.

Canister samples are analyzed promptly upon receipt of samples from the field, using GC/FID according to guidance provided by the EPA Method TO-15. The GC/FID response is calibrated in ppbC, using NIST Standard Reference Materials (SRM) 1805 (254 ppb of benzene in nitrogen). Based on the carbon response of the FID to hydrocarbons, the response factors determined from these calibration standards are used to convert area counts into concentration units (ppbC) for every peak in the chromatogram. Identification of individual compounds in an air sample is based on the comparison of linear retention indices (RI) with those RI values of authentic standard compounds. A DB-1 column (60 m long 0.32 mm i.d., 1 µm film thickness) is used for these analyses. Breath canisters are quantified for CO2, MTBE, and BTEX by the method of Pleil & Lindstrom using GC/MS.

Blank checks are performed once daily, while performance standards are executed three times per week. Our analysis plan and data processing standards call for the replicate analysis of approximately 10% of the samples. For canisters the replicate analysis is conducted at least 24 hours after the initial analysis to allow for re-equilibration of the compounds within the canister. The replicate analyses are flagged in our database and the programs we have for data processing extract these replicates and determine a replicate precision. Replicate analysis is important because it provides us with a continuous check on all aspects of each analysis, and indicates problems with the analysis before they become significant. A portion (5%) of the canisters is also analyzed by a second independent laboratory (Battelle-Columbus).

Solid adsorbent samples. Ethanol is quantified from solid adsorbent cartridges as well as canister methods. Although MTBE is stable in SUMMA canisters and can be quantified with high precision and accuracy, ethanol is relatively unstable and the replicate analyses of canister samples show a high degree of scatter (Goliff and Zielinska, 2001). Thus, the solid adsorbent samples are necessary for quantification of ethanol. For sample collection we use multibed adsorbent cartridges consisting of Tenax-TA, Carbotrap (or Carboxen) and Carbosieve (Shire et al., 1996; Tsai and Weisel. 2000; Vayghani et al., 1999). Prior to use the Tenax-TA solid adsorbent is cleaned by Soxhlet extraction with hexane/acetone (4/1 v/v) overnight and dried in a vacuum oven at ~ 80 °C. The dry Tenax is packed into Pyrex glass tubes together with Carbotrap and Carbosieve and thermally conditioned for four hours in an oven at 300 °C under nitrogen purge. Approximately 10% of the precleaned tubes are tested by GC/FID prior to sampling. After cleaning, the tubes are sealed with clean Swagelok caps (brass) with graphite/Vespel ferrules, placed in metal containers with activated charcoal on the bottom, and kept in a clean environment at room temperature until use.

After sampling at monitored flows of 200-300 ml/minute, tube samples are analyzed by a thermal desorption-cryogenic preconcentration method, followed by high-resolution GC/MS. A Chrompack Thermal Desorption-Cold Trap Injection (TCT) unit is used for sample desorption and cryogenic preconcentration. The compounds of interest are quantified by MS, using the response factors of authentic standards, prepared at five different concentrations with a static dilution bulb.

Carbonyl compounds. Formaldehyde and acetaldehyde are collected with Sep-Pak cartridges that have been impregnated with an acidified 2,4-dinitrophenylhydrazine (DNPH)

reagent (Waters, Inc), according to the EPA Method TO-11A. When ambient air is drawn through the cartridge at nominal flow rates of 1 L/min, carbonyls are captured by reaction with DNPH to form hydrazones, which are separated and quantified in the laboratory using HPLC (Fung and Grosjean, 1981). The ambient measurement results are subject to various artifacts due to sorbent interactions with ozone so ozone is removed with a honeycomb denuder coated with sodium carbonate/sodium nitrite/glycerol mixture (Koutrakis, et al., 1993). After sampling, the cartridges are eluted with acetonitrile. An aliquot of the eluent is transferred into a 1-ml septum vial and injected by autosampler into a high performance liquid chromatograph (Waters Alliance System) for separation and quantization of the hydrazones (Fung and Grosjean 1981).

1.2 BTEX by Solid Phase Microextraction (SPME)

1.2.1 Sampling

Carboxen/(poly)dimethylsiloxane (CAR/PDMS) coated (75 μm) quartz fibers are used for 10-minute BTEX sampling. SPME is a passive method, thus the rate of the fiber uptake is controlled by the diffusion rate of the analytes to the fiber. In a stationary environment without air movement, a concentration gradient is formed in the boundary layer between the fiber and the surrounding environment. This situation occurs during fiber calibration in a static system, such as a Tedlar bag. However, in an outdoor environment there is always some air movement and the sorption rate will be higher in this situation, since the thickness of the boundary layer will be smaller. This phenomenon explains some of the differences observed between canister and SPME samples collected in summer 2002. To improve the agreement between these methods the Summer 2003 SPME samples were obtained using the experimental set up in Figure 1. The outlet of the SPME sampling bulb was connected to the Tenax media sampling pump. Active sampling at low constant air flows was a suitable solution of outdoor field sampling variability on windy days. With these modifications, wind speed influence is avoided and a common air stream is being sampled by all instruments. The SPME was exposed to the air stream at a fixed flow rate of about 300 ml/min. The sampling bulb temperature is not controlled.

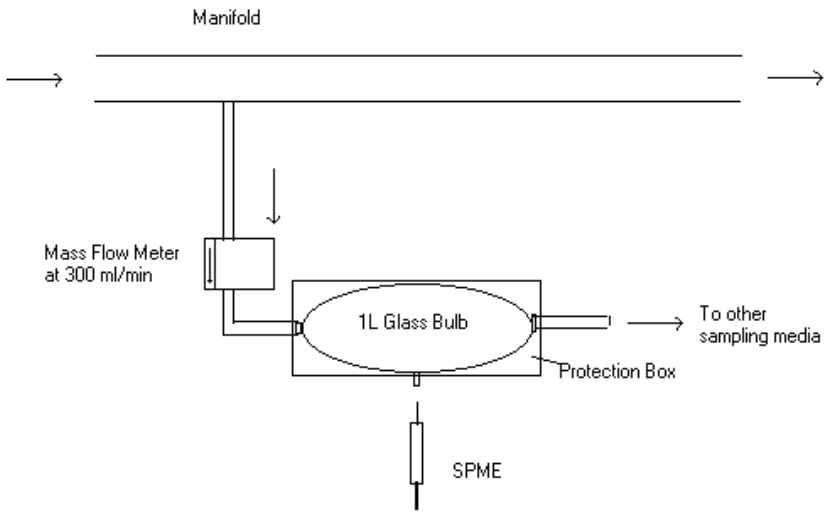

Figure 1. SPME Sampling System Set Up

1.2.2 Analysis

All SPME BTEX samples are analyzed in a mobile laboratory with a Model 8610C SRI Instruments GC equipped with a heated injection port suitable for SPME desorption, a CP-Sil 5 (Varian, Inc.) capillary column (60m, 0.32mm i.d.), and a PID detector. The heated flash vaporization injector is maintained at 250°C and the PID at 150°C. The column temperature was programmed at 60°C for 2 min, 8°C/min to 165°C (held for one minute), and then 45°C/min to 240°C. The helium carrier gas flow rate was 3 ml/min.

Blanks and calibration checks are performed daily on the SRI GC in order to determine the performance of the instrument. Fibers are kept in the injector port throughout the sample run to guarantee that the entire sample was desorbed and to begin the conditioning of the fiber. Fibers are further cleaned in a fiber conditioner at 300°C for at least one hour. One fiber per batch of 5 is checked for cleanliness after conditioning. The fiber conditioner consisted of a 70 cm x 16 cm stainless steel container with 5 ports and a Watlow heater/temperature controller capable of maintaining temperatures in the 200-300° C range. A helium flow of approximately 10 ml/min is maintained during fiber conditioning. Testing showed that the same fiber can be reused up to 40 times absent breakage of the fiber or failure of the fiber mounting mechanism.

The SRI GC is calibrated with 1 μl injections of liquid standards prepared in pentane with BTEX at different concentrations (1, 5, 10, 20, 40, 50, and 100 ng/μl). Carboxen/PDMS fibers are calibrated by introducing the SPME fiber for a defined time into a flowing standard gas containing the calibration component under the same flow-through conditions used for field sampling). The fiber is then analyzed by GC/PID. SPME gas calibrations are done throughout the study as necessary. BTEX calibration is performed with certified gas standards at different concentrations (20, 80, 100 and/or 200 ppbv for each compound).

The dependence of the SPME uptake rate on the sample flow rate is shown in Figure 2. The response changes logarithmically and reaches a plateau region after approximately 0.038 cm/s when changing flow has a lesser effect on the amount of extracted mass. Optimal flow was determined to be 0.038 cm/s. The linear velocities studied were low (0.0044-0.1126 cm/s) enough to characterize a "quasi static" environment. The flow profile showed two distinctive zones in Figure 2. In the first zone (0-0.0665 cm/s) mass transfer is controlled by diffusion through the well-developed fiber boundary layer; in the second zone (0.0665 cm/s and higher) transfer is controlled by diffusion through the fiber pores.

Sampling was performed within the plateau region where the SPME response is not greatly affected by changes in the flow.

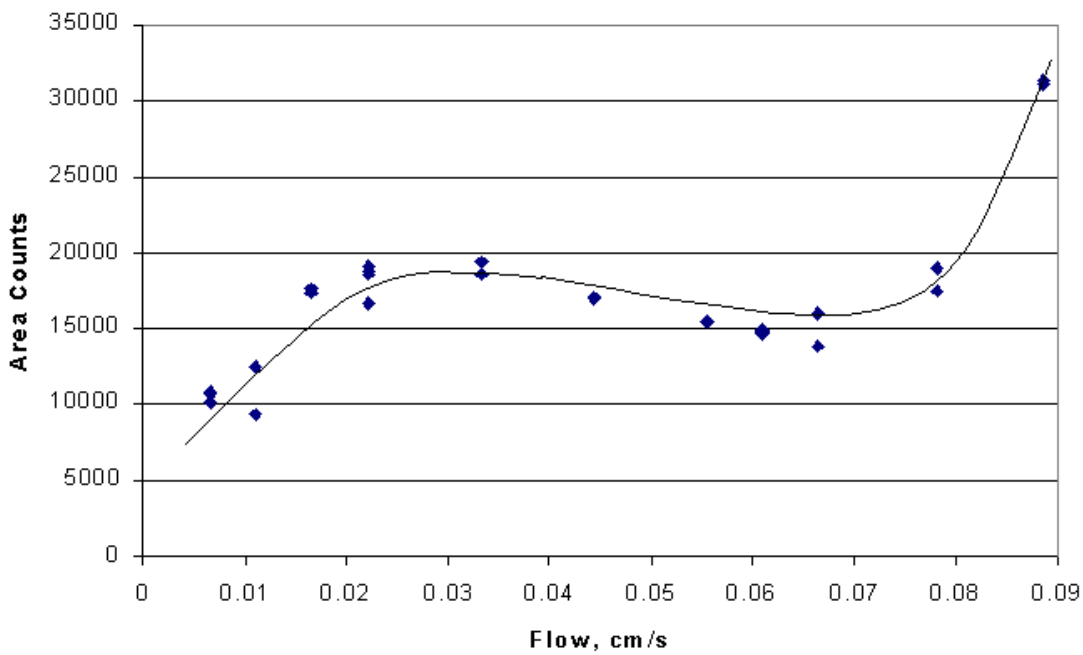

Figure 2. SPME Flow Profile

Sampling temperature and humidity are also important parameters affecting the SPME data. Temperature correction factors are obtained in the laboratory. The sampling bulb is temperature controlled with a cooling/heating system. Temperature inside the glass bulb is measured with a thermocouple. For introducing humidity, a heated injection port is added before the glass bulb entrance in order to inject water with a syringe pump to produce the desired relative humidity (Tuduri, et al., 2001; Nelson, 1992; Martos, P. and J. Pawliszyn, 1997, and Lodge 1989).

Chai and Pawliszyn, 1995, performed several experiments to determine the influence of relative humidity (RH) on the 100 μm PDMS partition coefficient (Boy-Boland, 1998). RH usually decreases the response factor (Kfg) of each individual compound. The decrease of the response is dependent on temperature. At lower temperatures humidity has a larger effect on the response factor. The highest effect of humidity was observed for a 0°C-10°C temperature range for 0% to 25% RH. Changes in the area counts at 0°C-25°C for 25%-75% RH were almost negligible. It is understood that humidity affects the fiber response because water at high concentrations competitively adsorbs into the coating of the fiber. Some compounds are less affected by humidity than others.

The 75 μm Carboxen/PDMS fiber showed no effect with RH at 100 ppbv of BTEX concentration. Experiments at 25°C and 12.5°C determined that RH does not affect the fiber uptake of BTEX compounds significantly. Figure 3 shows toluene response at 100 ppbv for different RH. All the other BTEX species behaved similarly. Data for BTEX showed a standard deviation between 5 to 13% for the range of humidity analyzed, 10% to 80% RH. Sensors are accurate as long as there is no condensation of water, which may happen above 85% RH). These differences in the response of the fiber are within the precision of the method. Low RH effects on the fiber sensitivity may be due to the low concentration ranges used for calibration. At low BTEX concentrations, water is probably not an important competitive molecule. More research in this area is suggested.

SPME Carboxen/PDMS coated (75 μm) fibers are used with portable or manual samplers. When manual samplers are used, the tip of the needle is closed with a septum or Teflon tape (Martos and Pawliszyn, 1997 and Chai and Pawliszyn, 1995). Prior to sampling, the pre-cleaned fibers are kept at ambient temperature within an activated charcoal protector. This storage method has been tested in the laboratory and BTEX backgrounds are stable up to 48 hours in storage following cleaning (the longest tested period). After sampling, fibers are kept in sealed Mylar bags inside a cooler with dry ice. Samples are analyzed 4-10 hours after sampling, on average, with a minimum of 1 hour and a maximum of 20 hours between sampling and analysis.

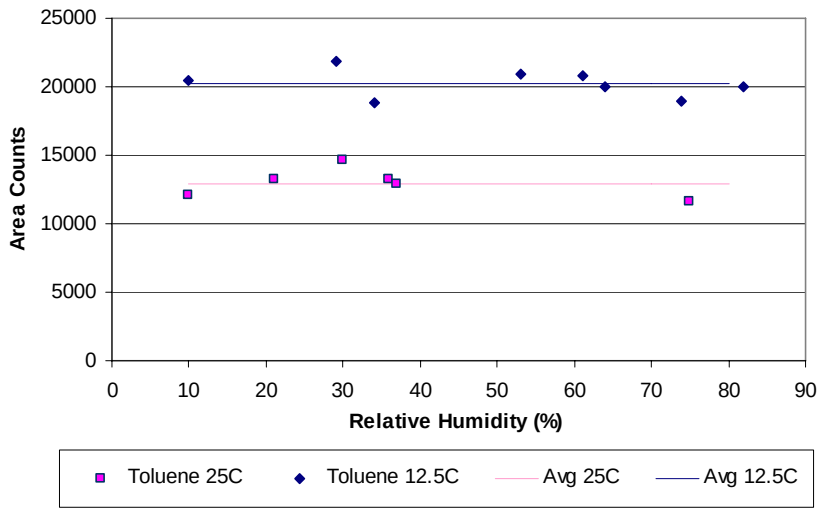

Figure 3. Humidity Effect in GC/PID response for a 100 ppbv BTEX standard at 25ºC and 12.5ºC (with a standard deviation of 5% for the 12.5 °C and 8% for 25 °C from the respective mean)

1.3 Continuous Methods

The continuous Kore MS200 is used to monitor BTEX on a one-minute basis, sampling during the initial 10 second portion of each 60 second period. This instrument uses a time-of-flight mass spectrometer to separate compounds of interest. Rather than using a gas chromatograph, this instrument uses a software solution and a library of 70 eV electron ionization fragmentation patterns to apportion the contribution of each parent species to the time-of-flight (TOF) mass spectrum recorded by the instrument. The software program does not distinguish between specific isomers so xylenes and ethylbenzene are reported together. The inlet uses a polydimethylsiloxane membrane preferentially to allow non-polar organic compounds into the analyzer while impeding polar species and air components to maintain the vacuum inside the analyzer chamber. The instrument performed well during the pilot studies and early field work, comparing favorably with the canister measurements for most samples, although it became increasingly unreliable in subsequent field studies. Given the corroborative role proposed for this device, we do not believe the information provided by this instrument, while desirable, is necessary to fulfill the goals of the screening study.

Carbon monoxide is monitored continuously by the Langan T15 electrochemical monitor for CO and by a nondispersive infrared (NDIR) analyzer. The response time of Langan T15 instrument is slower than the response of the infrared-based instruments. Prior to each period of field measurement the instrument is calibrated using a zero-air generator and

span gas to provide two reference points encompassing the expected range of concentrations anticipated during actual testing. The two-point calibration procedure is as follows:

1. Allow instrument to stabilize for a minimum of 15 minutes.
2. Record ambient concentration as determined by the instrument.
3. Connect inlet lines from the instrument to a zero-air source (for a passive sampler use the flooder cap provided by manufacturer) and check for a flow rate of >1 lpm with rotometer.
4. Let instrument stabilize, record current baseline, then adjust zero.
5. Connect inlet lines to a tank of span gas with an appropriate CO concentration for anticipated range and verify flow rate
6. Let instrument stabilize, record current reading, and adjust span to correct value.
7. Re-connect instrument to zero-air source, let stabilize and check baseline zero reading.
8. Repeat steps 4-7 if necessary.
9. Check a third concentration level with span gas if available.

During field measurements the passive sampler is checked against the reference unit, which has automatic baseline stabilization and an internal zero-air source. Baseline readings will be recorded at the beginning and end of each sampling day. If significant deviations are observed a re-calibration will be performed.

RAE Systems Model PGM-7240 (ppbRAE) portable PID monitors are used to continuously monitor ambient VOC levels in high end microenvironments. The monitor is sensitive to organic and inorganic gases that have an ionization potential of less than 10.6 eV, which includes most compounds of interest in this study. It does not respond to light hydrocarbons such as methane, ethane, propane, and acetyleneor to CO or formaldehyde.

A Continuous Formaldehyde Monitor was purchased from Alpha-Omega Power Technology, Ltd. (Albuquerque, NM). The Alpha-Omega (AO) a wet instrument that utilizes the Hantzch reaction, absorbing formaldehyde in acidified water, reacting it with 2,4-pentanedione and ammonia to form a cyclized product, 3,5-diacetyl-1, and 4-dihydrolutidene, which is continuously detected by fluorescence. The method is sensitive and highly specific for formaldehyde.

1.4 Breath Collection and Analysis

Breath is collected from technicians who participate in a scripted exposure. Since this study requires the use of human subjects, the final protocol was reviewed by an Institutional Review Board that is certified with the National Institute of Health.

Technicians were instructed to avoid exposure to materials that may compromise the exposure assessment prior to and during the scripted exposures. This includes avoiding alcohol ingestion (ethanol) and cigarette smoke for at least 3 days prior to the scripted exposures. Breath samples collected before the exposure were used to assess background levels in the technician.

The test subject takes the three breath samples. One sample is taken before initiating ME sampling for background purposes; the second sample, ten seconds (timed with a stopwatch) immediately after completing an active refueling task or experiencing a measured peak exposure in another ME, and the third sample 1 minute immediately following the second sample. The 3rd backup sample is analyzed in case there is a problem with the second sample. The technician takes a 1-liter canister, places the tube in his mouth, and breathes smoothly and regularly through the mouth around the tube until a resting breath pattern is established. At the end of a normal exhalation, the technician closes the mouth, opens the canister valve, and continues to expel the expiratory reserve. The canister vacuum will collect 1 L of the expiratory reserve. When the flow stops, the technician closes the canister valve to capture the sample (Pleil and Lindstrom, 1995; 2002). Breath samples are collected in 1 L silico-steel steel canisters (Restek, Inc). .

<u>Gas Chromatography-Mass Spectrometry.</u> The analysis of VOC in breath samples is conducted as described by Pleil and Lindstrom (1995, 2002). Prior to the commencement of sampling, the CO_2 level in alveolar breath of all technician subjects is measured using GC/FID. Since the FID does not respond to CO_2, this species is converted to methane by a methanator, positioned after the GC column, but ahead of the FID. Three breath samples are collected and analyzed, and the mean CO_2 value is used for further comparison. After breath sample collection, the CO_2 is measured using the same method. The target VOC (MTBE, 1,3-butadiene, ethanol, BTEX) is measured using a GC/MS technique. The GC/MS system includes an Entech 7100 preconcentrator, a Varian 3800 gas chromatograph with FID and column switching valve, and a Varian Saturn 2000 ion trap mass spectrometer.

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Appendix C

Characterization of Solid-Phase Microextraction and Gas Chromatography for the Analysis of Gasoline Tracers in Different Microenvironments

(Celballos, D., Zielinska, B., Fujita, E., Sagebiel, J. (2007) J. Air & Waste Manage. Assoc. 57: 355-365)

Link to JAWMA article: http://216.92.182.36/gsearch/journal/2007/3/ceballos.pdf

APPENDIX D

Section 211(B) Tier 2 High-End Exposure Screening Study Of Baseline and Oxygenated Gasoline – 1st Reno Pilot Study

APPENDIX D
First Reno Pilot Study

Section 211(B) Tier 2 High-End Exposure Screening Study Of Baseline and Oxygenated Gasoline – Pilot Study

Final Report

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1. INTRODUCTION

This report summarized the results of a pilot study that was conducted in Reno, NV, from February 25 through March 1, 2002 as part of a screening study of the high-end exposures to baseline and oxygenated gasoline. The study is being conducted for the American Petroleum Institute pursuant to Section 211(b) of the Clean Air Act. The objectives of the pilot study were to evaluate various monitoring methods under realistic field sampling conditions and to determine their suitability for use in the main exposure study to be conducted in Atlanta, Chicago, and Houston during the upcoming summer and winter seasons. We also evaluated biological sampling methods (breath and urine) for their applicability to the final study. In addition to DRI, personnel from Lovelace Respiratory Research Institute and Battelle participated in the pilot study. The refueling experiment was repeated on June 4, 2002 to evaluate the response of the portable mass spectrometer, which was not available for the refueling experiment during the pilot study. This report includes the results of the second refueling experiment.

1.1 Measurement Methods

During the pilot phase of the study, we evaluated the sensitivity, precision, accuracy, selectivity, power requirements, and portability of sampling and monitoring devices to be used in the main study. The evaluations included methods for continuous measurement of carbon monoxide (CO), methyl tertiary butyl ether (MTBE), formaldehyde (HCHO), benzene, toluene, ethylbenzene, and xylenes (BTEX), with time integration of 1-5 minutes, and time-integrated measurements of ethanol (EtOH), 1,3-butadiene, and acetaldehyde (CH_3CHO). The following continuous analyzers were used during the pilot study:

Background CO, Monitor Labs. Research-grade non-dispersive infrared detection for carbon monoxide. This was maintained in the mobile lab and measured CO during our runs. Property of DRI.

T15 CO, Langan products. Electrochemical monitor for CO. Quite small and portable, but it is temperature dependant. Property of DRI

Photoacoustic Gas Monitor, Innova. A photoacoustic instrument that uses infrared light to detect CO and total hydrocarbons (calibrated as propane). In addition, this instrument could provide CO_2 and water vapor (relative humidity). Property of Lovelace.

Continuous Formaldehyde Monitor, Battelle. This instrument monitors formaldehyde in a continuous mode via a reaction to a fluorescent species and detection in a fluorimeter. Property of Battelle.

Model TVA1000 FID, Thermo Environmental Instruments. This is a flame ionization based instrument for total hydrocarbons on a continuous basis. Sold primarily for leak detection at petrochemical plants. Property of TEI, on loan to DRI for the pilot study only.

MS200, Kore Technologies. An electron impact ionization time-of-flight mass spectrometer was used for the detection of VOC species. Rather than using a GC to separate species, this

instrument uses software to quantify species by apportionment of their mass fragmentation patterns. Property of DRI.

In addition to the continuous instruments, time-integrated samples were collected in stainless steel canisters and on 2,4-dinitrophenylhydrazine (DNPH)-impregnated silica gel cartridges and Tenax/Carbotrap solid adsorbent traps. These samples were collected over a one-hour exposure period. The DNPH cartridges were sampled with a potassium iodide coated denuder to remove ozone. The canisters were analyzed by gas chromatography with flame ionization detection for BTEX, MTBE, 1,3-butadiene, and total nonmethane hydrocarbons. The extracts of the DNPH cartridges were analyzed by HPLC/UV for formaldehyde and acetaldehyde. The Tenax/Carbotrap samples were analyzed for EtOH.

We also tested the solid phase microextraction (SPME) technique during the pilot study for the collection and analysis of BTEX, MTBE, ethanol, formaldehyde, and acetaldehyde. A 100 μm (poly)dimethylsiloxane (PDMS) fibers and 75 μm Carboxen/(poly)dimethylsiloxane (CAR/PDMS) fibers were used for BTEX, MTBE, and ethanol and 65 μm PDMS/divinylbenzene (DVB) fiber that was impregnated with o-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA) was used for carbonyl compound collection. The fibers were exposed in parallel for 15 to 30 min and were analyzed on a gas chromatograph with both FID and photoionization detector (PID). Some of the fibers were also analyzed by GC/MS.

1.2 Description of Microenvironments and Sampling Procedures

A summary of the samples collected is presented in Table 1-1. This table details the samples that were taken and a brief summary of the conditions at the time of sampling. In addition, the following notes detail the experiments. For the three driving exposures, we also collected GPS data showing location and time. Unless noted otherwise, each run last one hour. These are presented in the appendix.

<u>In-cabin Freeway (R02022607), Run #1</u>

For the first 15 minutes, the sampling van drove south on US 395 from Parr Boulevard to south Reno. This was a stretch of high rush hour traffic. The second 15 minutes, the van drove north from south Reno to Parr Boulevard. This was a stretch of low rush hour traffic. This loop was repeated for the third and fourth 15-minute periods. Data were not collected for the Innova photoacoustic instrument due to a failure of the pump. Only limited, hand logged, data were available for the TEI FID because of a failure of the internal memory of that instrument. A few data points are missing due to power problems at the beginning of the run.

<u>In-cabin Surface Streets (R02022612), Run #2</u>

For the first 15 minutes, the sampling van drove within the “urban canyon” loop, consisting of south on Sierra, east on 4th, north on Virginia, west on 5th. (This made a total of 4 left turns around the Silver Legacy Hotel/Casino.). The second 15 minutes, the van drove a surface street loop, consisting of going east on 4th to Wells, north on Wells to Oddie, south on Sutro, and west on 4th. The third 15 minutes began at 4th, went north on Center, stopped at

Table 1-1. API S211(b) Exposure Study - Reno Pilot Study

Run #	Test ID	Date	Start Time	End Time	Microenvironment Exposure Level	Location/Activity	Ventilation Condition
1	**R02022607**	**02/26/02**	**0710**	**0810**	**In-cabin - freeway**	395 from Parr to south Reno	
	R02022607a	02/26/02	0710	0725	higher -stop & go	SB 395 from Parr to south Reno	D&P-side windows open half inch, heater on and vent open to outside, keep temperature between 60 and 65.
	R02022607b	02/26/02	0725	0740	lower - free flow	South Reno to DRI via 395	
	R02022607c	02/26/02	0740	0755	higher -stop & go	SB 395 from Parr to south Reno	
	R02022607d	02/26/02	0755	0810	lower - free flow	South Reno to DRI via 395	
2	**R02022612**	**02/26/02**	**1200**	**1300**	**In-cabin -surface streets**		
	R02022612a	02/26/02	1200	1215	higher - urban canyon	S on Sierra, E on 4th, N on Virginia, W on 5th (4 left turns around Silver Legacy)	D&P-side windows open half inch, heater on and vent open to outside, keep temperature between 60 and 65.
	R02022612b	02/26/02	1215	1230	mixed - cross I-80 w/o stopping)	From urban canyon loop, go E on 4th to Wells, N on Wells to Oddie, S on Sutro, W on 4th	
	R02022612c	02/26/02	1230	1245	transect across I-80 with 10-min stop at bridge	From 4th, N on Center, stop at bridge over I-80 for 10 minutes, then go back to urban canyon loop	
	R02022612d	02/26/02	1245	1300	higher - urban canyon	S on Sierra, E on 4th, N on Virginia, W on 5th (4 left turns around Silver Legacy)	
3	**R02022616**	**02/26/02**	**1600**	**1700**	**In-cabin - freeway**	395 from Parr to south Reno	
	R02022616a	02/26/02	1600	1615	lower - free flow	SB 395 from Parr to south Reno	D&P-side windows open half inch, heater on and vent open to outside, keep temperature between 60 and 65.
	R02022616b	02/26/02	1615	1630	higher -stop & go	South Reno to DRI via 395	
	R02022616c	02/26/02	1630	1645	lower - free flow	SB 395 from Parr to south Reno	
	R02022616d	02/26/02	1645	1700	higher -stop & go	South Reno to DRI via 395	
4	**R02022708**	**02/27/02**	**0810**	**0910**	**Refueling/in-cabin**		
	R02022708a	02/27/02	0810	0825	baseline	Frontage Road just south of Gold Ranch	window open 1 inch
	R02022708b	02/27/02	0825	0840	refueling/in cabin	Gold Ranch Pump #10	window open 1 inch, close door once at start
	R02022708c	02/27/02	0840	0855	refueling/in cabin	Gold Ranch Pump #10	window half open, opened door once
	R02022708d	02/27/02	0855	0910	refueling/in cabin	Gold Ranch Pump #10	window half open

Run #	Test ID	Date	Start Time	End Time	Microenvironment Exposure Level	Location/Activity	Ventilation Condition
5	**R02022712**	**02/27/02**	**1200**	**1300**	Refueling/outside		
	R02022712a	02/27/02	1200	1215	baseline	Trailer park south of Gold Ranch	window open 1 inch
	R02022712b	02/27/02	1215	1230	refueling/outside	Van at Gold Ranch Pump #10, filled Suburu with midgrade gas on Pump #9	sampling line to pump
	R02022712c	02/27/02	1230	1245	refueling/outside	Van at Gold Ranch Pump #10, filled Corolla with regular on Pump #9, collected gasoline sample	sampling line to pump
	R02022712d	02/27/02	1245	1300	refueling/outside	Van at Gold Ranch Pump #10, filled Volvo with premium gas on Pump #9, collected gasoline sample	sampling line to pump
6	**R02022811**	**02/28/02**	**1100**	**1200**	Pedestrian walk	1 square block around Silver Legacy	
	R02022811a	02/28/02	1100	1115		Virginia St between 4th and 5th (southbound)	
	R02022811b	02/28/02	1115	1130		4th between Virginia and Sierra (westbound)	
	R02022811c	02/28/02	1130	1145		Sierra between 4th and 5th (northbound)	
	R02022811d	02/28/02	1145	1200		5th between Sierra and Virginia (eastbound)	
7	**R02022815**	**02/28/02**	**1500**	**1600**	Garage underground	Survey surrounding area, enter garage and survey upper level. Paused for 15 min to allow traffic to build up, then sampled for 1 hour.	D&P-side windows open 1 inch with heater on if necessary and vent open while outside of garaged, window fully open inside garage, and side doors open when stationary.
	R02022815a	02/28/02	1500	1515			
	R02022815b	02/28/02	1515	1530			
	R02022815c	02/28/02	1530	1545			
	R02022815d	02/28/02	1545	1600			
8	**R02030109**	**03/01/02**	**0935**	**1340**	Garage residential		
	R02030109a	03/01/02	0935	1005		Background 1	Use house fan located in center of room to circulate/mix air in garage and kitchen. Measure continuous instruments with 10-min cycle time between garage and kitchen. Sampling line through deadbolt hole.
	R02030109b	03/01/02	1005	1035		Background 2	
	R02030109c	03/01/02	1110	1140		Pull car in gar. open kitchen door 1 min and close	
	R02030109d	03/01/02	1140	1210		Kitchen door open.	
	R02030109e	03/01/02	1210	1240		Kitchen door closed, windows open	
	R02030109f	03/01/02	1240	1310		Open garage door and let icar dle for 30 min. open door to kitchen for 1 minute and keep close for remainder of period.	

	R02030109g	03/01/02	1310	1340		Post Exposure, back car out and close garage door	
Run #	**Test ID**	**Date**	**Start Time**	**End Time**	**Microenvironment Exposure Level**	**Location/Activity**	**Ventilation Condition**
9	R02030116	**03/01/02**	**1600**	**1630**	Generator Exhaust		
	R02030116a	03/01/02	1600	1605		Exhaust downwind (CO ~ 2-3 ppm)	
	R02030116b	03/01/02	1605	1610		Exhaust upwind (CO peak of 150 ppm)	
	R02030116c	03/01/02	1610	1615		Exhaust downwind (CO <10 ppm)	
	R02030116d	03/01/02	1615	1620		Exhaust upwind (CO 10-50 ppm)	
	R02030116e	03/01/02	1620	1625		Exhaust upwind (CO 20-150 ppm)	
	R02030116f	03/01/02	1625	1630		Exhaust downwind (CO <5 ppm)	
10	**R02060410**	**06/04/02**	**1010**	**1101**	**Refueling/outside**		
	R02060410a		1010	1025		Parking west of Gold Ranch- background	Sampling line outside of vehicle
	R02060410b		1031	1046		At Gold Ranch Pump#10, refueling Volvo (4 min) with premium gas on Pump #10	Sampling line at breathing high
	R02060410c		1047	1101		At Gold Ranch Pump#10, refueling Corolla (2 min) with regular on Pump#9	Sampling line at breathing high

bridge over I-80 for 10 minutes, then went back to the urban canyon loop. The van door was open during the stop at the freeway overpass. For the fourth 15 minutes, the sampling van drove the "urban canyon" loop again, completing another 4 turns around the Silver Legacy Hotel/Casino. Data were collected from all instruments , but the MS200 instrument shut down during the run due to vacuum becoming too low.

In-cabin Freeway (R02022616), Run #3

For the first 15 minutes, the sampling van drove south on US 395 from Parr Boulevard to south Reno. This was a stretch of low rush hour traffic. The second 15 minutes, the van drove north from south Reno to Parr Boulevard. This was a stretch of high rush hour traffic. This loop was repeated for the third and fourth 15-minute periods. Data were collected from all instruments, but a few data points are missing due to power problems at the beginning of the run.

In-cabin Refueling (R02022708), Run #4

For both refueling experiments a rural but high volume service station was used. The station is located near a major interstate (I-80), but is otherwise in a rural area. The station has 18 fueling pumps and sells between 20,000 and 40,000 gallons of gasoline per day. The mangers indicated they are the largest gasoline seller in northern Nevada.

For the first 15 minutes, the sampling van parked on the frontage road, near the I-80 freeway, away from the filling station to collect a background sample. The goal was to be approximately the same distance from the freeway as we would be at the fueling station. For the next 50 minutes, samples were collected while the van was parked at pump number 10, the center pump of the center island. Most equipment worked well, except that the MS200 had vacuum problems and had to be shut down.

Refueling at Pump (R02022712), Run #5

Similarly as with the first experiment, during the first 15 minutes, the sampling van parked on the frontage road, near the I-80 freeway, away from the filling station to collect a background sample. For the next 45 minutes, samples were collected in the breathing zone while the van was parked at pump 10, center of the center island. Breathing zone was at pump 9 (opposite side of a dual-side pump), while three cars were filled with fuel. First was a Subaru that was filled with regular. Next came a Toyota that was filled with mid-grade, and finally was a Volvo filled with super. No formaldehyde data were collected due to power failure. In addition, the MS200 was not run due to vacuum problems.

Refueling at Pump, Repeated (R02060410), Run #10

During the first 15 min the vehicle with sampling equipment was park on the quiet parking area, west of Gold Ranch and away from the filling station to collect a background sample. Only MS and SPME samples were collected. For the next 30 minutes, samples were collected in the breathing zone while the vehicle with sampling equipment was parked at pump 10, center of the center island. Breathing zone was either at pump 10 or at pump 9 (opposite side of a dual-side pump), while two cars were filled with fuel. First was a Volvo filled with super,

and next came a Toyota Corolla that was filled with regular grade. During 30 min one canister sample and two 15 min SPME samples were collected. MS200 was operating in a continuous mode.

Pedestrian Walk (R02022811), Run #6

All the monitoring equipment was placed on two mobile carts with batteries and inverters. For one hour, monitoring was conducted while the carts were slowly pushed around a large one square block area of central downtown Reno (the Silver Legacy Casino). The block was split roughly into equal times with approximately 15 minutes spent on each leg of the block. We started at 4th and Virginia, went south on Virginia, then west on 5th to Sierra, then north to 4th and back to the starting point.

Data was collected from all instruments, except that for the first 15 minutes, no formaldehyde data was collected possibly due to a light leak in the fluorescence detector. In addition, the TEI FID did not collect data, although it appeared to be on the entire time. The reason for this failure was never determined.

Underground Public Parking Garage (R02022815), Run#7

The van was parked in an underground parking garage for one and a half hours during the period of maximum car departure. This garage has two underground levels, however the van remained on the upper of these two levels for two reasons. The first is that this level was nearly full while the lower level had only a few vehicles. The second reason is that the traffic ramps in the garage would allow travel from the first underground level down to the second, but from the second level the van could only go up to the surface, not back to the first underground level. The van's position was relocated several times to try and capture the cold start exhaust from departing vehicles. Data were collected for the first 15 minutes, followed by a 15 minute zeroing, and then data collection for the next hour.

Residential Kitchen and Garage without Car (R02030109a,b), Run #8

For both residential exposures a home was used that had an attached two-car garage. The home and the garage share a common wall and there is a door from the garage into the kitchen. For the duration of these experiments a vented 2.5 gallon gasoline storage container was also present in the garage during the sampling period, located in the front center portion of the garage, closest to the house. The can was approximately half-full and the vent on the gas can was open. The sampling equipment was set up in a residential kitchen next to the door of the attached garage. For the first hour, the sampling was done with the garage door closed and no car. Samples were taken alternately for 10 minutes in the kitchen followed by 10 minutes in the garage for one hour.

Residential Kitchen and Garage with Car (R02030109c-g), Run #8

For these experiments the car used was a 1984 Honda Accord with a four-cylinder engine and it is carbureted. The vehicle is normally fueled with regular gasoline and annually passes the state smog check with no problems. Prior to parking the car in the garage, it was driven approximately 5 miles to warm the engine up. Once parked in the garage, the air cleaner cover

was removed, exposing the inlet of the carburetor and the oil filler cap on the valve cover was removed to allow additional evaporative emissions.

The sampling equipment had the same setup as the background samples. Separate integrated samples were collected in the garage and in the kitchen. The continuous instruments were switched between the garage and the kitchen at 10-minute intervals for 2.5 hours. The sequence of activities was as followed:

Time		Activity
1110	1140	Pull car in gar. open kitchen door 1 min and close
1140	1210	Kitchen door open.
1210	1240	Kitchen door closed, windows open
1240	1310	Open garage door and let car idle for 30 min. Open door to kitchen for 1 minute and keep closed for remainder of period.
1310	1340	Post Exposure, back car out and close garage door

Sample probe was on the following sequence:

garage	11:10-11:20
kitchen	11:20-11:30
garage	11:30-11:40
kitchen	11:40-11:50
garage	11:50-12:00
kitchen	12:00-12:10
kitchen	12:10-12:20
garage	12:20-12:30
kitchen	12:30-12:40
garage	12:40-12:50
kitchen	12:50-13:00
garage	13:00-13:10
garage	13:10-13:20
kitchen	13:20-13:30
garage	13:30-13:40

Generator Exhaust (R02030115), Run #9

In the DRI staging lot, the exhaust hose of a gasoline powered electrical generator was operated near the inlet of the sampling equipment. The generator exhaust hose was moved to a different location every 5 minutes. Adjusting its position relative to the instrument inlets; first downwind, then upwind, downwind, upwind, upwind closer to exhaust, and finally downwind.

2. RESULTS

The results from this study are presented in four parts: 1) continuous (or semi-continuous) instruments; 2) integrated samples; 3) SPME samples; and 4) biological samples. Where appropriate, comparisons are made between the continuous and the integrated samples. Results from the additional refueling experiment performed in June 2002 in Reno are summarized in Section 2.5.

2.1 Continuous Instruments

Figures 2-1 through 2-15 present the time series for the continuous analyzers. For the residential garage exposures (2-8 through 2-15) the plots are only 30 minutes, not 60 minutes as for the rest of the plots. This is because of the number of changes that took place during these exposures. Also, during the residential garage exposures, the sample probe was moved to measure the kitchen area and the garage area as per the schedule listed above in the description of the runs. This accounts for the sudden changes in concentration seen in the data.

The MS200 data is not presented in these time series. When we examined the raw MS data, without background correction, we found very high concentration levels being reported. The MS200 data appear high during all runs, especially compared to the integrated canister data, however, the structure of the data suggests that the MS200 is accurately responding to changes in ambient concentrations. Additional work was conducted with this instrument to help explain this effect. As a result of this work and discussions with the manufacturer (Kore), we have been able to better understand these data. The data that the MS200 reports is very dependent on the blank level. In addition, the membrane-based inlet and the relatively slow pumping mechanism appear to have the effect of slowing the 2-3 minute recovery time of the instrument, especially when the instrument is challenged with a high concentration. To test this we alternatively applied a high concentration standard and a zero air to the inlet of the MS200. On the basis of these experiments, we applied a correction that consisted of subtracting a background value consisting of a linearly sloping zero to the data, based on our experiments with the standards. This was difficult in the case of the residential garage where the instrument was switched every 10 minutes between the relatively high concentrations in the garage with the much lower levels seen in the kitchen. However, once these backgrounds were subtracted, the MS200 data generally showed agreement (within a factor of 2 at ppb levels) with the canister data, which will be discussed later. We are still working with Kore to develop a pre-concentrator inlet that will allow for a much lower detection limit, however, this will sacrifice time resolution.

An example of the correction applied is in chart 2-16 which shows the original benzene concentration, the zero function applied and the resulting corrected benzene concentration. The next figure, 2-17 shows the corrected data from this run for benzene, toluene, and the xylenes. In this chart, it is clear that the corrected plots track each other in structure, as we expected. The other data sets were similarly corrected and are summarized in Table 2-1 with the canister data. The comparison with the canister is quite favorable, except in the case of benzene at very low concentrations and in some runs where limited data was available. This was generally due to problems with the vacuum system in the MS200.

To compare the responses of the various instruments, we produced scatter plots, Figures 2-18 through 2-21. Figure 2-18 shows the comparison between the Innova CO and the T15 CO. There is reasonable agreement, but especially at lower concentrations, we find that the Innova occasionally is much higher than the T15. This may be due to the method the Innova uses, which is to take a grab sample into its internal chamber, measure the components of interest and then evacuate the chamber. If this grab sample is during a particularly high brief instant, this may result in the higher response seen.

Figure 2-19 compares the two continuous hydrocarbon (HC) measuring devices, the Innova and the TEI. There are two very high values from the Innova, which Figure 2-20 removes. The Innova data are adjusted upward by 10 to account for the expected difference in response from the photoacoustic vs. the FID. These two instruments use fundamentally different methods to measure hydrocarbons and may be hard to compare. In general, the two are tightly correlated, despite the different response factors.

The correlation between the Battelle continuous formaldehyde monitor and the T15 CO is presented in Figure 2-21, without the data from the generator which was significantly higher and dominated the plot. This shows a weak correlation, but includes some very high values. At more ambient concentrations, they are slightly better correlated. We should expect that these two would be correlated as they both are combustion-derived.

2.2 Integrated Samples

Integrated samples consist of canisters, DNPH cartridges (for aldehydes) and Tenax/Carbotrap solid adsorbent traps. Canister data and Tenax/Carbotrap data for ethanol are presented in Table 2-1. In addition to the values measured, we show the sum of the BTEX compounds. Of interest was to compare these values to the MS200; this comparison is presented in Table 2-2. In this table, the average values (canister) from the various exposures are presented along with the corrected MS200 values for these same exposures. The corrected data are calculated as described above (Section 2.1). Generally the averages agree better at higher concentrations, but lower concentrations are quite reasonable, considering we are working at or near the detection limit of the MS200. In the case of the residential garage exposures this was further complicated by the 10-minute cycle time between the garage (at high concentrations) and the kitchen (at much lower concentrations). In spite of all this, the correlations between the canister and the MS200 were on the order of $r^2 \sim 0.87$ and the slopes were ~0.75, with the MS200 reporting less than the canisters.

The DNPH samples were compared with the averaged data from the Battelle continuous formaldehyde sampler. This comparison is presented in Table 2-3 and Figure 2-22. The agreement is excellent for the 10 samples that are comparable. The correlation suggests that the Battelle unit is reading about 15% less than the DNPH cartridges are reporting.

Table 2-1: Canister and Tenax/Carbotrap Data (concentrations in ppbv)

Test ID	Date	Location	1,3-butadiene	Ethanol (T/C)	MTBE	benzene	toluene	ethyl benzene	m/p-xylene	o-xylene	Sum BTEX
R02022607	2/26/02	Morning Freeway Commute	1.02	0.79	0.07	4.32	10.77	0.95	3.65	1.28	20.98
R02022612	2/26/02	Urban canyon, surface	0.55	0.13	0.04	1.79	6.08	0.63	2.35	0.86	11.70
R02022616	2/26/02	Afternoon Freeway Commute	0.68	Missing	0.04	2.24	5.82	0.53	1.94	0.70	11.24
R02022708	2/27/02	In van, gas station	0.16	nd	0.12	1.14	6.72	0.63	2.63	0.99	12.11
R02022712	2/27/02	Gas station, refueling	1.58	nd	2.06	10.37	53.38	2.93	12.00	3.96	82.65
R02022811	2/28/02	pedestrian walk	0.16	0.47	0.01	0.69	2.29	0.22	0.85	0.31	4.35
R02030109a	3/1/02	Res. Garage, background	0.03	Missing	0.03	0.29	1.67	0.31	1.15	0.50	3.93
R02030109b	3/1/02	Kitchen, background	0.03	Missing	0.01	0.31	1.25	0.13	0.49	0.20	2.38
R02030109c	3/1/02	Residential garage	0.22	0.98	0.95	9.53	164.44	11.18	48.17	17.39	250.71
R02030109d	3/1/02	Kitchen	0.10	nd	0.36	3.66	55.34	3.60	15.54	5.68	83.82
R020301016	3/1/02	Mobile gas generator	17.38	nd	0.58	41.03	123.23	9.95	34.21	12.16	220.57

Nd = not detected
Missing – missing sample

Table 2-2. Comparison of MS200 with Canisters

		Canisters						MS200 Summary Corrected Values, ppbv			
Date	Location	benzene	toluene	ethyl benze	m/p-xylene	o-xylene	Sum Xylenes	Benzene	Toluene	Xylenes	
2/26/02	Morning Freeway Commute	4.32	10.77	0.95	3.65	1.28	4.93	4.38	10.69	5.15	
2/26/02	Urban canyon, surface	1.79	6.08	0.63	2.35	0.86	3.20	9.20	8.66	4.33	Limited Data
2/26/02	Afternoon Freeway Commute	2.24	5.82	0.53	1.94	0.70	2.65	12.53	5.89	4.90	
2/27/02	In van, gas station	1.14	6.72	0.63	2.63	0.99	3.62	9.17	4.71	4.82	Limited Data
2/27/02	Gas station, refueling	10.37	53.38	2.93	12.00	3.96	15.96				No Data
2/28/02	pedestrian walk	0.69	2.29	0.22	0.85	0.31	1.16	3.11	2.37	2.60	
3/1/02	Res. Garage, background	0.29	1.67	0.31	1.15	0.50	1.65	2.57	5.21	11.76	
3/1/02	Kitchen, background	0.31	1.25	0.13	0.49	0.20	0.69	8.69	5.84	10.40	
3/1/02	Residential garage	9.53	164.44	11.18	48.17	17.39	65.56	9.30	91.20	46.59	
3/1/02	Kitchen	3.66	55.34	3.60	15.54	5.68	21.22	13.95	66.25	32.15	
3/1/02	Mobile gas generator	41.03	123.23	9.95	34.21	12.16	46.37	38.33	115.25	51.79	

Table 2-3. Comparison of Formaldehyde Data

Date	Time	Test ID	DNPH-HCHO	Battelle-HCHO
2/26/02	0710	R02022607	6.66	7.9
2/26/02	1200	R02022612	9.66	7.9
2/26/02	1600	R02022616	6.84	6.2
2/27/02	0810	R02022708	4.13	5.5
2/27/02	1200	R02022712	4.62	
2/28/02	1100	R02022811	2.30	1.1
2/28/02	1503	R0202815	4.96	3.5
3/1/02	0935	R02030109a	3.56	4.6
3/1/02	0935	R02030109b	2.39	
3/1/02	1110	R02030109c	6.27	5.4
3/1/02	1110	R02030109d	4.15	5.2
3/1/02	1600	R020301016	23.29	20.7

2.3 Solid Phase Microextraction (SPME)

We tested the SPME technique during the pilot study for the collection and analysis of BTEX, MTBE, ethanol, formaldehyde, and acetaldehyde. A 100 μm (poly)dimethylsiloxane (PDMS) fibers and 75 μm Carboxen/(poly)dimethylsiloxane (CAR/PDMS) fibers were used for BTEX, MTBE, and ethanol and 65 μm PDMS/divinylbenzene (DVB) fiber that was impregnated with o-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) was used for carbonyl compound collection. The fibers were exposed in parallel for 15 min, with exception of the residential garage microenvironment where the fibers were exposed for 30 min. The fibers were analyzed by injection into a GC housed in the mobile laboratory. Some of the fibers were also analyzed by GC/MS. The analysis was performed immediately after collection, when possible. However, some of the fibers had to be stored on dry ice in the cooler for a period of several hours.

The initial SPME results from the pilot study are more qualitative than quantitative. The technique is new method for us and requires additional calibration work in the laboratory. Our major findings from the pilot study include:

- 75 μm CAR/PDMS fibers are more sensitive than 100 μm PDMS fibers and are thus more suitable for ambient measurements. We will be using 75 μm PDMS fibers in the main study for the measurements of MTBE and BTEX.

- Although ethanol peak was observed in all chromatograms, the ethanol concentrations were clearly too high. This is most probably due to the adsorption of ethanol from breath into the fibers. We measured up to 200 ppbv of ethanol concentration in the breath samples collected during this pilot study. The fibers were situated in the breathing zone during each experiment.

- Formaldehyde and acetaldehyde concentrations are too high as well when compared with continuous formaldehyde analyzer data and integrated DNPH cartridge data. This may also be due to the presence of acetaldehyde in breath (we measured up to 25 ppbv of acetaldehyde in the breath samples). In addition, formaldehyde may be present in the mobile lab where the PFBHA impregnation of the PDMS/DVB fibers took place. We are getting the continuous formaldehyde analyzed from Battelle, thus we do not see any need to monitor formaldehyde with SPME technique and we propose to drop this analysis. Acetaldehyde data are less important for this study and we will obtain this data from integrated DNPH cartridge method.

In summary we are still working on the development of the standard procedures for the SPME technique. The calibration, storage, and optimal sampling time are being addressed. We will be ready for the main study starting in June and we propose to use the SPME method for measurements of BTEX and MTBE.

2.4 Biological Samples

2.4.1 Breath VOC Concentrations

Breath concentrations are portrayed in Table 2-4 and Figures 2-23 through 2-25 for two separate subjects during three separate scripted exposures. For the pilot project the subjects were two of the technicians collecting samples for micro-environmental concentrations. The objectives of this pilot program for the breath monitoring were to 1) evaluate the ability to analyze breath concentrations of VOC's according to methods developed by Pleil and Lindstrom (1995), 2) to see differences between full and alveolar breath collections, 3) to assess breath concentrations between two subjects prior to and after scripted environmental exposures, and 4) to develop a recommendation for the final sampling protocol and biological monitoring technique of choice. All of the samples shown and discussed are "alveolar" samples unless designated as "full-breath" samples. Alveolar samples were collected to represent material that has undergone gas exchange in the lung. These samples were collected by breathing the end part of a breath directly into an evaculated cylinder (1 or 3L). The results of the breath measurements are described below.

Refueling

Subject 7: The out of cabin re-fueling experiment showed the highest average exposure concentrations for all of the samples where biological samples were collected, by at least a factor of 5 for most analytes. As expected from results published by Philips and Greenberg (1992), all of the analytes (except MTBE) show a negative alveolar gradient (concentration in breath lower than ambient air) relative to the average exposure concentrations of 60 minutes. Unfortunately there is no real time data for these compounds, and the elimination rate via breath is rapid enough that real-time levels towards the end of exposure would be most important for these compounds. For subject 7 there is an observed exposure effect, with post exposure alveolar concentrations higher than pre-exposure concentrations by at least a factor of 2. With the exclusion of MTBE and ethyl benzene, this exposure effect was not observed for most compounds in subject 3. Exposure for the outside refueling was terminated at 1300 hours. The mobile lab was located approximately 1-2 minutes walking distance away from the exposure area and the exposure subjects were also responsible for much of the sampling responsibilities. Expired breath was not collected from subject 7 until 1302, and not from subject 3 until 1304. These short differences in times between samples may explain the lack of an exposure effect observed in subject 3. This can be confirmed by the breath elimination half-lives published to be between 1 and 3 minutes for MTBE, benzene, and toluene (Lindstrom and Pleil, 1996).

In-Cabin Refueling

Subject 7 was the only subject sampled for both pre and post samples of the in-cabin refueling exposure. With the exception of MTBE, there is no exposure effect. This is most likely due to the fact that the post-exposure breath sample was not collected until 0919, 9 minutes after exposure. This may be enough time to eliminate back down to background levels.

Table 2-4. Concentrations (ppbv) of volatile organic compounds in breath and micro-environments.

Sample	Collection Time	Location	Subject	MTBE	benzene	toluene	ethylbenzene	m/p xylene	o-xylene
Breath	800	In Cabin fueling PRE	7	0.32	0.92	2.05	0.33	0.84	0.23
Breath	919	In Cabin fueling POST	7	0.79	0.82	1.92	0.33	0.89	0.23
microenvironment		van, Verdi gas station	microenviront conc.	0.12	1.14	6.72	0.63	2.63	0.99
Breath	1149	Refueling PRE	7	0.35	0.75	1.74	0.33	0.85	0.27
Breath	1302	Refueling POST	7	3.99	1.83	5.73	1.06	3.70	1.58
Breath	1415	Midday Background	7	0.08	0.58	1.41	0.00	1.01	0.32
Breath	1150	Refueling PRE	3	0.22	1.34	2.62	0.00	1.86	0.41
Full Breath	1304	Refueling POST	3	1.54	1.52	3.16	0.67	1.76	0.44
Alveolar Breath	1305	Refueling POST	3	1.84	1.24	2.53	0.48	1.29	0.31
microenvironment		Verdi gas station, refuel	microenviront conc.	2.06	10.37	53.38	2.93	12.00	3.96
Breath	1415	Midday Background	3	0.47	1.10	2.26	0.55	1.44	0.33
Breath	1422	Midday Background	7	0.80	0.76	1.83	0.00	0.86	0.25
microenvironment		pedestrian walk	microenviront conc.	0.01	0.69	2.29	0.22	0.85	0.31
Breath	924	Morning Background	3	0.28	1.18	2.42	0.63	1.63	0.00
Breath	1043	Walk PRE	3	0.69	1.56	0.00	0.65	1.70	0.43
Breath	1201	Walk POST	3	0.31	1.44	3.00	0.73	1.87	0.45
Breath	1047	Walk PRE	7	0.79	0.99	2.34	0.41	1.30	0.42
Breath	1200	Walk POST	7	0.32	0.84	2.18	1.16	5.25	2.18
Full Breath	1623	Direct Exhaust Exposure	3	0.12	1.36	2.73	0.41	1.20	0.33
Alveolar Breath	1623	Direct Exhaust Exposure	3	0.09	1.38	3.79	0.59	1.56	0.42

Pedestrian Walk

Again for the pedestrian walk there is very little exposure effect observed from subject 3 while subject 7 shows at least a factor of 2 increase in alveolar concentrations after exposure for ethyl benzene, m/p xylene, and o-xylene. Similar to the refueling samples, subject 3 was did not give their sample at the same time as subject 7. There was a one-minute difference between subject 3 (1201) and subject 7 (1200). There was a negative exposure effect for MTBE in both subjects, suggesting that pre-exposure background or residual subject concentrations are higher than the exposure. The un-observable exposure effect for benzene and toluene are not explainable, as the exposure to these compounds was actually higher than the compounds where an exposure effect was observed.

Full versus Alveolar Breath

Figure 2-26 shows the relationship between full and alveolar breath. Full and alveolar breath are defined here by how the sample was collected. Full is the entire breath blown into the canister sample, while the "alveolar" breath consists of partially reserved tidal volume and some expiratory reserve. The alveolar sample is collected at the end of a regular breath. As observed the agreement between the two breath collection methods are reasonable, but vary slightly by analyte. Agreement is between 15-25% for MTBE, benzene and toluene; and about 40% for ethyl benzene and the xylenes. In general, the difference is higher for compounds where the concentrations are less, indicating some contribution from measurement uncertainty may affect observed differences. Since the observed concentrations are higher in the full breath samples (with the exception of MTBE), it is obvious that there are levels of these compounds in the "dead-space" region of the subject that has not undergone any gas exchange. CO_2 measurement between the two samples shows a difference of 10%, which is 5% less than the difference observed by Pleil and Lindstrom (1995). 15% is the expected amount, based on a 15% dilution of a 1 liter tidal volume. The full and alveolar breath sample in this pilot study was taken from a 3 liter evacuated canister, which is different than the 1 L canister used by the second subject and in the Pleil and Lindstrom paper. Additional experiments should be completed comparing full/alveolar breath CO2 dilution between the 1 and 3 liter canisters.

2.4.2 Urine VOC Concentrations

Urinary concentrations of MTBE, benzene, toluene, ethylbenzene, and the xylenes were measured for backgrounds and pre/post exposure levels in two subjects from three scripted exposures. Shown in Table 2-5 are the urinary concentrations of benzene, which was the only urinary constituent consistently above the analytical limit of quantitation of 100 ng/L. The objectives of this pilot study was to apply the technique of 1) Fustinoni (1999) to measure urinary volatile organic compounds, 2) to measure concentrations (and variability) in two separate subjects, and 3) to evaluate results in terms of their ability to relate to exposure concentrations. In the original proposal one objective was also to measure urinary creatinine levels. This was not conducted for this report because this is not conducted in the contemporary literature to report urinary concentrations of VOC's. "Older" literature used to measure creatinine in order to normalize urinary components for dilution. The current belief is that this is not necessary. The benzene results are discussed below for each scripted exposure.

In-cabin Refueling

Subject 3 had a high pre-exposure background (208 ng/L) prior to the in-cabin refuel. There was a negative exposure effect after the in-cabin exposure (<100 ng/L), and a higher concentration one hour after exposure (138 ng/L) than immediately after exposure. This sample was similar to the next pre-exposure concentration taken one hour later (120 ng/L). Subject 7 had both pre and post exposure levels for the in-cabin re-fuel that were below the detection limit of 100 ng/L (3 x baseline).

Table 2-5. Urinary benzene concentrations in two subjects exposed to three micro-environments

Time	Date	subject	activity	Benzene ng/L
520	227	3	background	118.3
520	227	3	background	141.8
755	227	3	preexpos in cabin refuel	208.1
920	227	3	postexpos in cabin refuel	90.4[a]
1010	227	3	mid background	139.8
1148	227	3	preexpos refuel	118.6
1308	227	3	post expos refuel	3.1[a]
1417	227	3	post expos refuel	166.3
1524	227	3	post expos refuel	465.8
1645	227	3	post expos refuel	1100.6
950	228	3	pre walk	276.7
1225	228	3	post walk	335.5
445	227	7	background	163.9
752	227	7	preexposin cabin refuel	26.4[a]
924	227	7	postexpos in cabin refuel	0.0[a]
1150	227	7	preexpos refuel	15.4[a]
1312	227	7	post expos refuel	11.4[a]
1424	227	7	post expos refuel	18.1[a]
1620	227	7	post expos refuel	101.8
545	228	7	background	0[a]
1229	228	7	prewalk	106.5
1415	228	7	post walk	131.0

a: below the limit of quantitation of 100ng/L

Refueling

Subject 3 showed a negative exposure effect immediately after exposure, but saw a steady increase in urinary benzene excretion throughout the day. Measurements were made approximately every hour until 1645, and the hourly concentrations were 166, 465, and 1100 ng/L at 1417, 1524, and 1645, respectively. This indicates that for these samples the time course for urinary excretion is much slower than it is for breath, and there is a lag in the excretion. The exposure concentrations observed for subject 7 were all below 100 ng/L, with the exception of the post exposure sample collected at 1620, where the concentration was about 100 ng/L. These results are comparable to MTBE data reported by Lee and Weisel (1998) who showed an increase in urinary MTBE after exposure (1 ppm for 10 min) at about 1 hour, remaining about the same at 3.5 hours and dropping several-fold by 6 hours.

Pedestrian Walk

There was a slight positive exposure effect for benzene in both subjects from the in-town walk. Subject 3 had a pre-exposure urinary benzene concentrations of 276 ng/L and post-exposure concentrations of 335 ng/L, while subject 7 had levels of 106 and 135 ng/L. For both subjects the starting background was different, and their increase was approximately the same for this exposure.

2.5 Results of Additional Refueling Experiment (June 4, 2002, Reno)

This experiment was conducted in order to test the response of MS200 (since we were not able to operate the instrument during the refueling experiment in February) in this microenvironment and to repeat breath and urine testing to confirm the conclusions drawn from the pilot study. There were important differences between this refueling and the one conducted for the pilot study. Most importantly:

- We only filled the canister during the actual exposure period of 30 min. During the pilot study, we filled the canister over 1 hour, which consisted of 15 min of background plus 45 min of exposure.
- Used one exposure subject rather than two.
- Refueled two vehicles instead of three.
- The MS200 data output was adjusted to sum the xylenes and ethyl benzene using a single library spectra. The reason for this is that there is very little difference between the spectra of these four compounds and we found that the software did not do well trying to separate them.

In addition to the MS200 and the canister, we also collected 5 breath samples and 8 urine samples that were analyzed by LRRI. The five breath samples were: Pre test; 15 min into test; approximatelly 2 min post test; 5 min later; and 10 min later. The urine samples included: pre-test; approximately15 min post exposure (no urinary output between these two); approximately

every hour thereafter for 6 more hours. All the voids from the test subject between the hours of 0730 and 1800 were collected.

2.5.1 MS200 and Canister Results

Figure 2-27 shows the time series of the concentrations of benzene, toluene and the sum of xylenes and ethylbenzene in parts per million by volume, ppmv. The data are one-minute averages recorded by the MS200. To convert this unit to canister data units (which are parts per billion of carbon or ppbC), multiply by the number of carbons and by 1000 to adjust ppm to ppb. For example, the highest spike seen (at appx 21 min) is 0.173 ppmv for toluene, which is equivalent to 1211 ppbC. Benzene in the same spike is 0.104 ppmv or 624 ppbC. Sum of xylenes highest reading at about 22 min is 0.135 ppmv or1080 ppbC.

The averages of the MS200 data are in good agreement with the canister measurements. The data are as follows (units are ppbC):

Compound	**MS200 (ppbC)**	**Canister (ppbC)**	**% error** **(difference/can value)**
Benzene	128.2	142.1	9.7
Toluene	413.8	438.4	5.6
Sum Xyl+EBz	336.6	368.2	8.6

2.5.2 Breath Sample Results

As explained above, the breath samples were collected in 1-liter stainless steel canisters from one subject. Table 2-6 below lists the results obtained from these samples (the units are ppbC):

Table 2-6 Breath Data in ppbC

Site/Compound	Pre refueling breath	Middle of run breath	Post exposure breath #1 (2 min)	Post exposure breath #2 (5 min)	Post exposure breath #3 (10 min)
sample_time (hr)	0945	1046	1103	1107	1111
sample_date	6/4/02	6/4/02	6/4/02	6/4/02	6/4/02
1,3-butadiene	0.21	0.83	7.46	0.44	0.41
MTBE	0.00	3.03	1.34	1.91	1.14
benzene	2.65	14.76	7.82	10.76	9.78
toluene	5.98	47.32	123.54	27.59	25.17
ethyl benzene	0.83	1.01	2.77	8.46	7.75
m/p-xylene	2.61	14.12	18.77	28.75	46.36
o-xylene	1.66	5.59	3.82	7.03	16.88

These data are consistent with the data obtained during the pilot study, confirming very short breath elimination half-lives of the compounds measured. In addition, this elimination time is different for every compound. Whereas benzene concentration is the highest in the middle point of the exposure, and declines significantly two minutes after exposure, toluene concentrations are the highest 2 min after exposure, declining sharply five minutes after the exposure. Thus, breath data obtained after an integrated exposure period of an hour will not accurately measure the biological uptake that occurs under variable condition during the exposure period.

2.5.3 Analysis of Urinary VOC Concentrations

Urinary concentrations of MTBE, benzene, toluene, ethyl Benzene, and the xylenes were analyzed utilizing the same methods described for the Reno pilot study protocol. In addition, for these data we analyzed urinary creatinine values and urinary ethanol. Creatinine values were obtained using a standard creatinine analysis kit on a Monarch 2000 clinical chemistry instrument. Ethanol data were obtained utilizing the same solid phase extraction fibers that were used for the other chemical species.

Table 2-7 lists the concentrations of measured species, including creatinine, and Figure 2-28 shows the data for BTEX and MTBE. Urinary concentrations of all of the measured VOC's except ethanol were present in detectable limits in most of the samples. The absence of ethanol may be due to the high detection limits of (0.5 ng/L) relative to the other analytes, which are detectable in much lower concentrations. If urinary ethanol is to be monitored in follow on studies additional method development will be conducted to decrease the limits of detection on this assay.

Concentrations of the other volatile organics reported here are complicated by the relatively high concentration observed in the pre-exposure samples. Concentrations post-exposure increased throughout the day for benzene and toluene, which is similar to what was observed in the pilot study. However, at their peak, the concentrations of these compounds were only slightly larger than the pre-exposure backgrounds. The concentrations observed in the urine for benzene were consistent with what was observed during the pilot study and in the literature, with values in the range of 100-200 ng/L. The concentrations post-exposure did not increase much beyond 200 ng/L for benzene. These low post-exposure concentrations are consistent with the results from subject 7. While the highest urinary concentrations for subject 7 in this study do not reach levels reported for subject 3 in the pilot study, subject 7 does show an increase in urinary benzene and toluene throughout the day, which is consistent with subject 3 in the pilot study. The currently reported results do show concentrations of toluene that are increased relative to benzene, which is consistent with the higher concentrations of toluene that the subject was exposed to. The toluene concentrations do not, however, increase well above the pre-exposure background concentrations.

Creatinine was measured during this follow-on study in response to some criticism from an external reviewer that creatinine values would help determine concentration effects resulting from dilution. As reported in the pilot study report, the concentrations of urinary VOC's in the contemporary literature are typically not normalized to creatinine concentration. One example of the rationale for not using creatinine correction is given in Albertine et al. (2001), where

statistical relationships between exposure and urinary concentrations of butadiene biomarkers were more significant when not normalized.

Table 2-7
Concentrations of Ethanol, MTBE and BTEX in urine samples (ng/L)

Re-do of Refueling Experiment

Sample #	Subject	Time	Date	Description	Ethanol	MTBE	Benzene	Toluene	Eth Benzene	p/m xylene	o-xylene	Creatinine mg/dL
					Concentrations in ng/L							
1	7	820	6/4/02	pre exposure-morning	nd	0.024	0.165	0.265	0.062	0.057	0.080	7
2	7	1115	6/4/02	post exposure	nd	0.052	0.103	0.112	0.039	0.039	0.066	33
3	7	1215	6/4/02	post exposure	nd	0.030	0.135	0.149	0.057	0.057	0.098	56
4	7	1327	6/4/02	post exposure	nd	0.033	0.089	0.135	0.047	0.046	0.066	23
5	7	1430	6/4/02	post exposure	nd	0.021	0.143	0.202	0.051	0.035	0.066	26
6	7	1522	6/4/02	post exposure	nd	0.017	0.203	0.283	0.042	0.042	0.066	13
7	7	1624	6/4/02	post exposure	nd	0.009	0.238	0.279	0.051	0.044	0.071	13
8	7	1718	6/4/02	post exposure	nd	0.013	0.106	0.114	0.046	0.040	0.070	22

3. RECOMMENDATIONS

This section describes the equipment and protocols we recommend for this program. We first summarize the equipment in Table 3-1 and then discuss each individually.

Table 3-1
Recommendation Summary

Instrument	Recommendation	Notes
Battelle HCHO	Yes	We have requested Battelle build one for DRI.
Kore MS-200	Yes	Needs protocol development and possibly preconcentrator.
TEI TVA1000	No	Not sensitive enough.
Innova Photoacoustic	No	Grab sampling method; overlap with other instruments.
Langan T15 CO	Yes	Need to develop temperature dependence.
Integrated Samples	Yes	
SPME	Yes	Would be used only for MTBE and BTEX

3.1 Exposure Measurements

Formaldehyde Monitor. The Battelle instrument appears to have performed quite well. We evaluated a similar commercial instrument made by Alpha Omega during a three-day evaluation period at the end of May 2002. The evaluation consisted of collocated measurements with our CO analyzer, Kore MS200 analyzer and integrated DNPH measurements using microenvironmental exposures similar to those used during the pilot study. Base upon the results of this evaluation, we concluded that the Alpha Omega HCHO monitor would be suitable for the main study.

Kore MS200. The MS200 appears to have performed rather well in the pilot study. We are currently refining the protocol for using this instrument, based on the results from the field study as well as the results of many experiments we have conducted since that time. We hope to install an automated system for zeroing the instrument during the run times to confirm the zero point of the instrument as it changes during the day. In addition, we will be standardizing the zeroing procedure and are working on methods to automate the background subtraction process. We recommend the use of the instrument in the main study.

TEI TVA1000. The TVA1000 is a FID based detector for total hydrocarbons. As such it responds approximately equally to the concentration of oxidizable carbon in the air. In the present experiment that means it has the challenge of measuring small amounts of the hydrocarbons of interest in the presence of a relatively high concentration of methane. In

addition since there is no speciation, we are not obtaining any information about the relative contribution of any of the components. Also, the baseline is not very stable and we do not think it adds a lot of useful information. Our recommendation is to not use this instrument.

Innova Photoacoustic. This instrument can measure CO, CO_2, total hydrocarbons and water vapor (dew point). However, the instrument is not a true "continuous" monitor, but rather it takes grab samples, measures that sample and then takes another grab sample. This means that the value determined may not accurately represent the average over the time period it is applied to. We feel that a better way to obtain total hydrocarbons is to compare CO and BTEX from continuous instruments to the same compounds in the canisters. Our recommendation is to not use this instrument.

Langan T15 CO monitor. This instrument appears accurate and easy to use in addition to being portable with very low power consumption. It is, however, temperature dependant and we will need to develop a temperature based calibration to maintain accuracy. In addition, it appears to have a slower response time, especially post-exposure to a high concentration, but this was only noticeable in the extreme case of the generator at DRI where concentration changes were over 100 ppm in less than 1 minute. We do recommend using this instrument.

Integrated Samples. We recommend collecting integrated samples as a check on the continuous samples and to get more detailed speciation of VOCs. The association between the continuous CO and BTEX data with the data from time-integrated measurements can provide estimates of the time series for species without feasible methods for continuous measurement such as 1,3 butadiene, acetaldehyde, ethanol, MTBE, and total nonmethane hydrocarbons..

SPME. Based on our pilot study, we consider this technique as very promising. We propose to use SPME for MTBE and BTEX, but not for ethanol, formaldehyde and acetaldehyde. We are currently working on perfecting our calibration procedure. We are also performing the series of experiments to determine the optimal exposure time and the dependence of measured concentrations on storage conditions.

3.2 Recommendations for Measurements of VOC in Breath

During the pilot study breath concentrations of MTBE, benzene, toluene, ethylbenzene, and the xylenes was successfully conducted. Analysis of alveolar and full breath showed that the sampling technique to target alveolar breath excluded contributions of VOC's present in the "dead-space" air present in a full breath because their concentrations were lower. Breath concentrations between the two separate subjects differed in many cases most likely because of slight differences in the time of sample collection. This is because the breath elimination half-lives of the compounds measured are between 1 and 3 minutes (Lindstrom and Pleil, 1996), so slight differences in the time of collection can make large differences in observed breath concentrations. This can also explain why for many of the samples there was little or no exposure effect observed. These samples were generally collected minutes after the end of the exposures, after which much of the target compounds would have been eliminated. This effect was observed by Lioy et al. (1991), who saw little correlation with breath benzene concentrations and microenvironmental exposure concentrations, and attributed their lack of agreement to the short time course of benzene elimination via breath.

When collected in exposure environments where the concentrations are above background (e.g. refueling) there is an observable exposure effect when the sample is collected very close to the end of exposure. However, these breath concentrations will only reflect what the subject is exposed to in the last portion of the exposure, as the majority of the one-hour exposure will have been eliminated by the time the samples are collected. Therefore single breath measurements at the termination of exposures are not a good index of cumulative one-hour exposures. Therefore, we do not recommend breath measurements for urban exposure experiments during the main study.

3.3 Recommendations for Measurement of VOC in Urine

The method of Fustinoni (1999) based on a sensitive SPME technique was developed for application to this study. Work at LRRI was conducted with the same instrument as used in that study, but the published quantitation limits of 12-34 ng/L were not attainable. We were able to observe good signal/noise for all of the analytes in what would likely be the sensitivity range published by Fustinoni (1999). However, the deuterated internal standards utilized for quantitation had small amounts of the parent (un-deuterated) compound present that limited the limit of detection. The area counts of the parent compound in blanks showed integrated area counts from the mass spectrometer of approximately 600 for benzene, when the 100 ng/L standard had area counts of about 2500. The use of the internal standards is necessary to reduce sample to sample variability in the uptake of the VOC's by the SPME fiber.

Because of the low exposure concentrations observed in this study, the amount of urinary benzene and other VOC's were extremely low. Although published excretion rates vary, a typical amount of un-metabolized benzene relative to exposure is on the order of 0.1% (Waidyanatha et al. (2001)). Fustinoni (1999) showed urinary concentrations of benzene to be around 114 ng/L after an approximate 3.5 ppb exposure, and Waidyanatha et al. (2001) have shown 145 ng/L concentrations in "non-exposed" subjects from an occupational exposure study. Similarly, Ghittori et al (1995) showed background levels of benzene in non-smokers of approximately 131 ng/L (geometric mean). Most of the urinary benzene concentrations observed in the currently reported pilot study are in the range of the low level exposures from previous studies described above. Since the scripted exposures were low there was no strong correlation between exposure and urinary benzene in the pilot study. This is slightly in contrast to published results of Waidyanatha et al. (2001), who saw an exposure effect with benzene, but the exposure concentrations were in the ppm range.

After the highest exposure there was a relatively strong exposure effect observed in one subject and a lesser exposure effect observed in a second subject. There was a time course in the elimination of benzene that showed urinary benzene concentrations increasing with time. These results are comparable to MTBE data reported by Lee and Weisel (1998) who showed an increase in urinary MTBE after exposure (1 ppm for 10 min) at about 1 hour, remaining about the same at 3.5 hours and dropping several-fold by 6 hours. Here urinary concentrations were only measured 3 hours post exposure, so we were not able to observe the start of elimination from the body. Because of an inability to see the decay of urinary benzene after exposures, and the slight inconsistency in the two subjects (one showed much higher urinary benzene), we repeated this highest end exposure on June 4, 2002, to see if the urinary VOC concentration data

can be linked strongly to an exposure effect at these levels and to see the full time course of elimination.

Because the additional measurements of urinary MTBE/BTEX from the second refueling experiment were promising, we recommend this measurement as the biomonitoring technique of choice. We will pay special attention to the pre-exposure background urine sample collection, making sure that the subject is not exposed to gasoline exhaust at least 10 hours prior to sample collection. Since we were not able to discriminate urinary benzene concentrations in low-level exposures (e.g. walking down street), we propose to only conduct biomonitoring experiments from projected “high-end” exposures such as refueling. Monitoring will be conducted similar to the pilot study, with pre and post exposure collections of the subject’s urine.

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FIGURE FOR SECTION 2

Figure 2-1 Concentration Time Series, Freeway AM

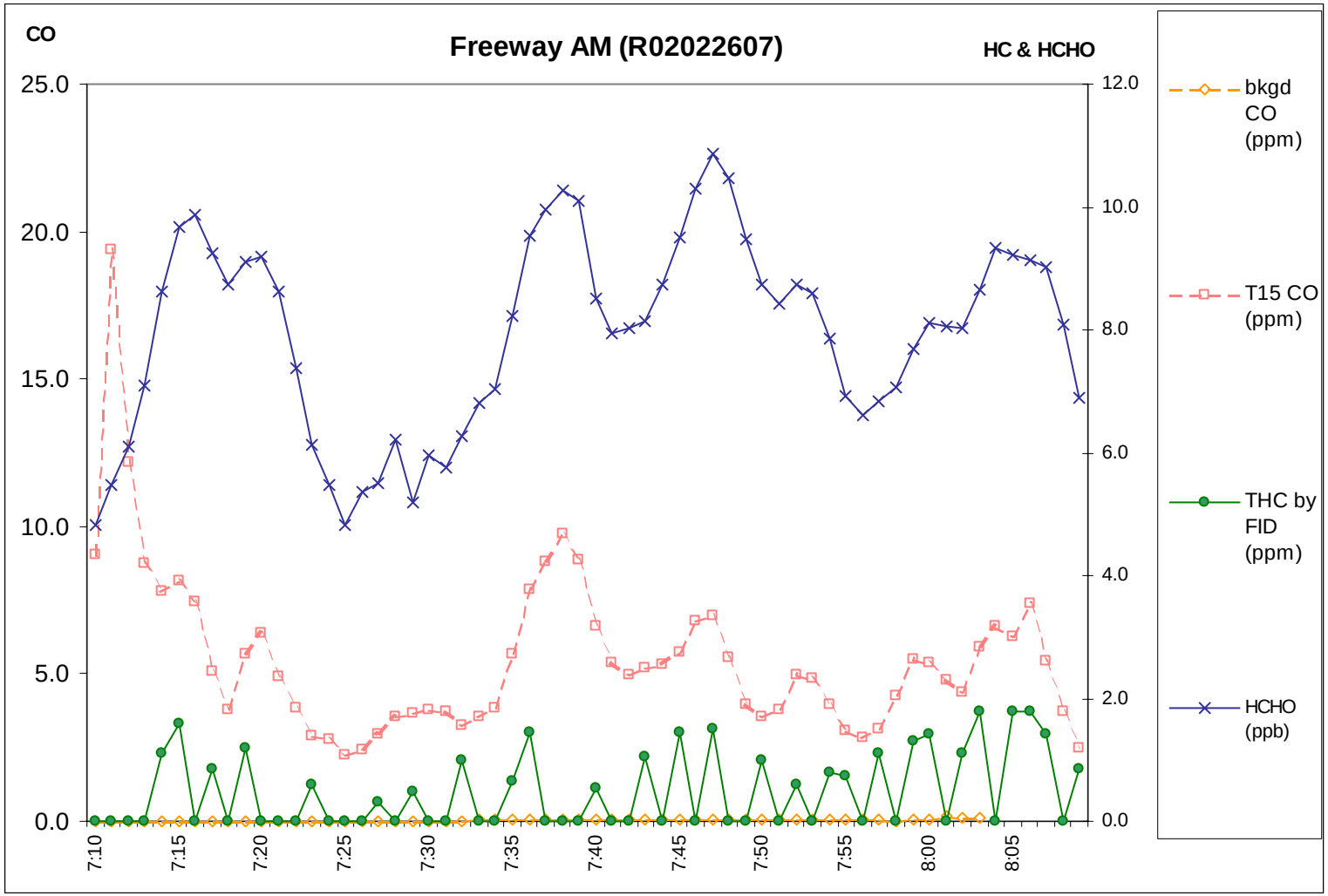


Figure 2-2 Concentration Time Series, Surface Streets

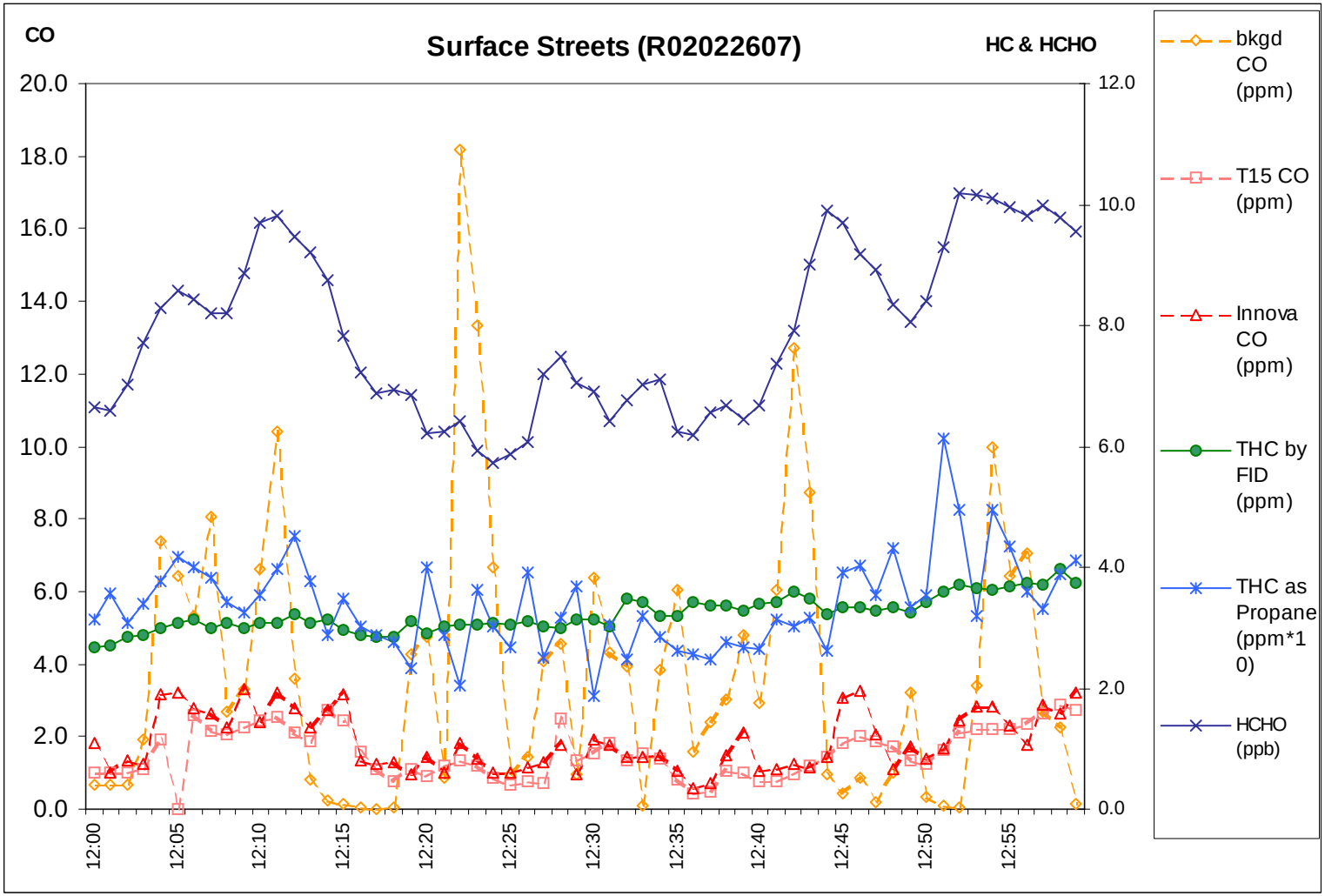


Figure 2-3 Concentration Time Series, Freeway PM

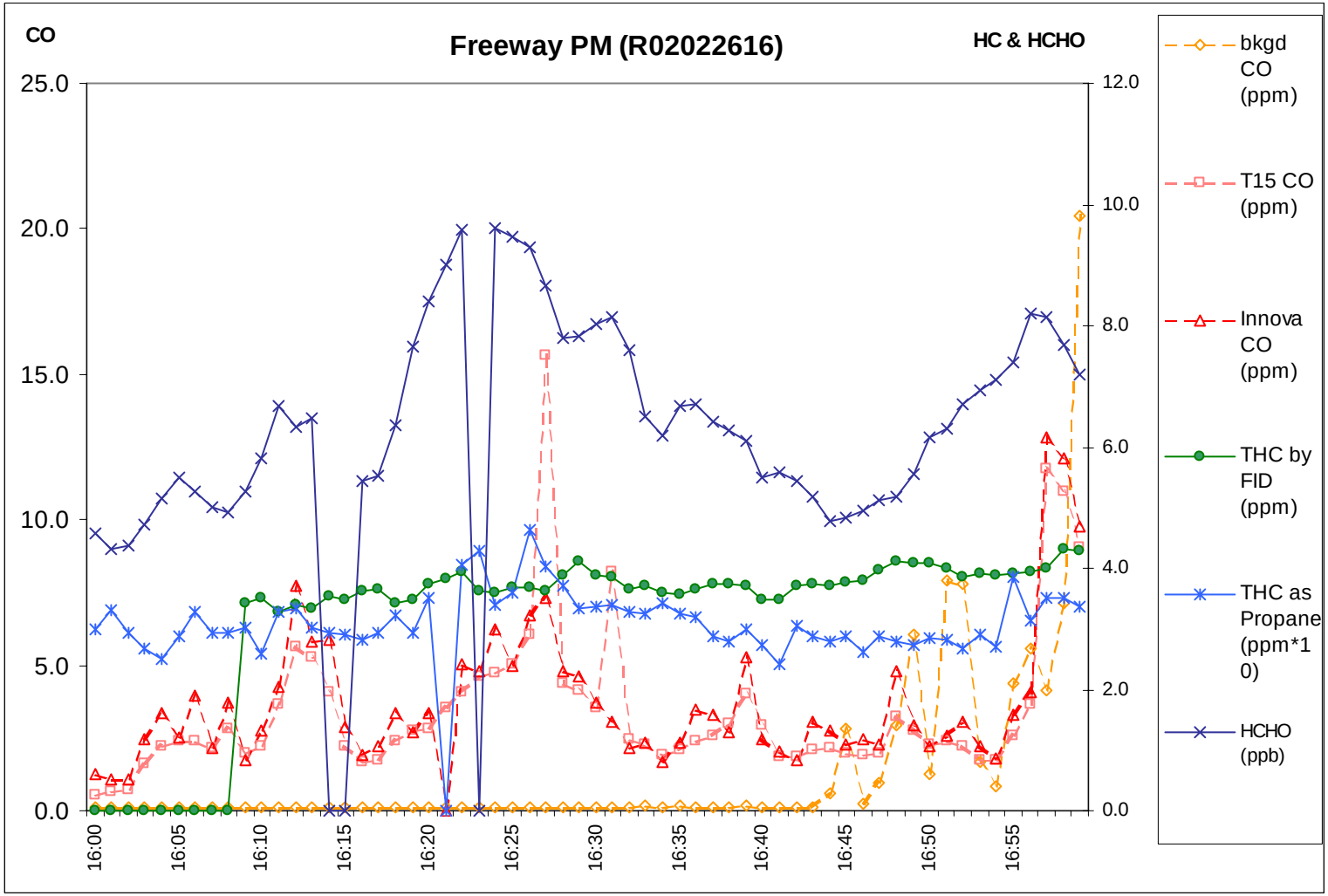


Figure 2-4 Concentration Time Series, Refueling In-Cabin

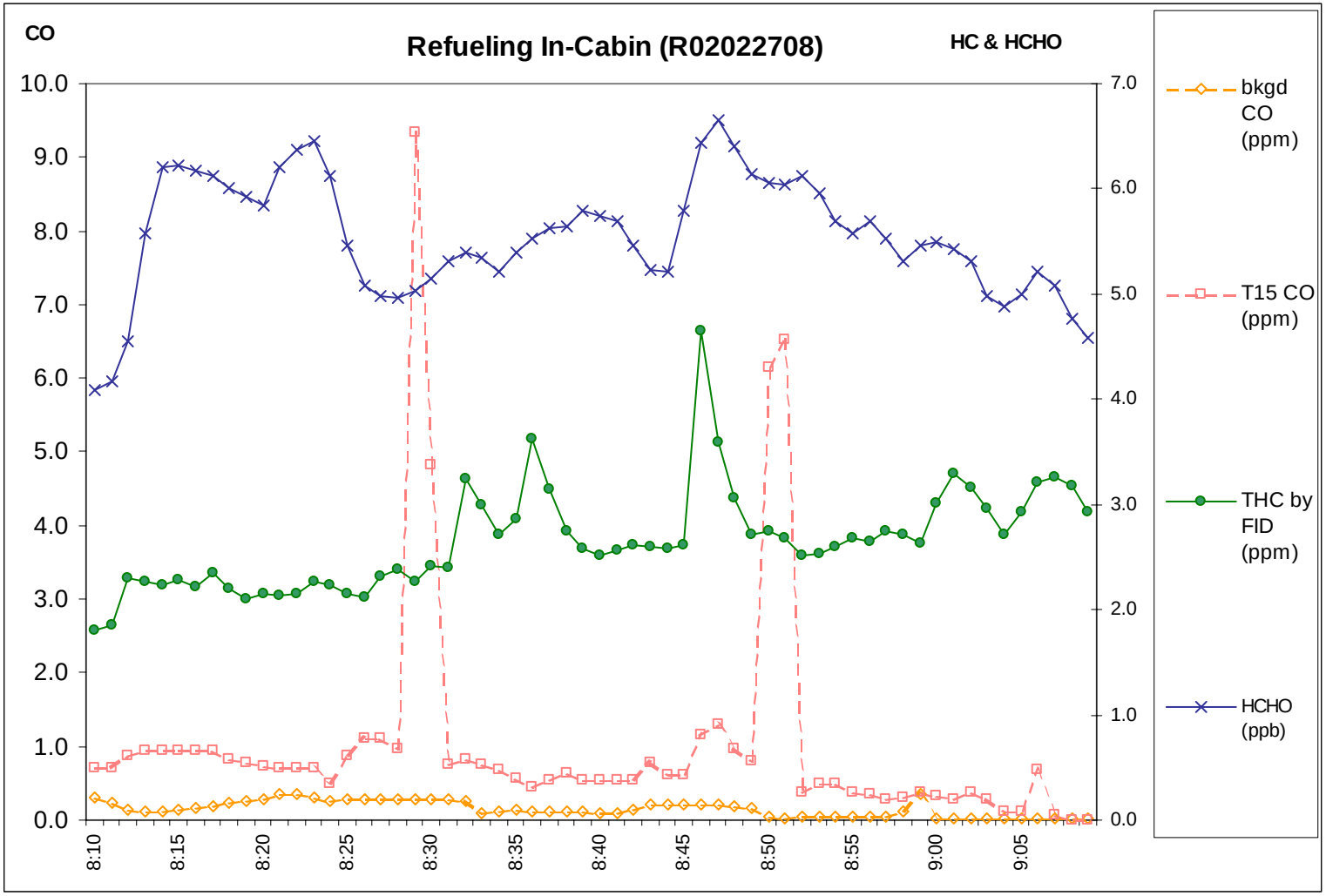


Figure 2-5 Concentration Time Series, Refueling out of cabin

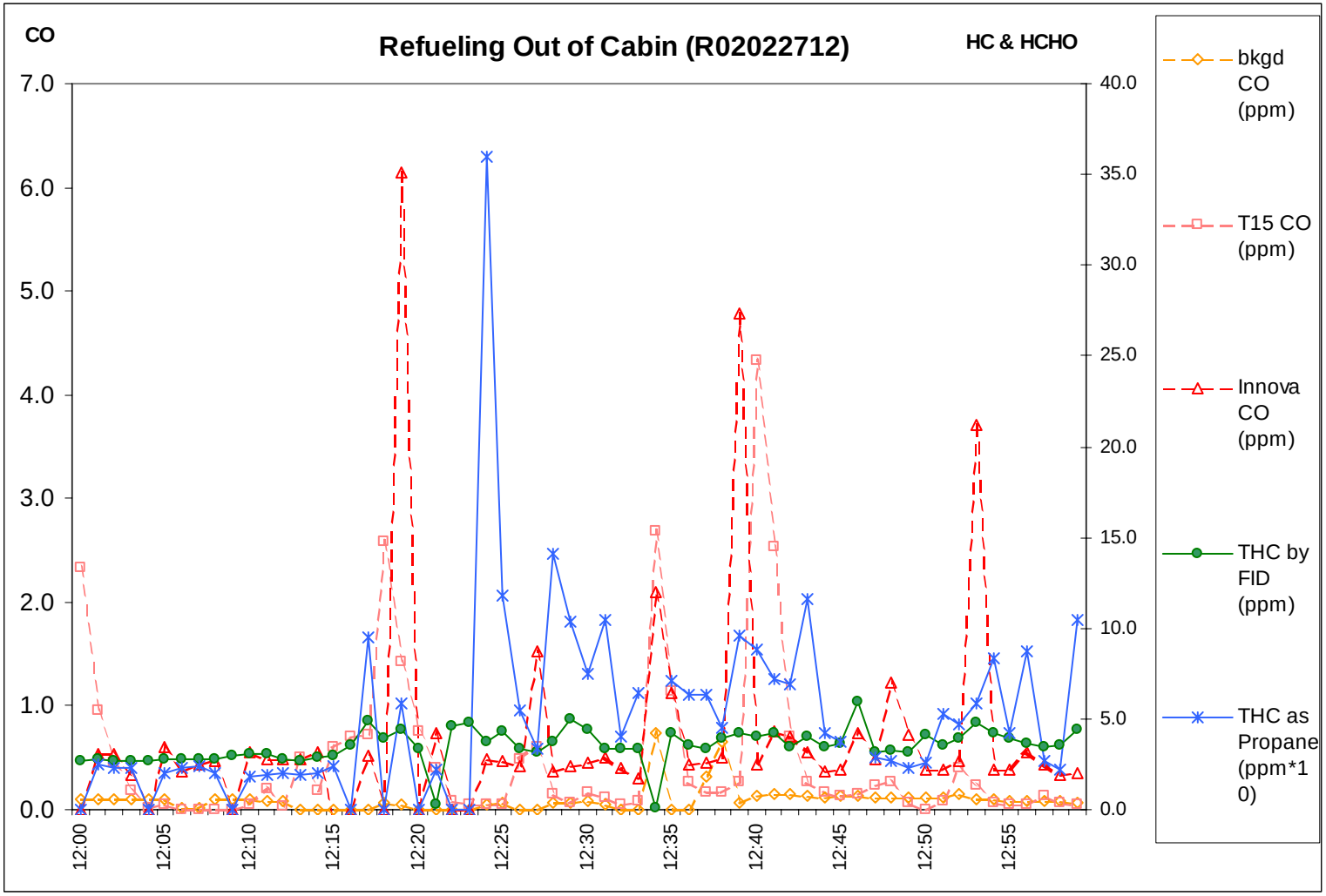


Figure 2-6 Concentration Time Series, Walking Downtown

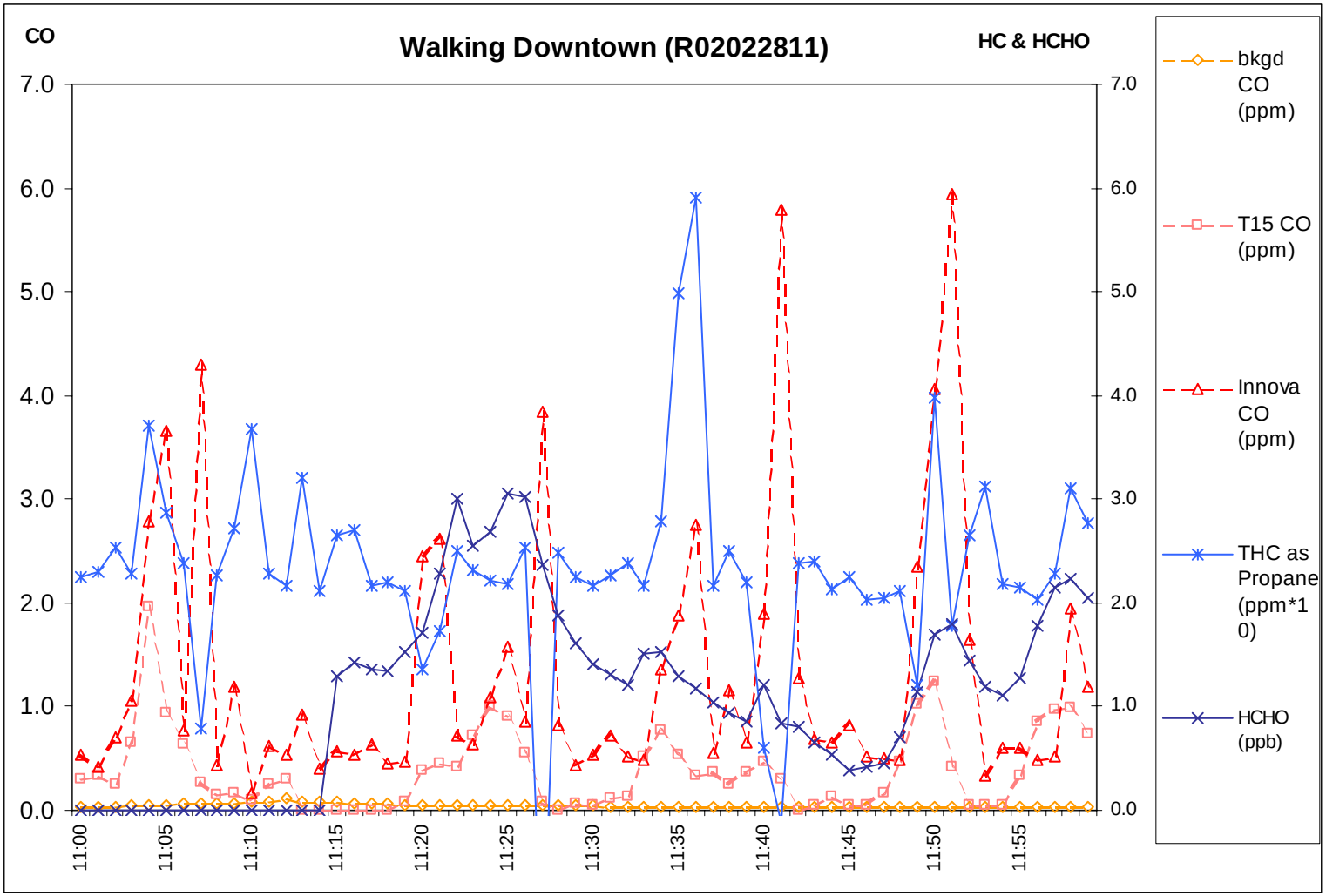
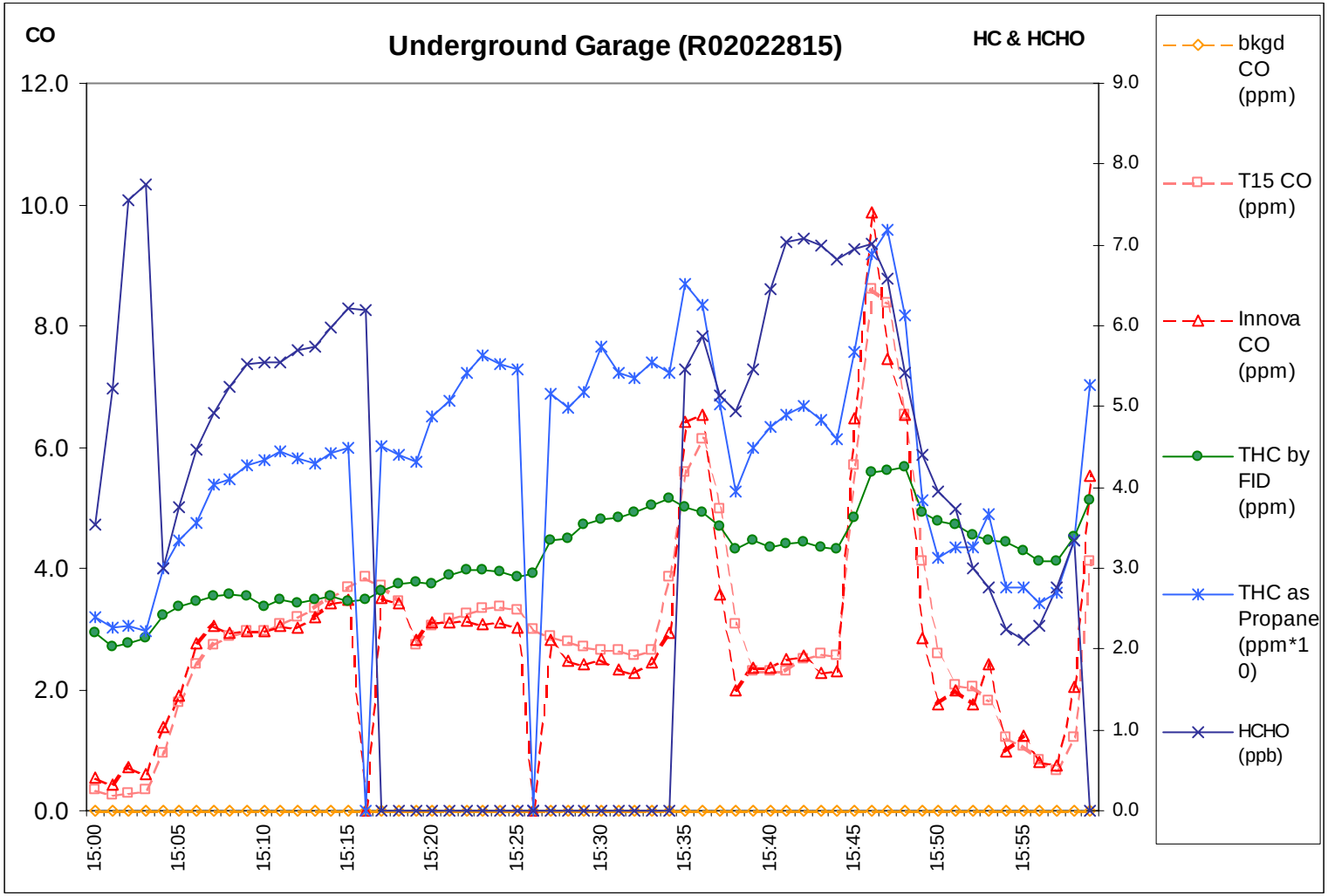


Figure 2-7 Concentration Time Series, Underground Garage



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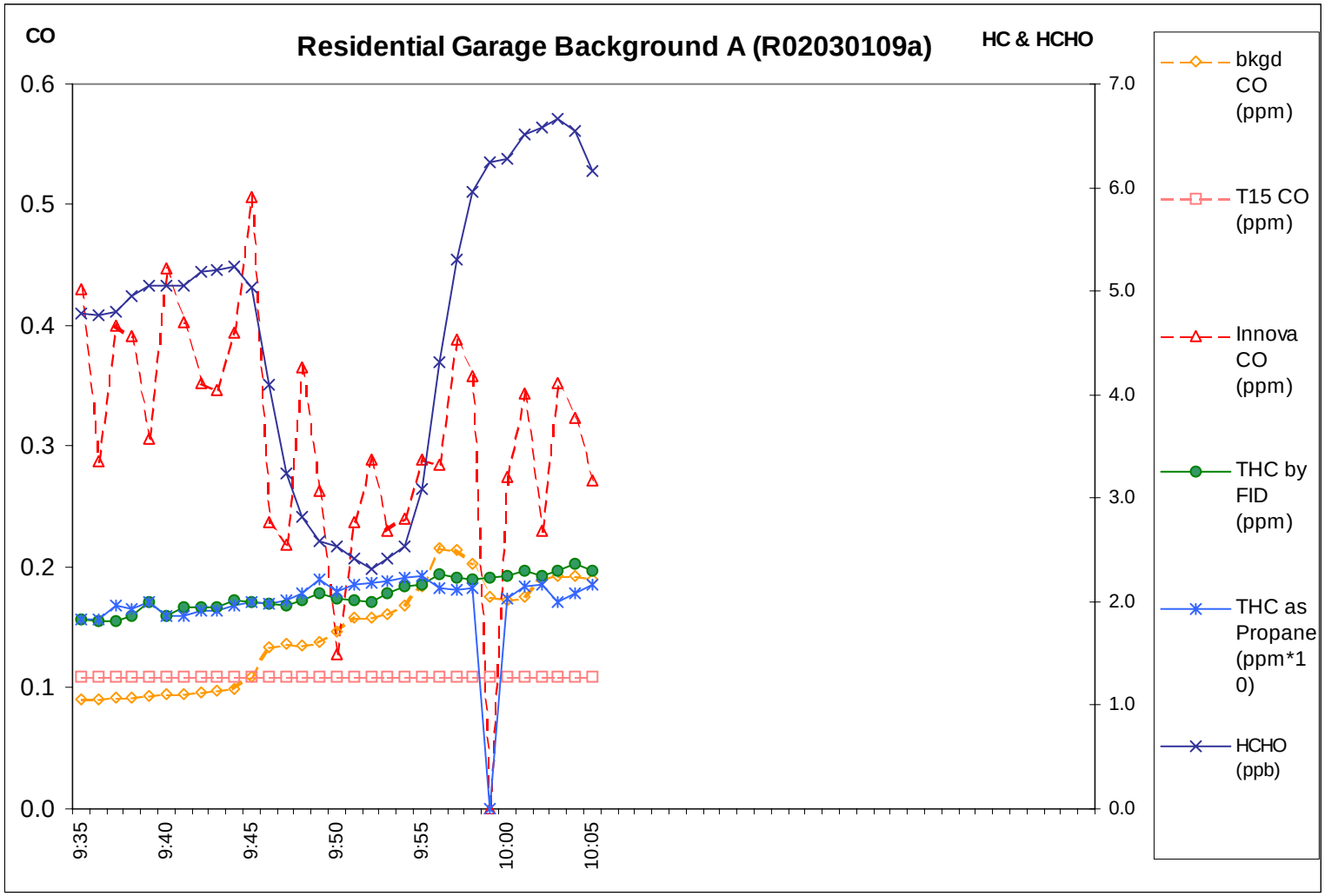

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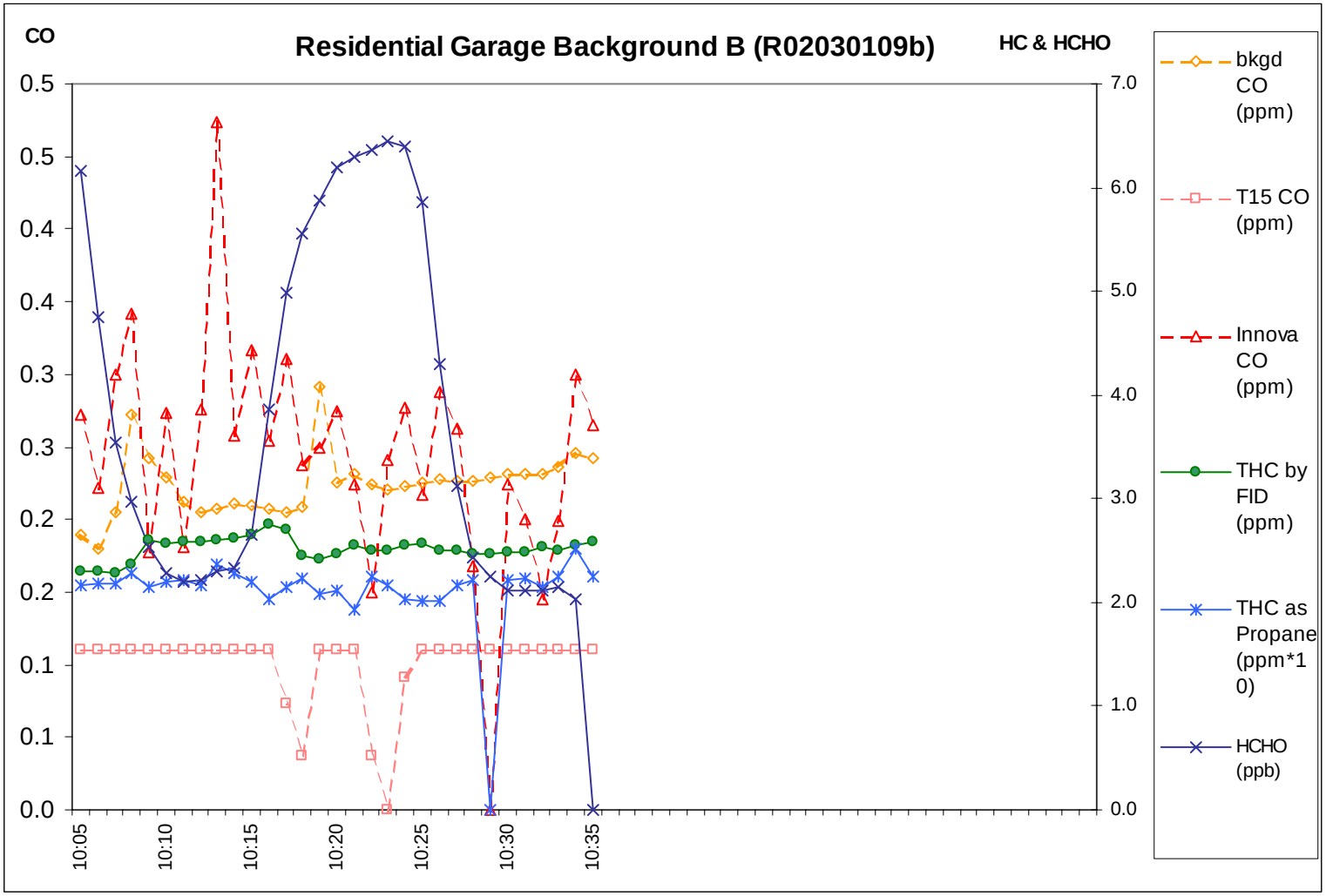

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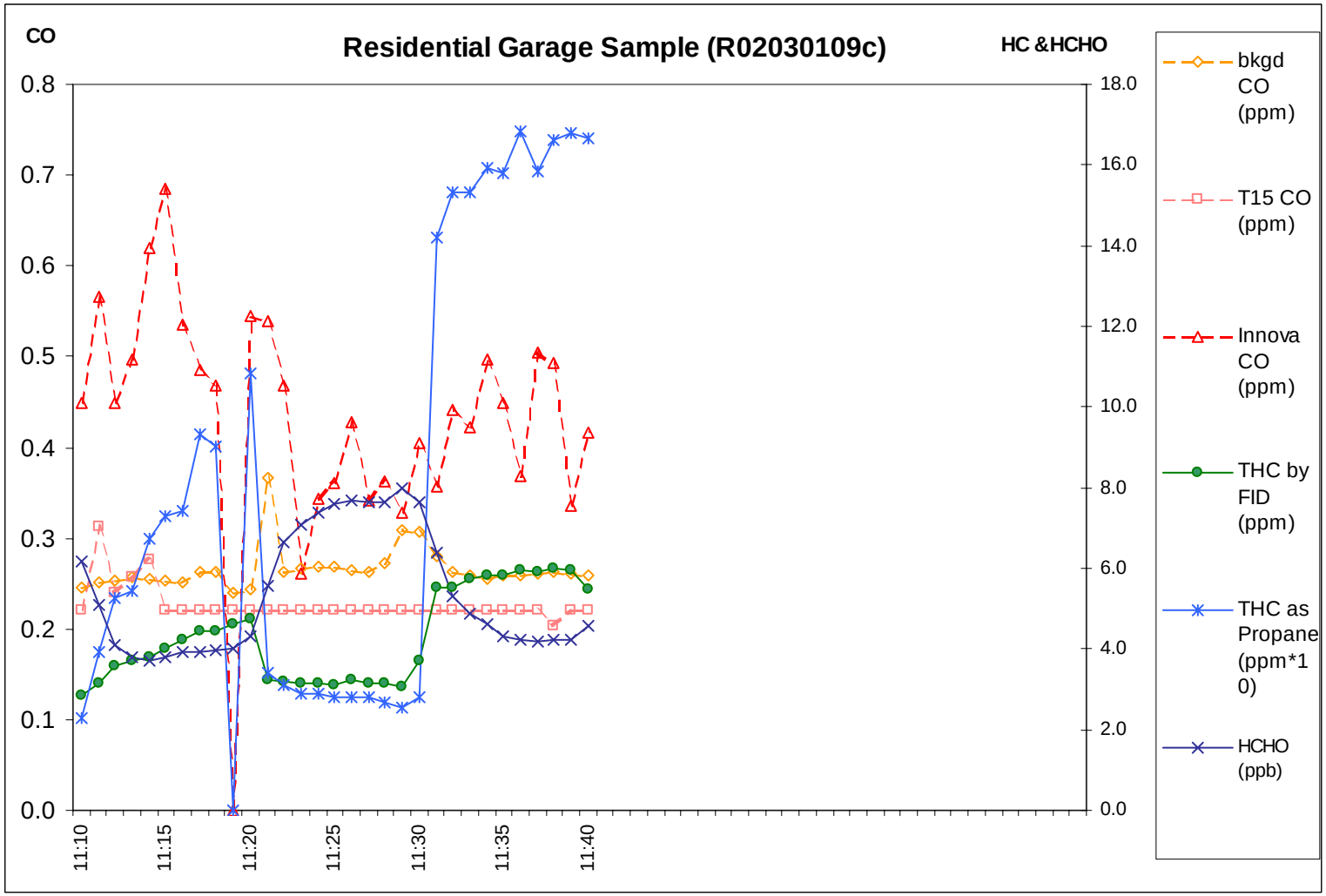

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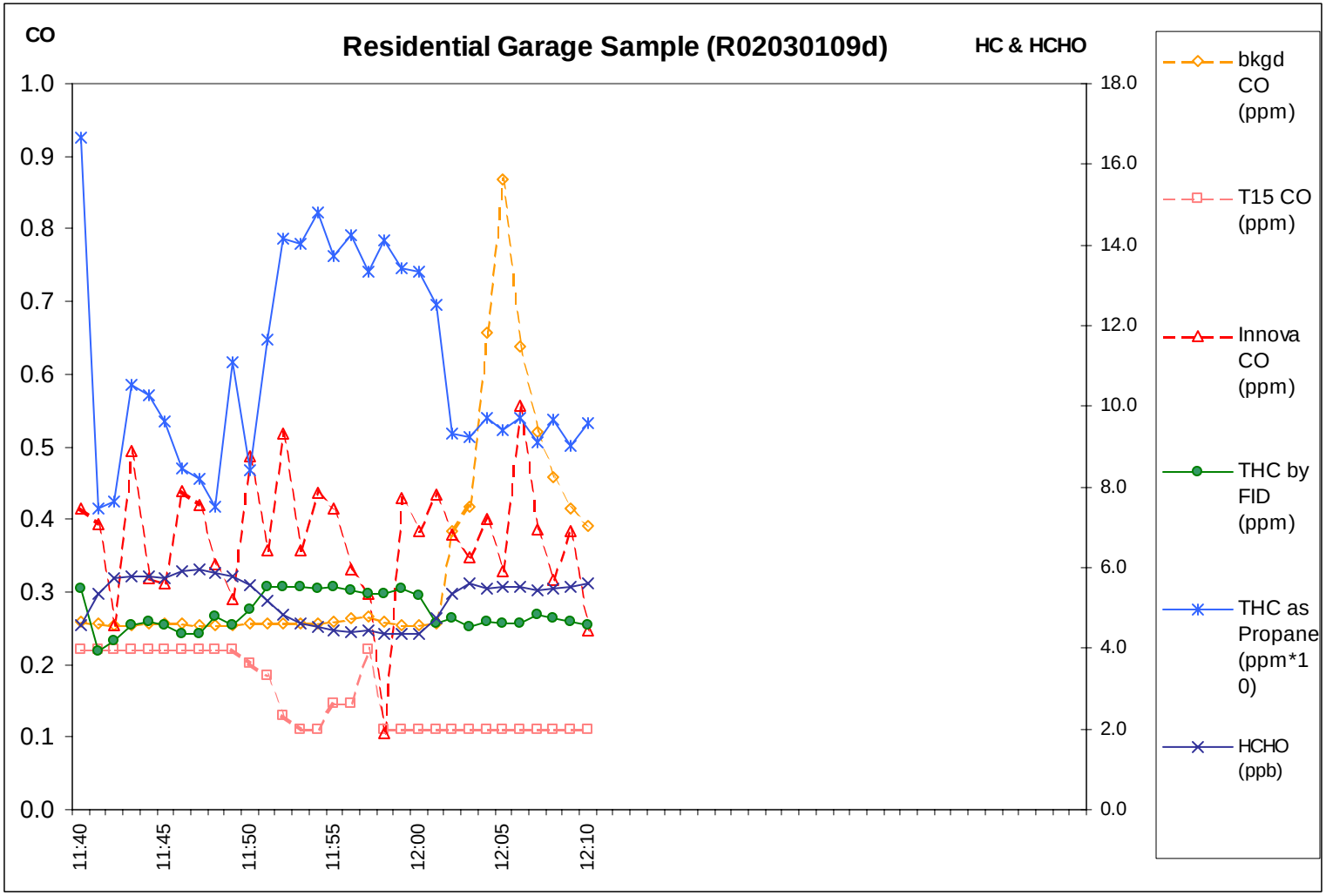

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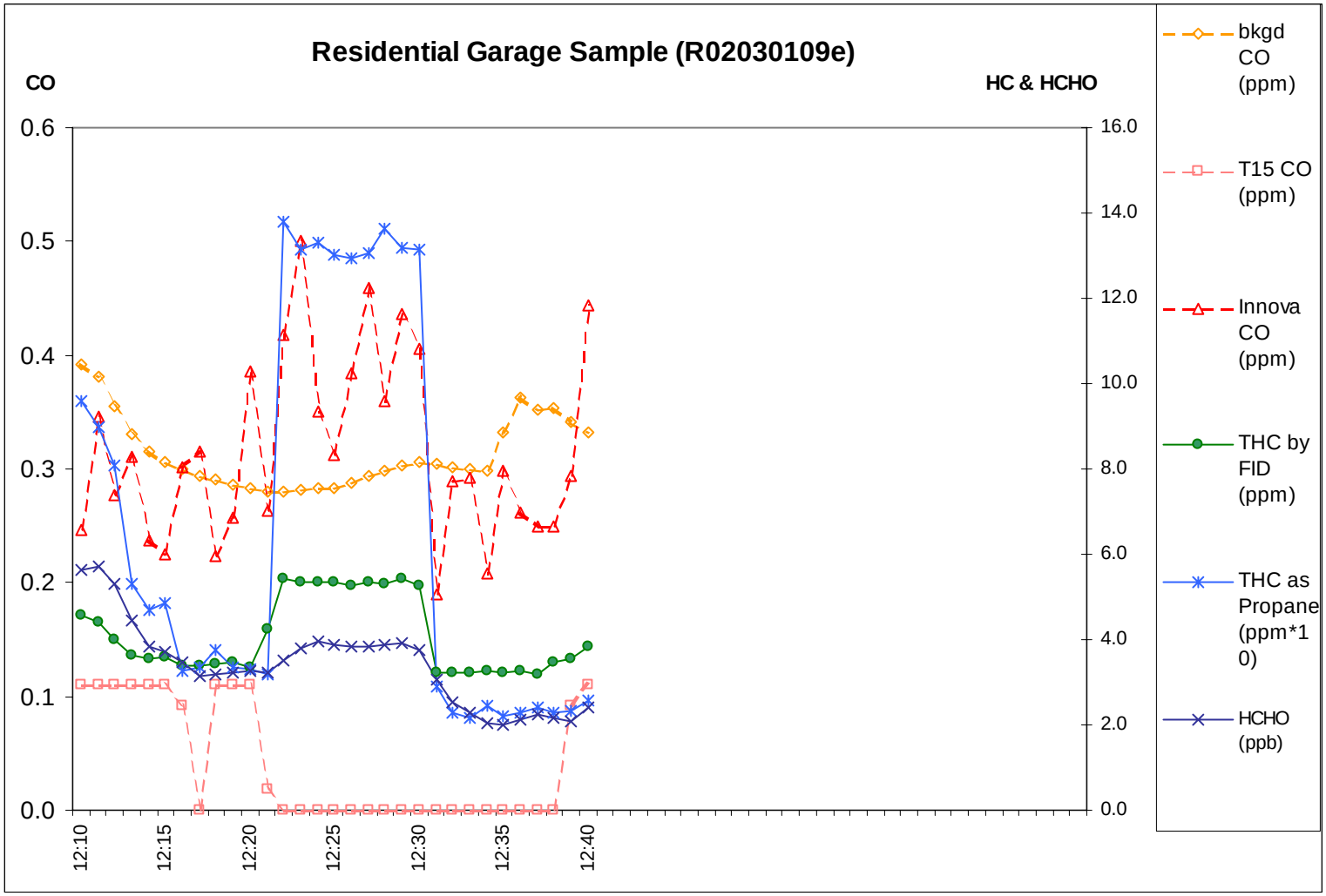

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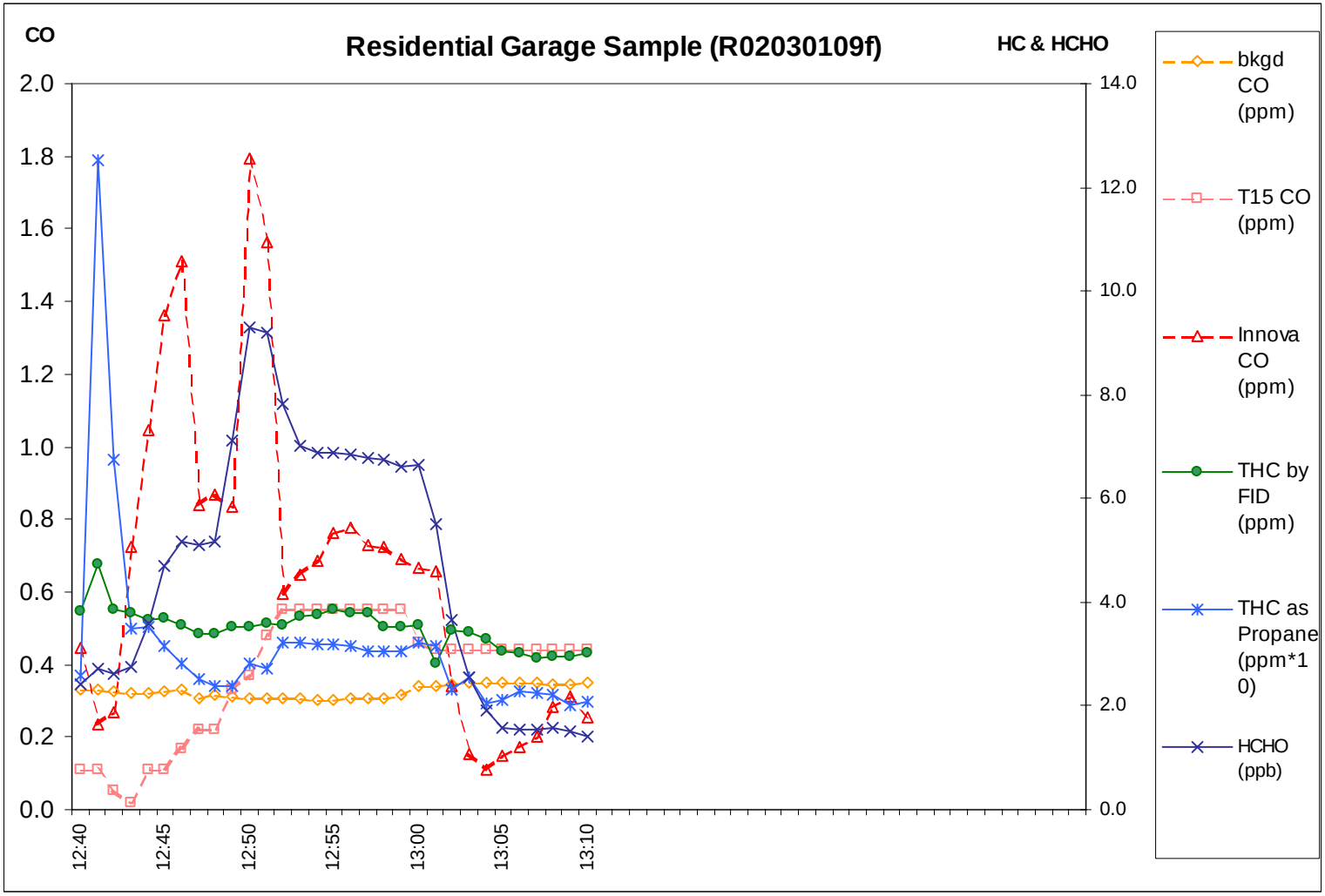

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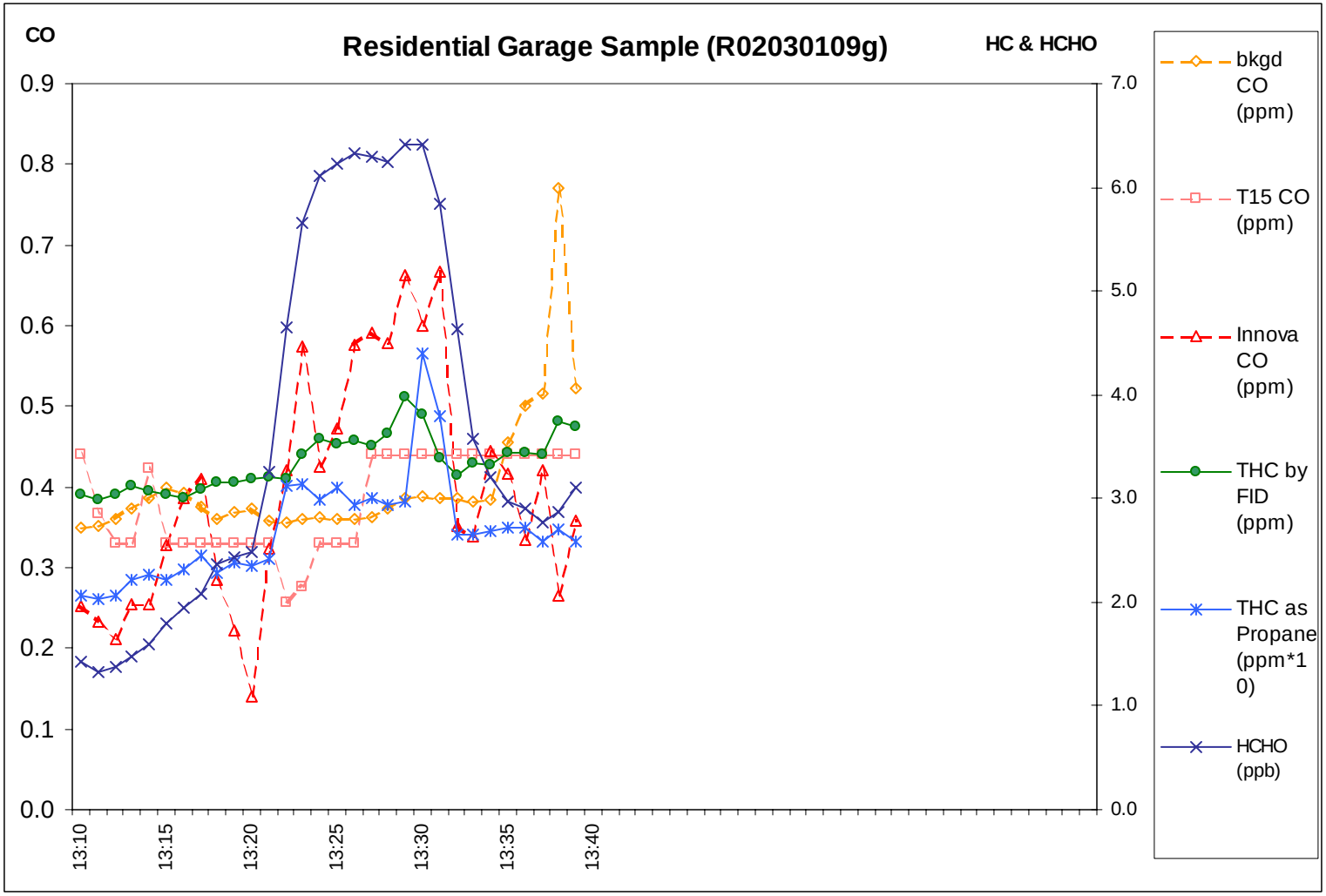

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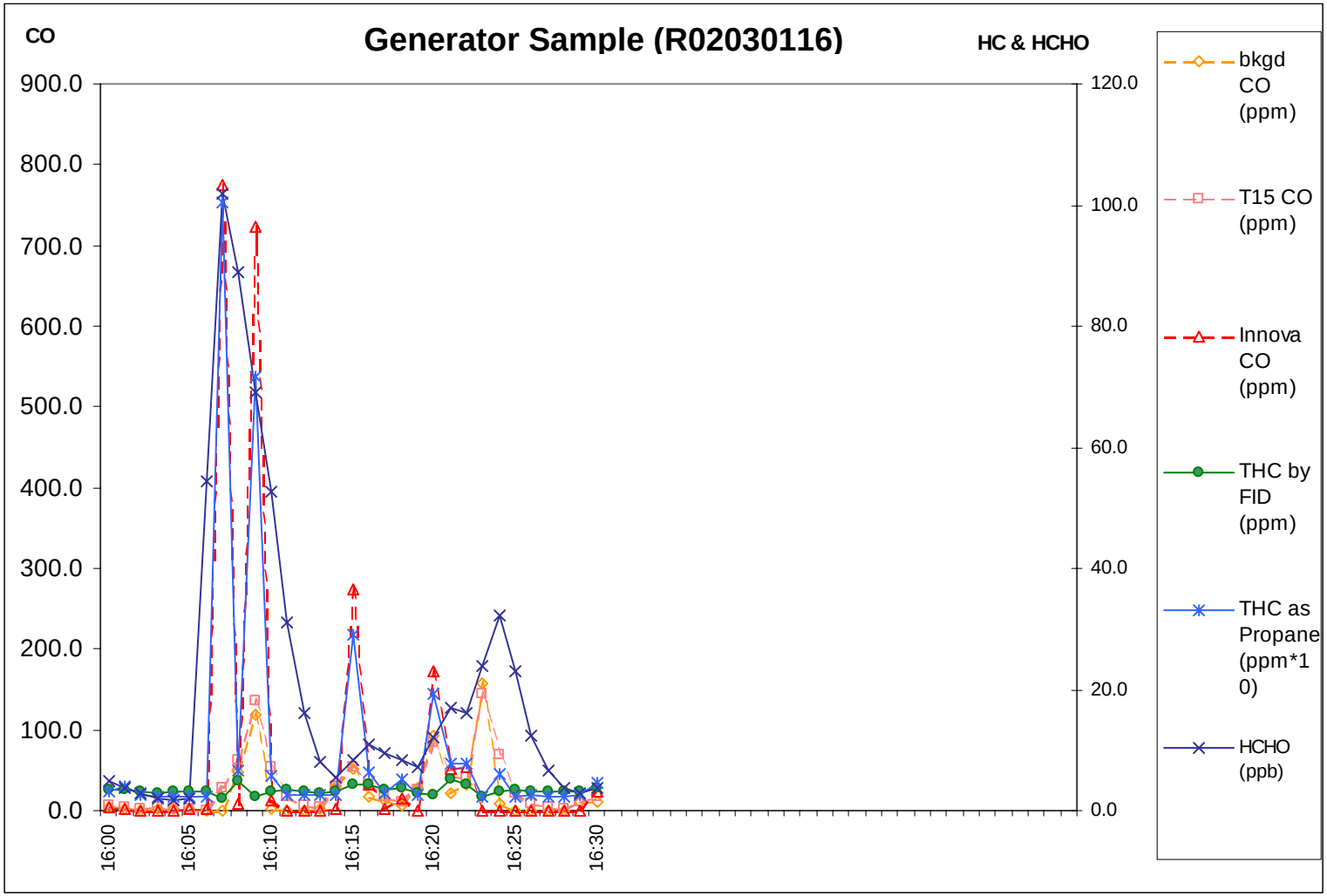

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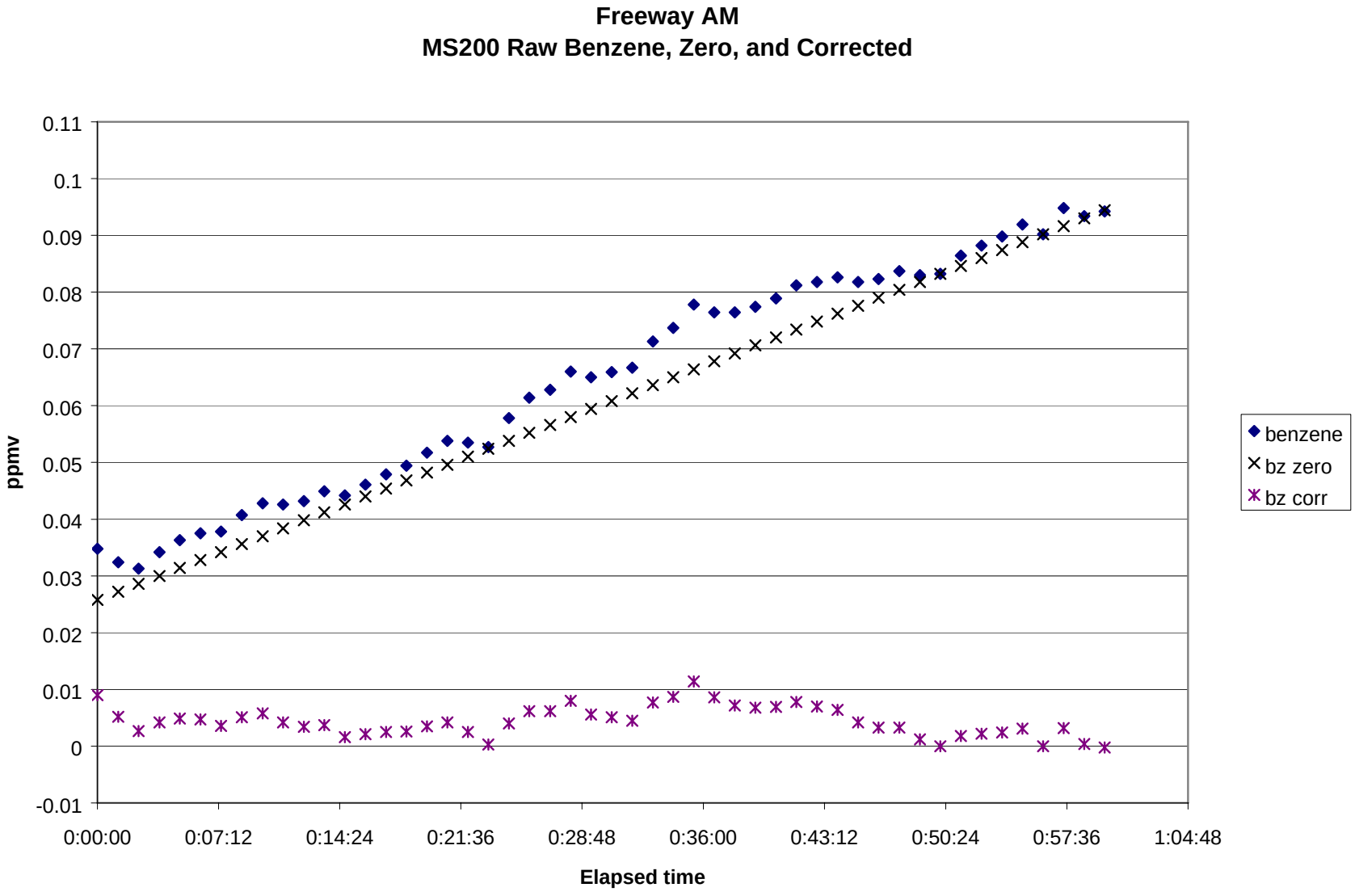

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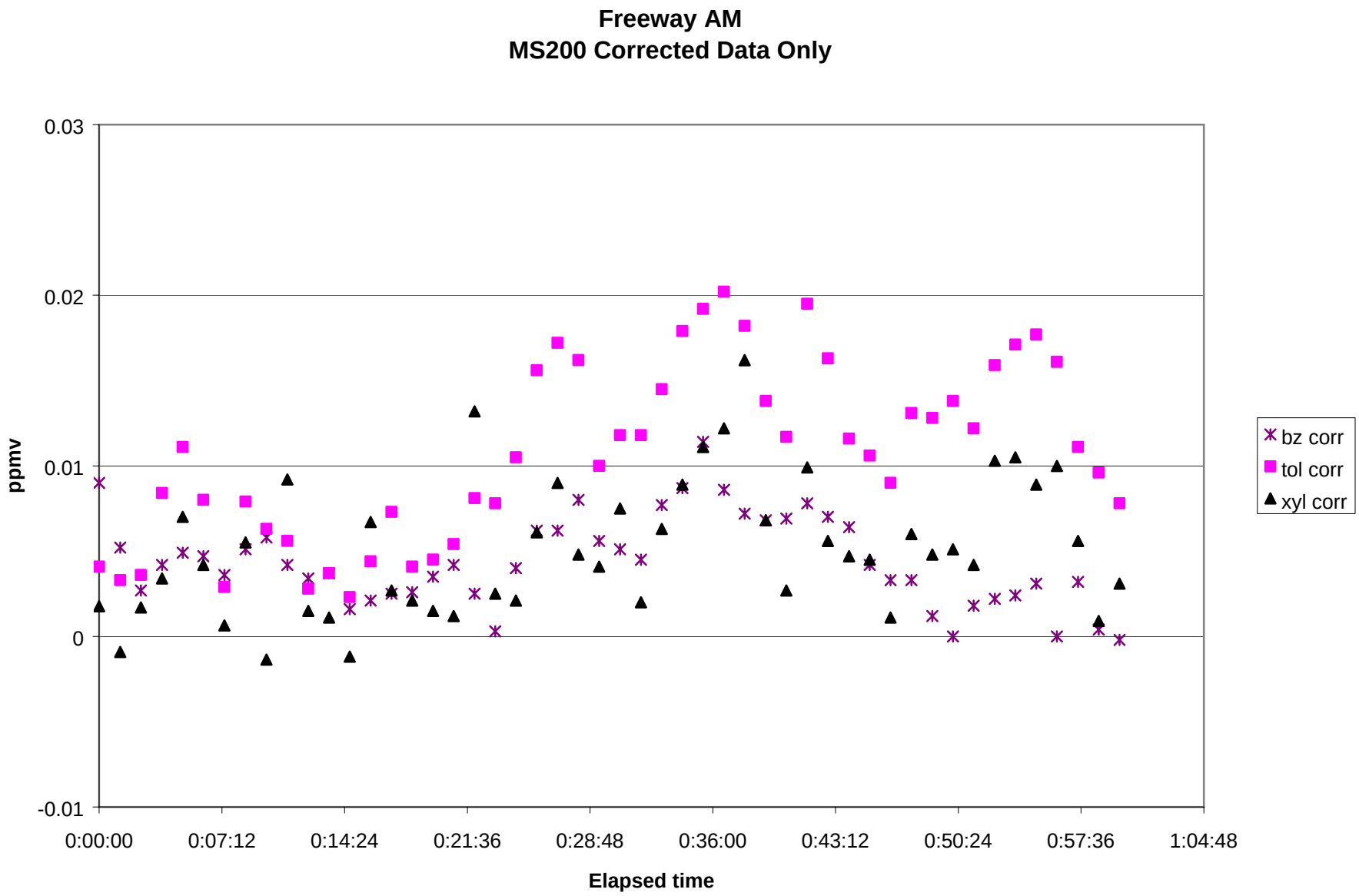

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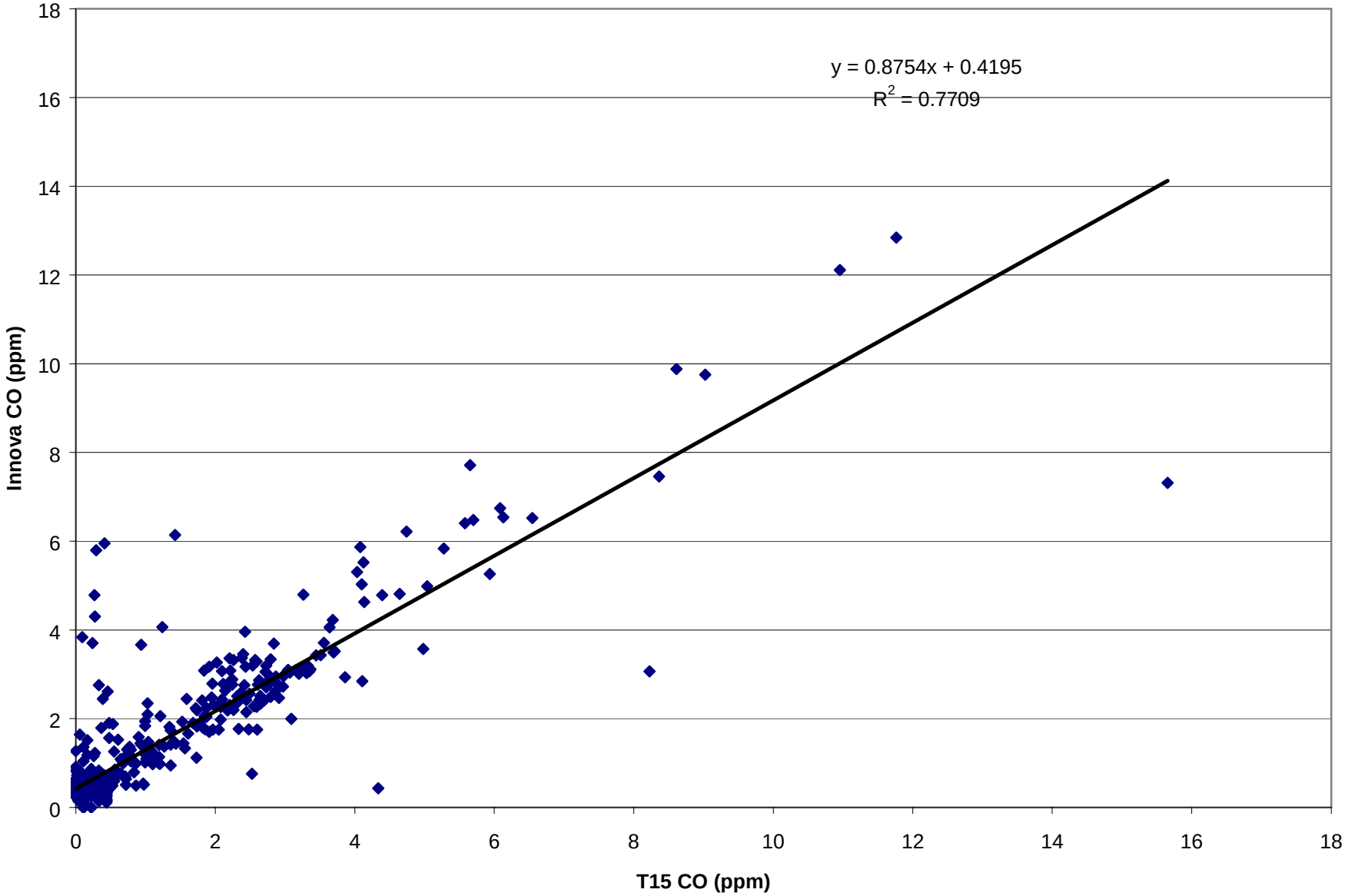

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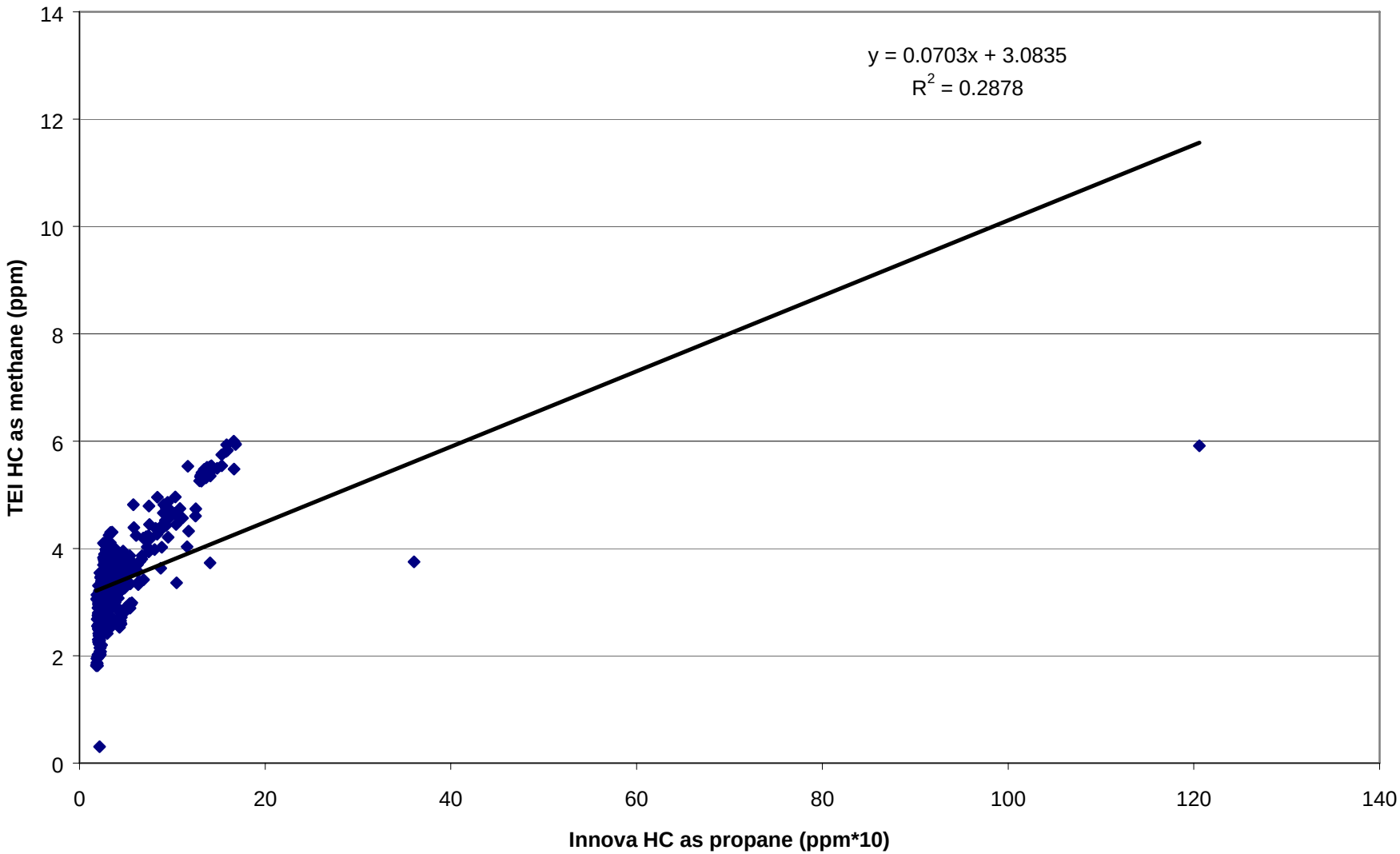

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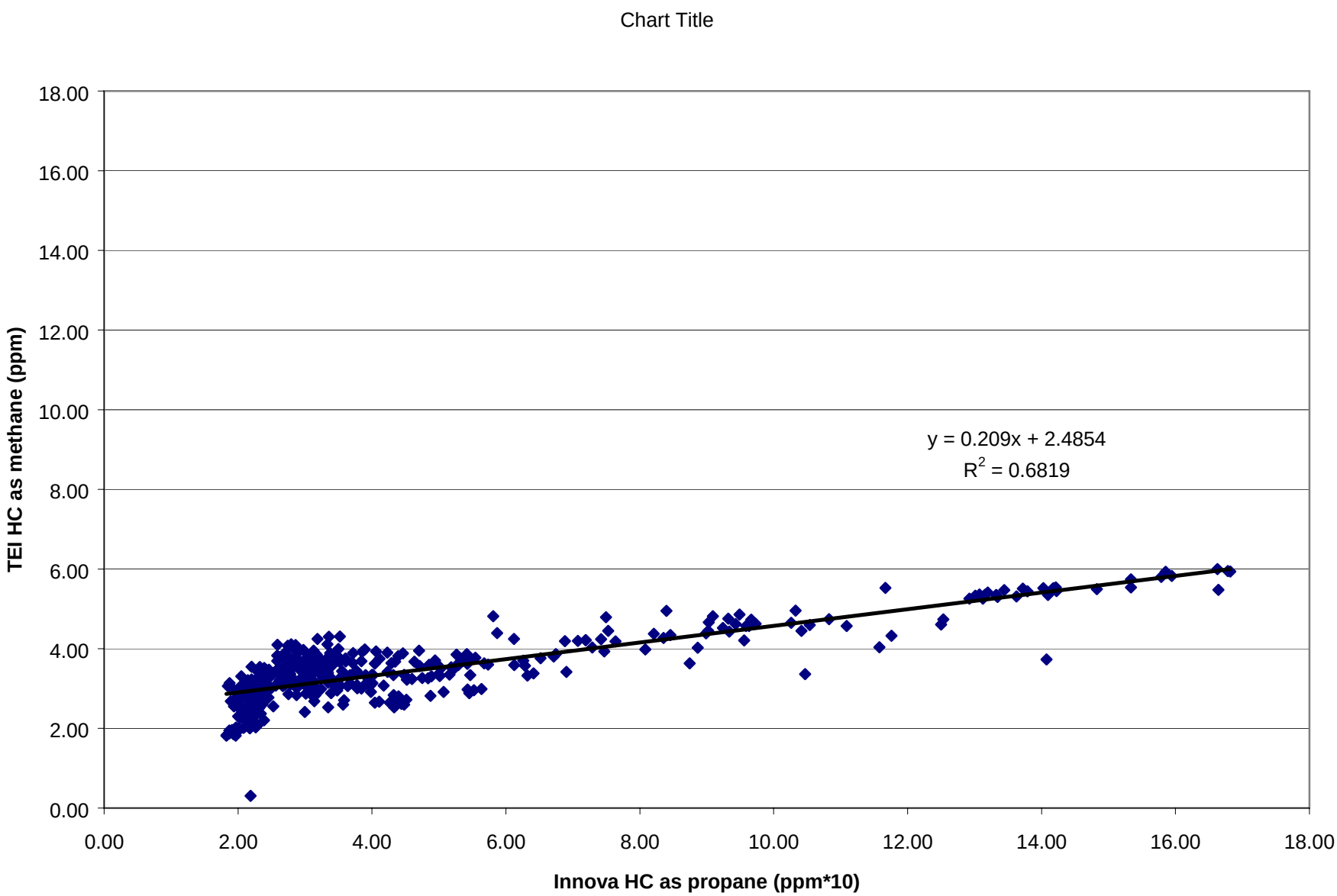

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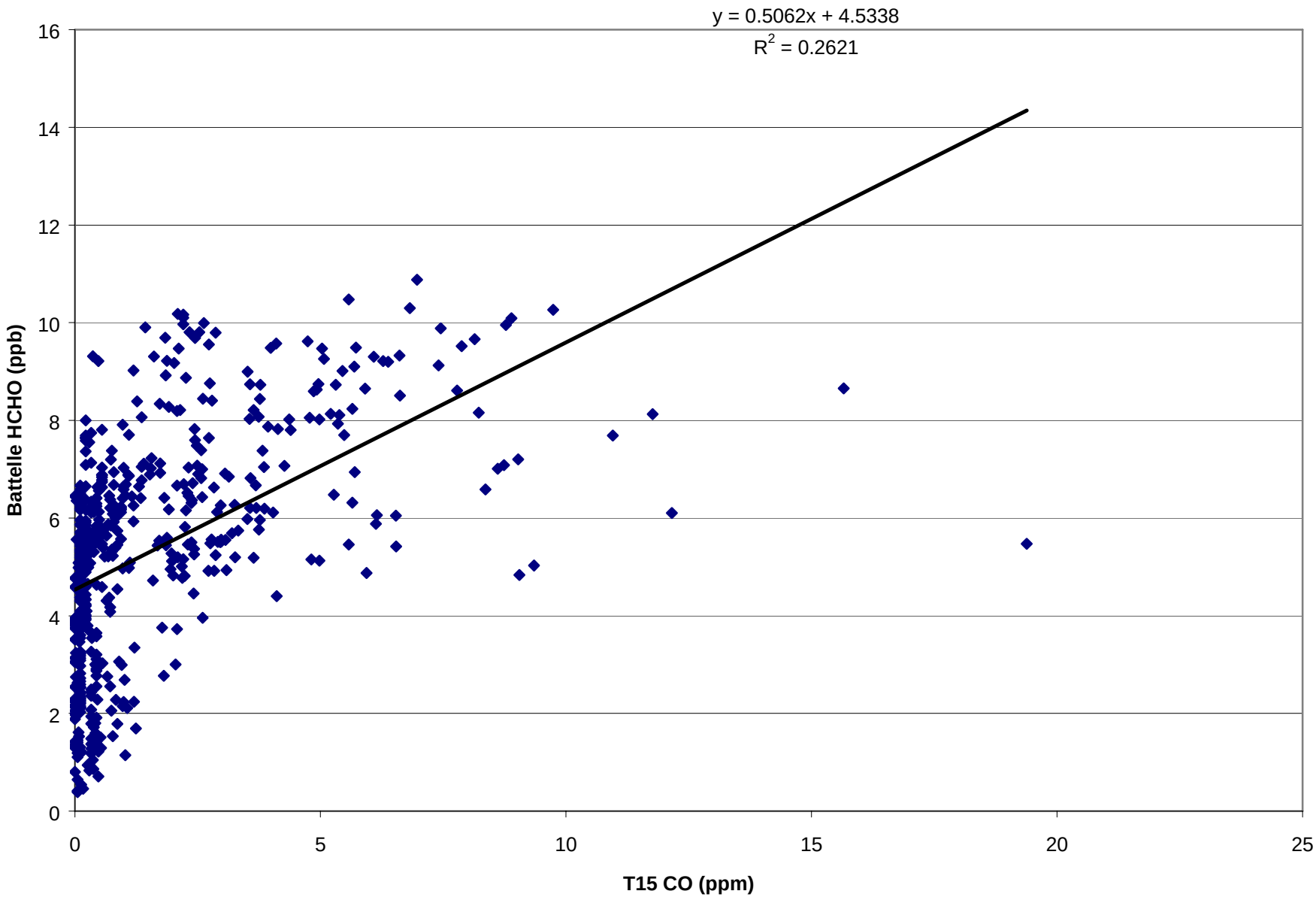

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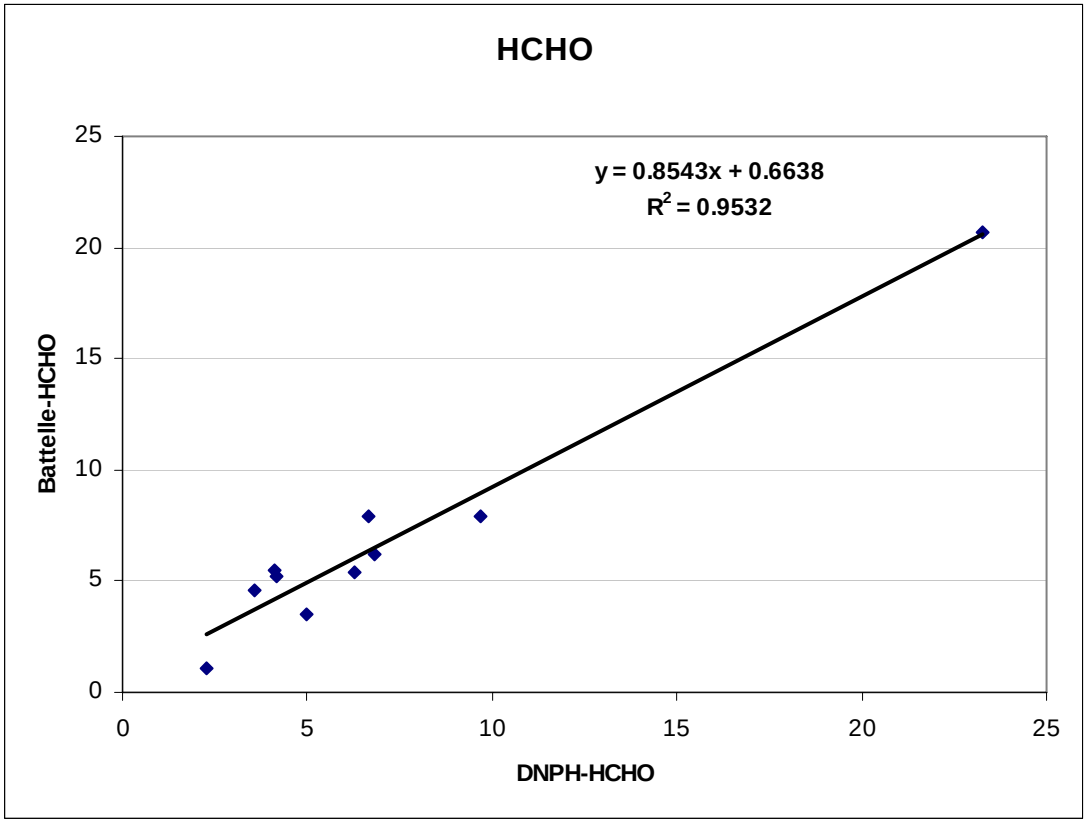

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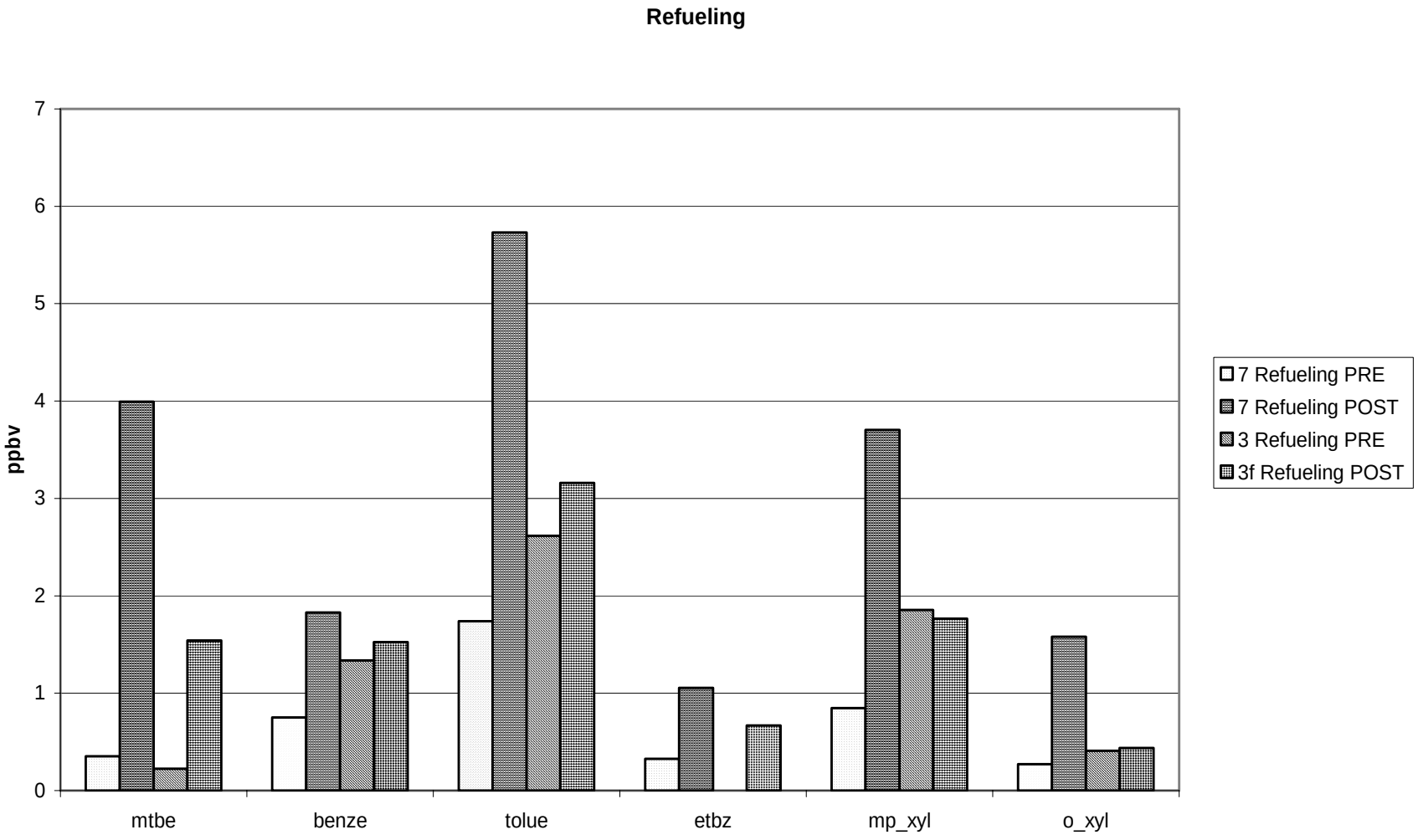

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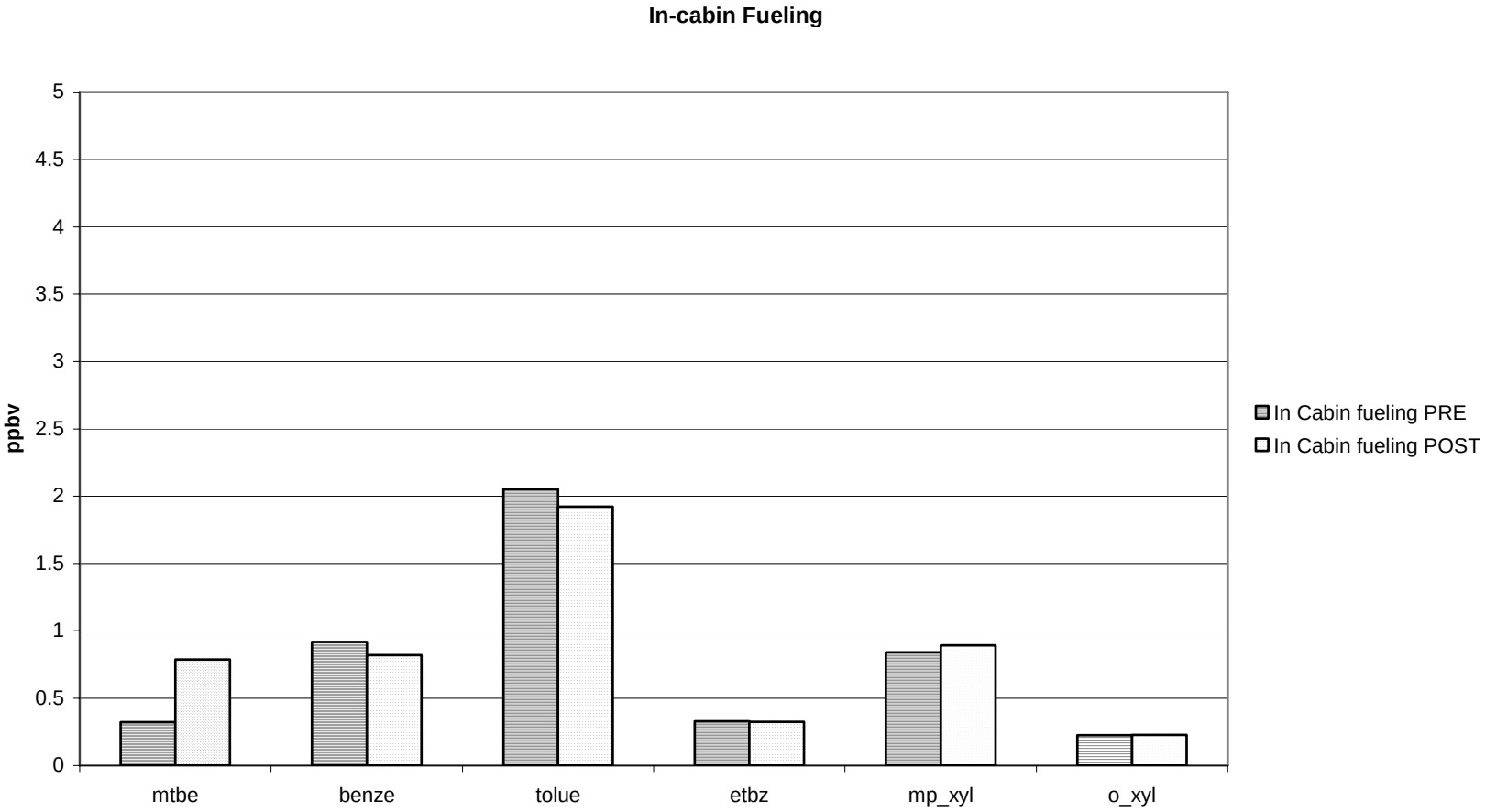

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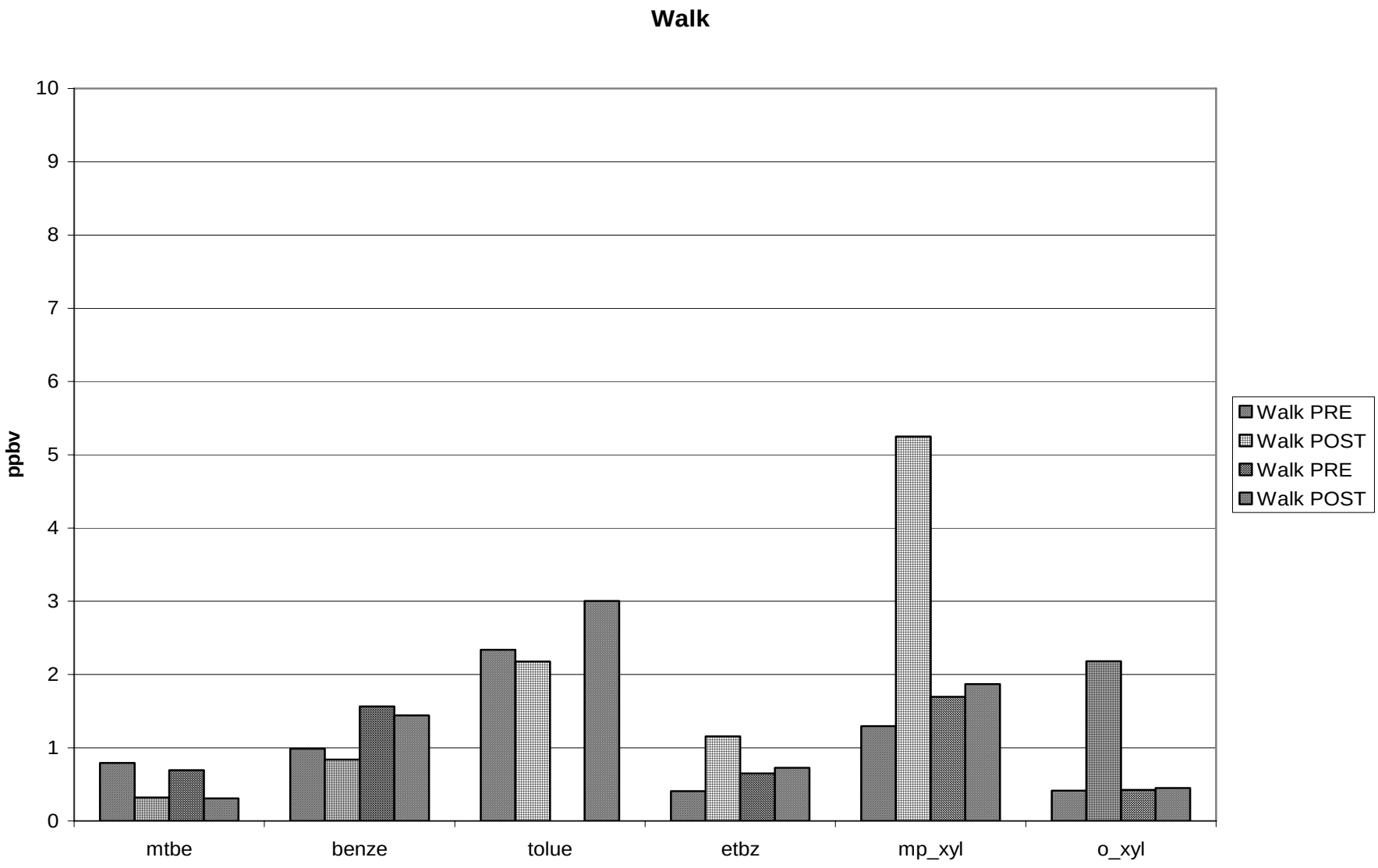

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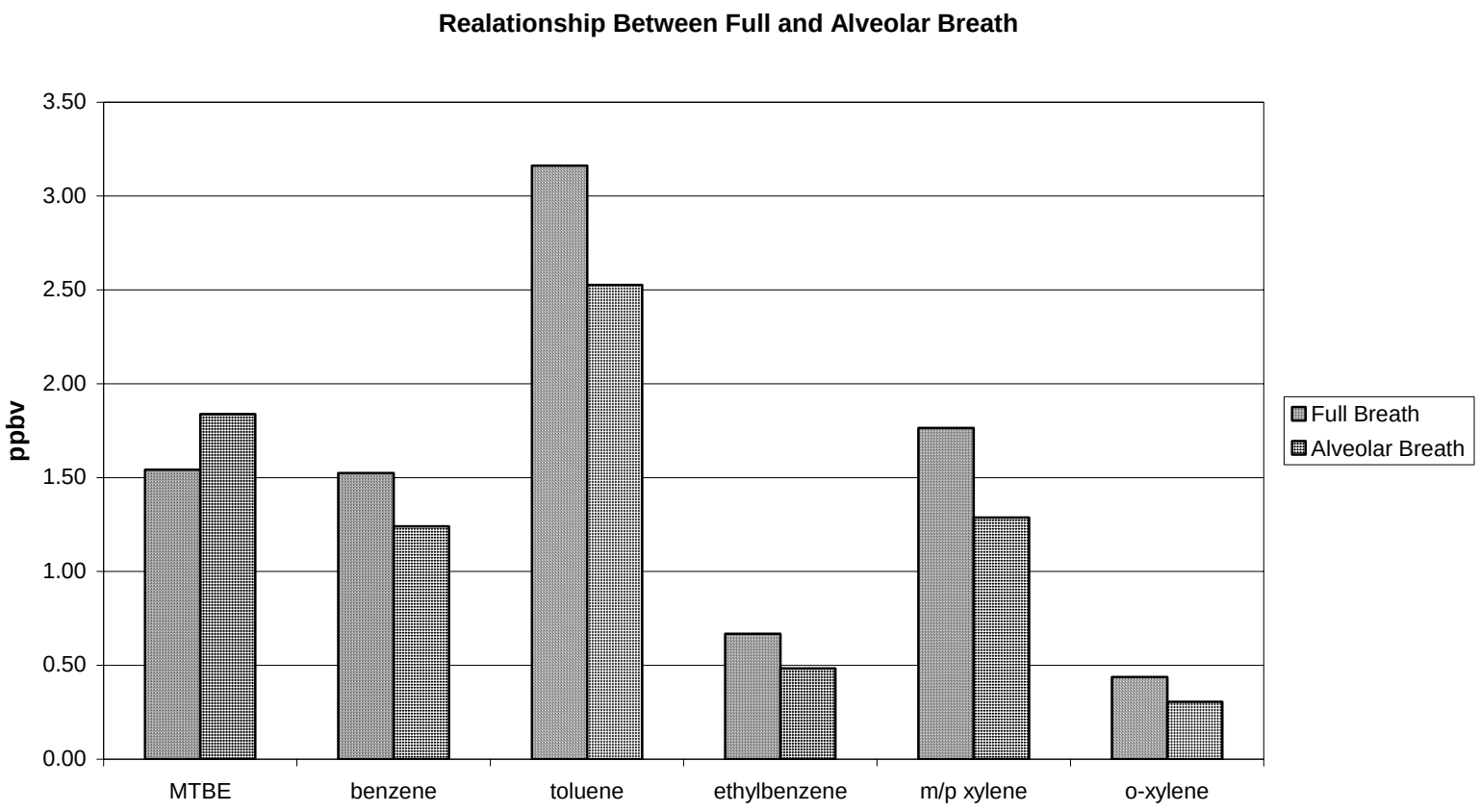

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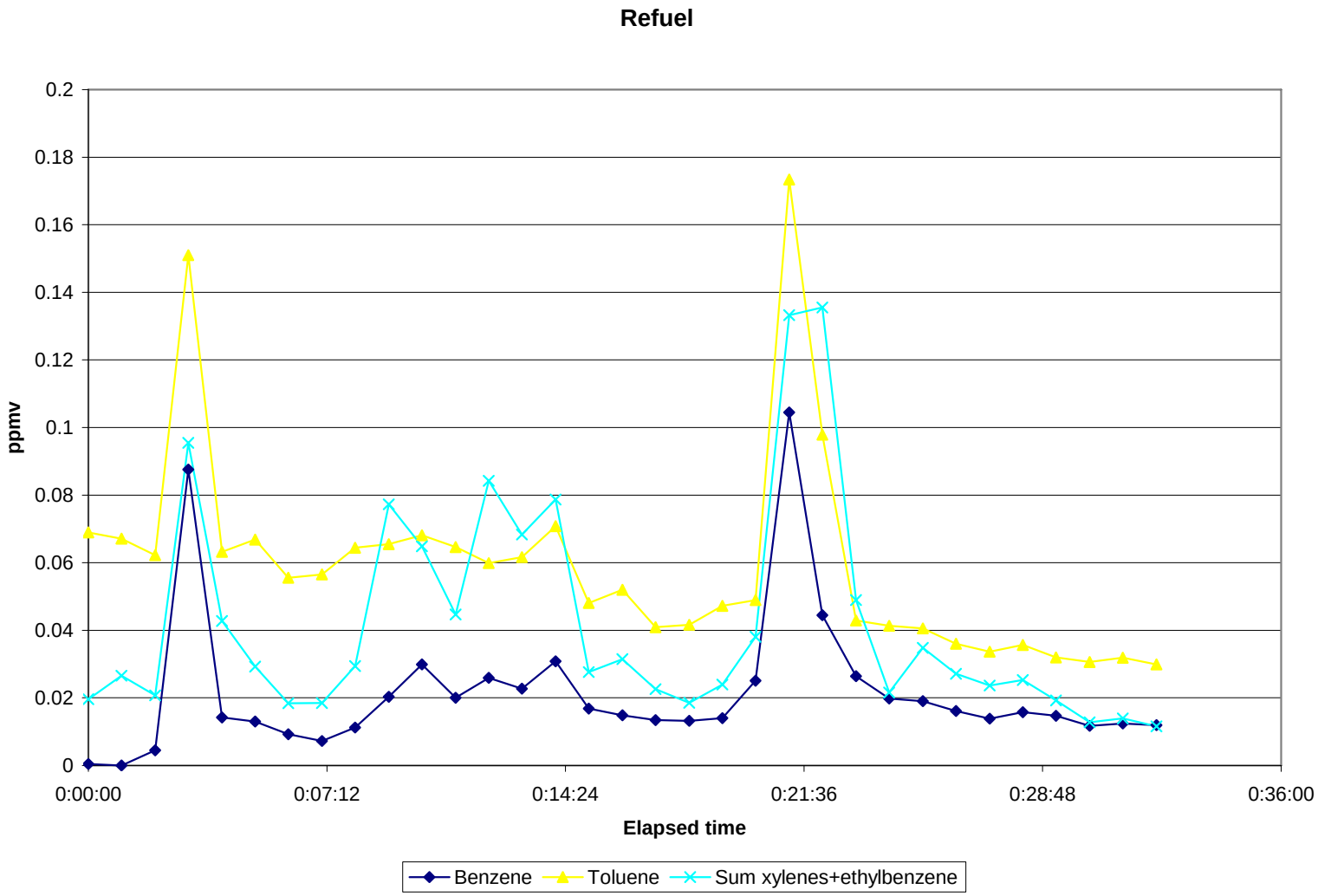

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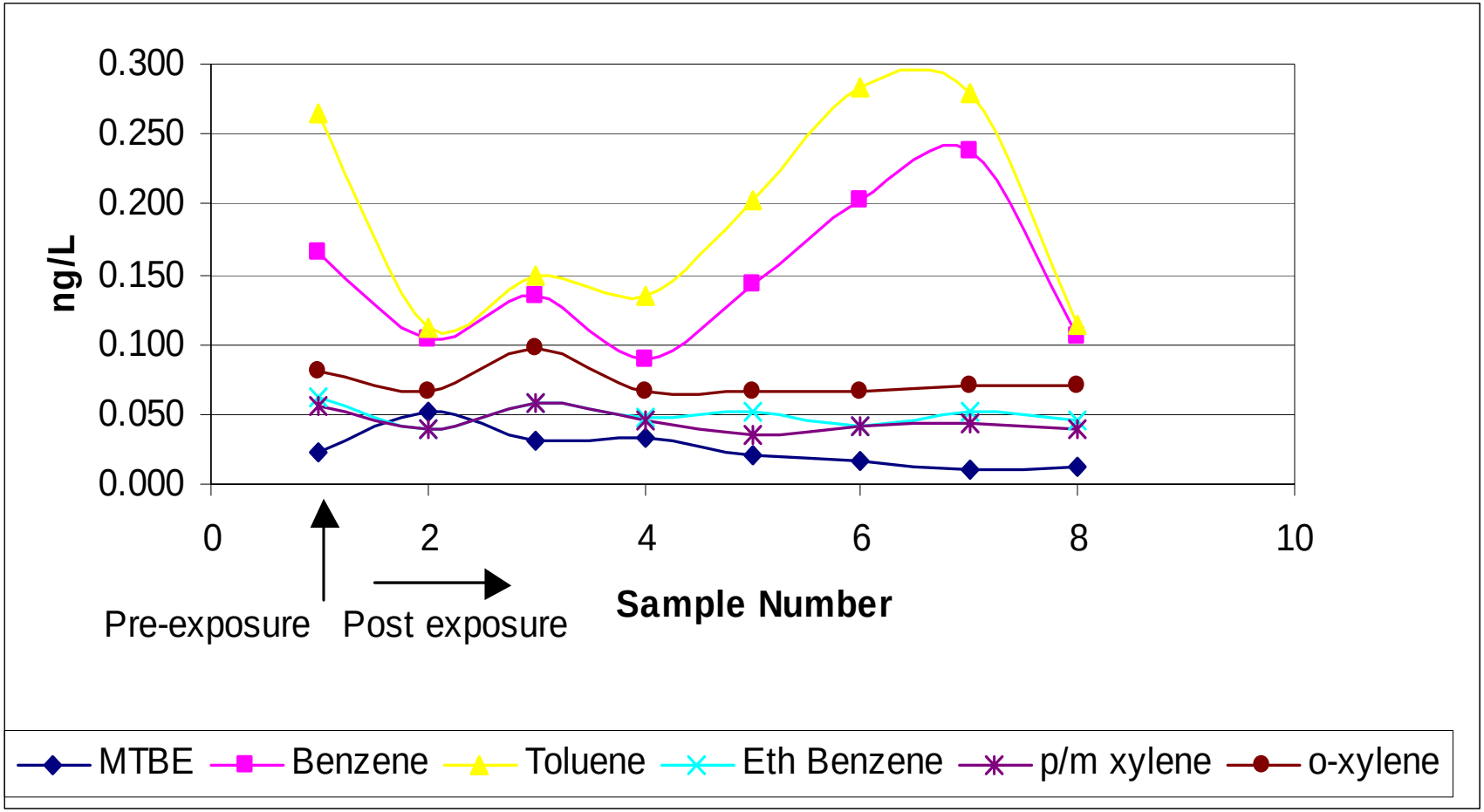

Appendix E

Section 211(B) Tier 2 High-End Exposure Screening Study of Baseline and Oxygenated Gasoline – 2nd Reno Pilot Study

SECTION 211(B) TIER 2 HIGH END EXPOSURE SCREENING STUDY OF BASELINE AND OXYGENATED GASOLINE –2ND RENO PILOT STUDY

DRAFT REPORT

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1. INTRODUCTION

The U.S. Environmental Protection Agency (EPA) has recently issued requirements for a test program in accordance with the Alternative Tier 2 provisions of the fuels and fuel additives (F/FA) health effects testing regulations, which are required pursuant to Section 211(b) of the Clean Air Act. In response to these requirements, the American Petroleum Institute (API) contracted with a research team consisting of the Desert Research Institute (DRI), Southwest Research Institute (SwRI), Lovelace Respiratory Research Institute (LRRI), and TRJ Environmental, Inc (TRJ) to conduct a screening study of the high-end distribution of inhalation exposures to evaporative and combustion emissions of baseline- and oxygenated gasoline. The exposure protocols and measurement methods, sampling & analytical procedures are described in the June 13, 2002 Exposure Protocol and Study Plan. The field measurements in San Antonio, Houston, and Atlanta were completed in adherence to this written protocol during summer 2002. The work in Chicago was postponed pending further evaluation of the measurement protocol and assessment of the data collected to date.

The overall approach for the exposure study is based upon the draft S211b Tier 2 Exposure Study Protocol that was developed in May 2001 by the API Section 211(b) Research Group and reviewed by the EPA. DRI and LRRI conducted a five-day pilot study in Reno, NV during February 2002 to test alternative measurement approaches in the field under conditions that are similar to those that will be encountered in the main study. TRJ and API provided input in the design of the pilot study and reviewed the results and findings. The evaluations included available measurement methods for continuous and time-integrated measurements of carbon monoxide (CO), total volatile organic compounds (TVOC), and designated VOC species. DRI and LRRI also evaluated the stability of the designated VOC species in breath and urine samples during the pilot study. Results of the pilot study are summarized in our pilot study report (Zielinska et al., 2002). The draft exposure protocols were appropriately modified based upon the results of the pilot study.

The work conducted last summer was summarized in two interim data reports, one reporting on data collected in San Antonio, Houston and Atlanta, and one conducting detailed data analysis from Atlanta. Based on these reports, in order to assess and identify the necessity for further refinement and adjustments to the study protocol prior to the commencement of the next phase of the study EPA asked to conduct the 2nd Pilot Study in Reno during the April – May 2003 time frame.

1.1 Study Overview and Technical Objectives

The main goal of the 2nd Reno Pilot Study was to demonstrate proper operation and reliability of analytical instrumentation and comparability of time-integrated, semi-continuous and continuous methods for compounds of interest. Four microenvironments were selected for this study, as follows:

1. **Morning rush hour commuter traffic (ME1).** This test was conducted on US395. Due to the limited rush hour period in Reno, a relatively small city, we sampled for

only 40 minutes. The driving route was from Parr Blvd in the north to Villanova Dr. in the south. During the test we attempted to follow a high emitting vehicle that was supplied by one of our DRI coworkers (Datsun 280Z, 1975). We sampled inside the van under high (first 20 min) and low (second 20 min) ventilation conditions. In low ventilation condition, we used recirculated air, windows closed, fan on high and in high ventilation conditions we had windows open, with fresh air, recirculated air off. During this ME a second PID monitored the air outside the van.

2. **Parking garage (ME2).** Due to lack of a suitable below ground parking structure in Reno, we used an above ground parking garage. We selected the Galleria parking garage in downtown Reno, a site that is used by county workers in a nearby building whose workday ends at 5:00 PM. Consequently, this location had a pulse of cold-start traffic emissions at 5:00 PM as workers attempted to leave at the same time. Due to our limited city size and modest traffic density, we anticipated the evening exit rush from the garage to be over promptly and employed one-half hour of sampling (approximately 1645 to 1715) from the van parked at a location near the only garage exit. Thus, all cars had to pass our sampling location as they exit the garage. The sampling inlet was located at the breathing zone immediately next to the van.

3. **Outdoor refueling with Stage 2 vapor recovery at the pump (ME3).** We conducted refueling of one vehicle (our 1996 sampling minivan) during a 20 min period. The fuel tank of the van was modified to enable the fuel to be drained from the van prior to refueling. Our objective was to dispense approximately the same amount of fuel each time. The vehicle was driven prior to refueling to raise the monitored temperatures on the outside surface of the fuel tank. The refueling tests were performed at the service station in Reno (corner of Sun Valley Dr. and Dandini Blv.), which has stage 2 vapor recovery nozzles. While removing the nozzle from the vehicle filler tube, we spilled a few drops of liquid gasoline on the ground near the vehicle. The amount of the spill was noted. The refueling was done under calm wind conditions (i.e., wind speed below 5 mph). Wind was monitored by hand-held anemometer. Monitoring was done at the breathing zone of the person fueling the van.

4. **Outdoor refueling without vapor recovery at the pump (ME4).** This test was conducted at a small gas station in Reno that does not have stage 2 vapor recovery nozzles. Because this station sells a relatively low volume of fuel, it has not been required to upgrade to the stage 2. As noted above, we refueled one vehicle during the 20 min test at the gas station. While taking the nozzle from the vehicle filler tube, we caused a spill of a few drops of liquid gasoline on the ground near the vehicle. The amount of the spill was noted. The refueling was done under calm wind conditions (i.e. wind speed below 5 mph). Monitoring was done at the breathing zone of the person fueling the van.

Figure 1-1 shows the sampling locations. The US395 driving segment is marked in blue.

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2. EXPERIMENTAL METHODS

2.1 Measurement Approach

Our sampling strategy consists of a three-tiered approach shown in Table 2.1-1, which lists the overlapping measurement methods used in the Section 211(B) Tier 2 High-End Exposure Screening Study and their intended application. The applications are classified in one of three tiers: reference, surrogate, and confirmatory. The base set or "reference" (R) measurements consist of three well-established time-integrated measurements. These include: 1) canister sampling and analysis by gas chromatography with flame ionization detection for methanized CO, BTEX, 1,3-butadiene, MTBE, and nonmethane hydrocarbons (NMHC); 2) 2,4-dinitrophenylhydrazine (DNPH) cartridge sampling and analysis by high performance liquid chromatography with UV detection for formaldehyde and acetaldehyde; and 3) solid adsorbent sampling and analysis of ethanol by gas chromatography with mass spectrometry detection. These three methods combined measure all species of interest over the entire sampling period within each microenvironment. Although these integrated methods do not characterize peak exposures in microenvironments with highly varying exposure levels. They provide a basis for validating continuous and semi-continuous data. They also provide a basis for deriving correlations between the integrated values and continuous "surrogates" (S), such as CO and photoionizable VOC (10.6 eV - photoionization detector) PID data, in order to reconstruct their time series. For example, data for BTEX, 1,3-butadiene, and MTBE from the canister measurements can be correlated to continuous CO and PID data to reconstruct their time series in exhaust-dominated environments. The same method is used for ethanol and NMHC. In a similar manner, the time series of acetaldehyde and formaldehyde can be reconstructed from the correlation of the integrated DNPH samples with CO or PID. Outdoor afternoon samples should be excluded due to possible contribution of carbonyl compounds formed from atmospheric reactions of hydrocarbons. Table 2.1-1 shows the other correlations that can be used in this manner.

Three continuous methods were employed to monitor: 1) the aromatic hydrocarbons benzene, toluene, ethylbenzene, and the xylenes (BTEX), 2) carbon monoxide, and 3) formaldehyde. These methods were also combined with component concentration ratios from contemporaneous time-integrated samples to reconstruct the expected time series for species that did not have continuous instruments, e.g., 1,3-butadiene (BD), ethanol (EtOH), and methyl tert-butyl ether (MTBE).

<u>The Kore MS200</u> instrument was used to monitor BTEX on a one-minute basis. This instrument uses a time-of-flight mass spectrometer to separate compounds of interest. This instrument also uses a software solution incorporating the 70 eV electron impact ionization fragmentation patterns of each compound to apportion the contribution of each component of interest to the time-of-flight (TOF) mass spectrum seen by the instrument. The software does not distinguish between specific isomers, thus xylenes are reported together. The inlet uses a polydimethylsiloxane membrane preferentially to allow non-polar organic compounds into the analyzer while maintaining the vacuum inside the analyzer chamber. This membrane inlet

does limit the types of compounds that can be analyzed, however. Common air constituents and polar organic molecules do not pass the membrane quickly.

Carbon monoxide was monitored by the Langan T15 CO monitor and the API Model 300 and ML9830 CO NDIR analyzers. The Langan T15 is an electrochemical monitor for CO. The response time of this instrument is somewhat slower than infrared-based instruments. Both the API and ML instruments are specified in the EPA List of Designated Reference and Equivalent Methods (March 24, 2000) as a federal reference method operating at any temperature in the range of 15 ºC to 35 ºC (59 ºF to 95 ºF). (www.epa.gov/ttnamti1/files/ambient/criteria/criteria/0300co.pdf)

Continuous Formaldehyde Monitor (Alpha-Omega Power Technology, Ltd., Albuquerque, NM) absorbs formaldehyde in acidified water, reacting it with 2,4-pentanedione and ammonia to form a cyclized product, 3,5-diacetyl-1,4-dihydrolutidene, which is continuously detected by fluorescence. The method is highly specific for formaldehyde and very sensitive. However, since this instrument did not performed well during the summer study we introduced several improvements, as follows. The original instrument case, detector, electronics, valves, some of the fittings were retained. Major modifications included removal of the original four channel peristaltic pump necessary for reagent delivery and fluid flows to the detector. This pump was found to be incapable of maintaining consistent flows and was susceptible to failure when pump tubing would rupture or pull away from the connection fittings. In addition, flow rates had limited adjustability, making it not suitable for the additional modifications that were performed on the instrument. The peristaltic pump was replaced with four milliGAT piston pumps (Global FIA) with microprocessor-controlled motors capable of delivering a broad range of precisely metered flow rates. Another major modification was replacement of the diffusion scrubber assembly with a scrubbing coil similar to the design described in Kelly and Fortune (1994). The original diffusion scrubber was susceptible to malfunction when scrubbers or driers were heavily used or contaminated by the reagents. In contrast, the scrubbing coil is simple to operate and maintain, and is reported as being 100% efficient at removing gaseous formaldehyde from the air stream being sampled. An in-line debubbler (Global FIA) was installed between the heated reaction cell and the detector to remove any bubbles from the sample stream before entering the detector. This was necessary because bubbles may be generated elsewhere in the system or when the sample mobile phase is heated in the reaction cell. Finally, calibration of the instrument was performed using a gaseous formaldehyde standard (1 ppm in $N_{2(g)}$, Apel-Reimer) diluted to the desired concentration (5 to 250 ppb) with UHP zero air (Airgas) and plumbed to the sample inlet of the scrubbing coil. Calibration curves were linear (R^2>0.99). The instrument response time was determined to be 6 minutes from the time of sample introduction to equilibration at the detector. Instrument background was determined by periodically installing a DNPH cartridge (Waters) on the inlet of scrubbing coil to remove any formaldehyde from the sample stream in order to observe the detector baseline response.

Table 2.1-1. Measurement methods used in the 2nd Reno Pilot Study.

Data applications for specific methods are classified as reference, confirmatory, and surrogate.

	Continuous					Semi-Cont	Integrated		
Method	T15 CO	NDIR CO	ppbRAE	MS200	HCHO	SPME	Canister	DNPH	Adsorbent
Applicable Environments	all	all	all	higher end	all	all	all	all	all
Time Resolution	seconds	seconds	seconds	1 min	1-2 min	10 min	30 & 40 min	30 & 40 min	30 & 40 min
Detection Limits	0.1 ppm	0.04 ppm	1 ppb	1-3 ppbv	1 ppbv	0.2 ppbv	0.05 ppbC	0.1 ppbv	0.2 ppbv
Data Application [1]	S	S	S	C	C	C	R	R	R
CO	SC	SC					R		
PID [2]			SC						
BTEX	S (a)	S (a)	SC (c)	C		C	R		
1,3-Butadiene	S a)	(S a)	(S (c)				R		
MTBE	S a)	(S a)	(S (c)			C	R		
Formaldehyde	S (b)	S (b)	S (d)		C			R	
Acetaldehye	S (b)	S (b)	S (d)		S (g)			R	
Ethanol	S (e)	S (e)	S (f)						R
NMHC	S a)	(S a)	(S (c)				R		

1. Category of data application include surrogate (S), confirmatory (C) reference (R), and surrogate compounds or signal (SC)
2. Sum of molecules ionizable at 10.6 eV and detected by photoionization detector.
S (a). Time series will be reconstructed from the canister/CO ratio for exhaust-dominated samples.
S (b). Time series will be reconstructed from the DNPH/CO ratio for exhaust-dominated samples except outdoor daytime samples.
S (c). Time series will be reconstructed from the canister/PID ratio for exhaust- or evap-dominated samples in outdoor MEs.
S (d). Time series will be reconstructed from the DNPH/PID ratio for exhaust-dominated samples except outdoor daytime samples.
S (e). Time series will be reconstructed from the solid adsorbent/CO ratio for exhaust-dominated samples.
S (f). Time series will be reconstructed from the solid adsorbent/PID ratio for exhaust and evap-dominated samples.
S (g). Time series will be reconstructed from $CH3CHO_{DNPH}/HCHO_{Cont}$ ratio for exhaust dominated samples.

Photoionization detector (PID) measured the total signal from molecules ionizable at 10.6 eV. We used two PID monitors for the pilot study. For the freeway runs, one PID sampled outside air, and the other sampled in-cabin air. For the remaining runs, only one PID was used, but for comparison purposes we ran both of them side-by-side for selected runs.

The time-integrated and semi-continuous collection methods (canisters, solid adsorbent cartridges, DNPH-integrated cartridges and SPME) were described in detail before (Zielinska et al, 2002, 2003). Depending on the type of sorbent (C18 or silica gel) in the DNPH cartridge, the carbonyl compound ambient measurement results are subject to various artifacts due to interaction with ozone. Consequently, the ozone denuder is recommended for sample collection. For this pilot study, we used a honeycomb denuder coated with sodium carbonate/sodium nitrite/glycerol mixture (method developed by Dr. Koutrakis from the Harvard School of Public Health). For canister sampling, ambient NO_2 is of concern, since it might react with 1,3 butadiene. Thus, we were using a honeycomb denuder coated with triethanoloamine (TEA) to remove NO_2 (a method developed by Dr. Koutrakis).

In addition, we collected breath samples in all microenvironments. We used 1 liter silicosteel canisters (Restek, Inc.) and a collection method described by Pleil and Lindstrom, 1995. Breath samples were collected for the refueling MEs immediately before and 10 seconds after refueling the vehicle to provide an estimate of the highest cumulative exposure. For the commuter traffic and garage MEs, breath samples were collected before, and at 10 seconds after a peak exposure indicated by the PID, and at the end of the ME sampling time. Two breath samples were collected at refueling MEs (total of 20) and three during each commuter traffic and garage tests. This is a total of 50 breath samples. The CO2 level in the breath sample of persons conducting the breath test was measured prior to the pilot study.

2.2 Improvement in Sampling Platform

The most significant change made to the sampling platform was the combination of all sampling inlets at a single location. For the mobile ME (freeway driving), the inlets are all located in the breathing zone near the driver's right shoulder. Figure 2.2-1 shows the current configuration of the inlets. The line in this figure labeled "Sample Inlet" provides sample to the NDIR CO, the MS200, the formaldehyde instrument, one of the two PIDs and all of the integrated samplers (canister, DNPH and solid adsorbent). The SPME fiber, the main inlet and the temperature and relative humidity sensor are all within 3 cm of each other. The T-15 (electrochemical) CO instrument is also very close. This configuration was designed to minimize or eliminate potential variability associated with concentration gradients inside the van. In addition, we recorded the fuel tank temperature by way of a temperature probe secured to the outside of the fuel tank and insulated to prevent influence from the ground or air heat. The video camera recorded the view out the front windshield during the driving ME and was used to record other significant activity at the other MEs. For example, in the garage, the camera was used to record traffic driving by the sampling point.

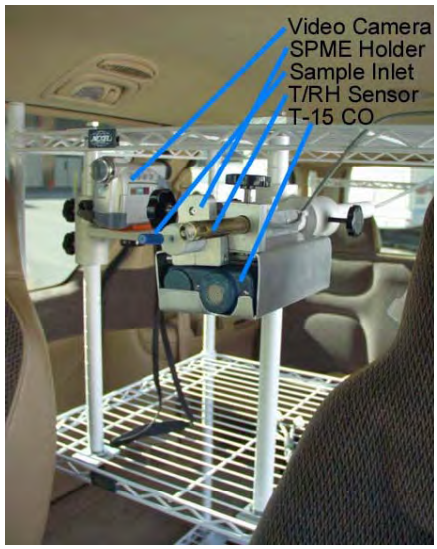


Figure 2.2-1. Van inlets

For the stationary MEs (refueling and garage), the inlet was mounted on a tripod to allow for placement at an appropriate location outside the van. In this case, the temperature and relative humidity probe was relocated as well. This was accomplished by an additional piece of Teflon tubing for the inlet and an extension cable for the temperature and relative humidity probe. This allows the sampling system to be switched from one configuration to the other relatively quickly without disturbing the instruments and samplers. Figure 2.2-2 shows a close-up of the tripod and details the locations of the sample inlet, the T/RH probe, and the SPME fiber. The proximity of all three ensures that no small-scale variations in concentration are influencing the sample.

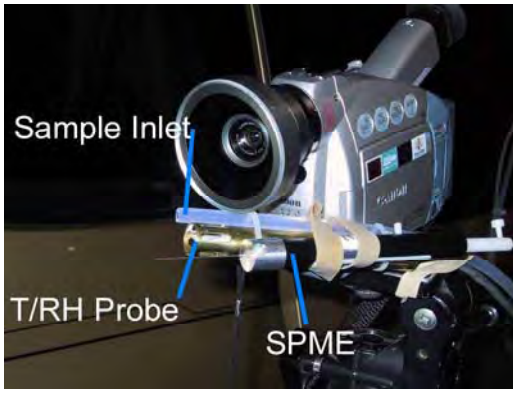


Figure 2.2-2. Inlets mounted on the tripod.

In addition, there were several other modifications made to the van to improve it for the sampling program. Among these were the addition of racks to safely and securely hold the equipment, the upgrading of the power supply, and the addition of a pump and lines to

withdraw the fuel from the fuel tank in between the refueling MEs. A computer-based data acquisition system was also installed to acquire as much of the data as possible in one system. This was used to log all temperature and other environmental parameters, analog outputs from the CO instruments and the formaldehyde instrument, and position, speed and direction information from the GPS unit.

The power system was significantly upgraded to provide power and to eliminate the suspected artifact seen on the T-15 CO under low ventilation conditions. In these experiments, no artifact was observed on the T-15 CO monitor, and thus we are confident that this potential contamination has been eliminated. However, the power system proved incapable of providing enough power for the API NDIR CO monitor. Once we discovered what was wrong (the instrument did not give an error message, rather it began giving very erratic results), we added a set of lead-acid batteries outside the van to provide the power necessary to supply this one instrument.

2.3 Analytical Methods

Most of the analytical methods employed during this pilot study were described in detail before (Zielinska et al., 2002a,b; 2003). The exceptions are the analysis of the breath samples that was performed similarly to the method of Pleil and Lindstrom, 1995, by gas chromatography/mass spectrometry (GC/MS), and the determination of the dependence of SPME concentrations on temperature and relative humidity. The sections below describe these two analytical procedures.

2.3.1 Breath Samples Analysis

The GC/MS system included: Entech 7100 preconcentrator, Varian 3800 gas chromatograph with FID and column switching valve, and Varian Saturn 2000 ion trap mass spectrometer. The Entech preconcentrator consisted of three traps: 50% glass beads/50% Tenax, held at –100 °C during sample transfer, 100% Tenax held at –40 °C and a final focusing trap (a piece of silico-steel capillary) held at –180 °C. The sample is desorbed from the first trap at 10 °C, from the second trap at 200 °C and from the third one at approximately 70 °C to a transfer line heated to 110 °C and connected to the head of the first column. The sample was injected at the head of a 60 m x 0.32 mm polymethylsiloxane column (CPSil-5, Varian, Inc.) held at 30 °C. This column was connected to the switching valve leading into a 30 m x 0.53 mm GS-GasPro column (J&W Scientific). After approximately 7 min the valve was switched so that the effluent from the first column eluted onto a second 15 m x 0.32 mm polymethylsiloxane column connected to the mass spectrometer. The column switch was timed so that the C2 and C3 compounds eluted on the FID and all C4 and higher compounds eluted on the mass spectrometer. The GC program was as follows: 30 °C held for 2 min, then 8 °C/min up to 260 °C.

Calibration of the system was conducted with a mixture that contained the most commonly found hydrocarbons (75 compounds from ethane to n-undecane, purchased from Air Environmental), MTBE, and halocarbons (23 compounds from F12 to the dichlorobenzenes, purchased from Scott Specialty Gases). The standards were prepared in 6 L Silco-Steel

canisters (Restek, Bellefonte, PA) by mixing three different standards through a multi-valve manifold using a Baratron absolute capacitance manometer (MKS Instruments, Andover, MA) to determine the pressure each standard added to the mixture. Prior to mixing, approximately 0.2 ml of ultrapure water was added to the canister to humidify the mixture (for mixture stability). The concentrations in the mixture were in the range of 0.2 to 10 ppbv. Three point external calibrations were run prior to analysis, and one calibration check was run every 24 hours. If the response of individual compounds were more then 10% off, the system was recalibrated.

Carbon dioxide (CO2) from breath samples was determined using GC/FID. Since the FID does not respond to CO and CO2, these species are converted to methane by a methanator, positioned after the GC column, but ahead of the FID. The methanator comprises a firebrick powder impregnated with nickel catalyst, through which a stream of hydrogen gas flows continuously at ~550 °C. For compound separation, a 20-foot x 1/8-inch inner-diameter (i.d.) column, packed with a 60/80 mesh of Carboxen 1000 (Supelco) is used. This column provides sufficient separation between CH4 and CO, without retaining CO2. Five ml samples were injected using a constant volume loop. The minimum detection limit for both CO and CH4 is ~20 ppbv, whereas for CO2 it is ~3 ppmv. The precision of measurements is generally better than 10%.

2.3.2 SPME Methodology

During the Reno 2nd pilot project, SPME fibers were calibrated and analyzed as described before (Zielinska et al, 2002, 2003). However, the gas calibration had to be corrected for temperature, since static (Tedlar bag) calibration is performed at room (25º C) temperature and the sampling temperature ranged from 4º C to 30º C (average 16º C). At lower temperature the fiber uptake is higher, therefore SPME values were expected to be higher than canister data. The temperature correction factors were obtained experimentally in the laboratory in a dynamic flow-through system constructed for the control of temperature and humidity of certified BTEX standards. Humidity corrections are not addressed in this report because the experimental data obtained so far doesn't show a significant change in the SPME response due to the change in humidity.

2.3.2.1 Temperature and Humidity Calibration Experimental Setup

Figure 2.3-1 shows the experimental setup for temperature and humidity calibration. It consisted of a 1L glass bulb that had two stopcocks on each side to let the calibration gas flow through and an injection port covered with a sleeve septum to allow the introduction of a SPME fiber. The bulb was temperature controlled with a cooling/heating system. The temperature inside the glass bulb was measured with a thermocouple. For introducing the desired humidity, a heated injection port was added before the glass bulb entrance in order to inject water with a syringe pump (Harvard Apparatus), Ludovic et al., 2001; Nelson, 1992; McLaren and Zhou, 2000; Martos and Pawliszyn, 1997). The water-dispensing rate can be calculated from the theoretical saturation ratio obtained from a skew T diagram:

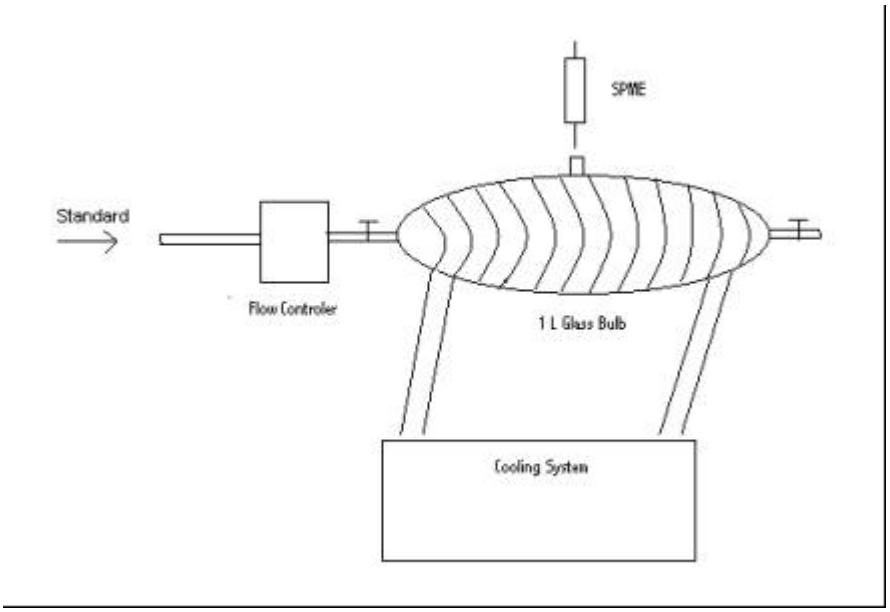
$$RH = 100\ w/ws$$

$$ws = ws(T,P)$$

$$w \text{ is set with the water-dispensing rate as g water/Kg air} = RH*ws/100$$

The experimental humidity was measured with a humidity sensor (Dickson FH121).

Data from the static calibration was compared to the data obtained in the dynamic system to determine a correction factor that could be applied to the sampling data. Tedlar bag calibrations are valid for the type of environments we are measuring where wind should not exceed 4 miles/hour. However, temperature calibration is a better approached in a dynamic system because temperature is the only variable that changes, while in a static system pressure and volume must be adjusted as explained by the ideal gas law and makes the system very imprecise. Some advantages of a dynamic system are greater reproducibility and stability of the standards at lower concentration ranges (Nelson, 1992; Lodge 1984).



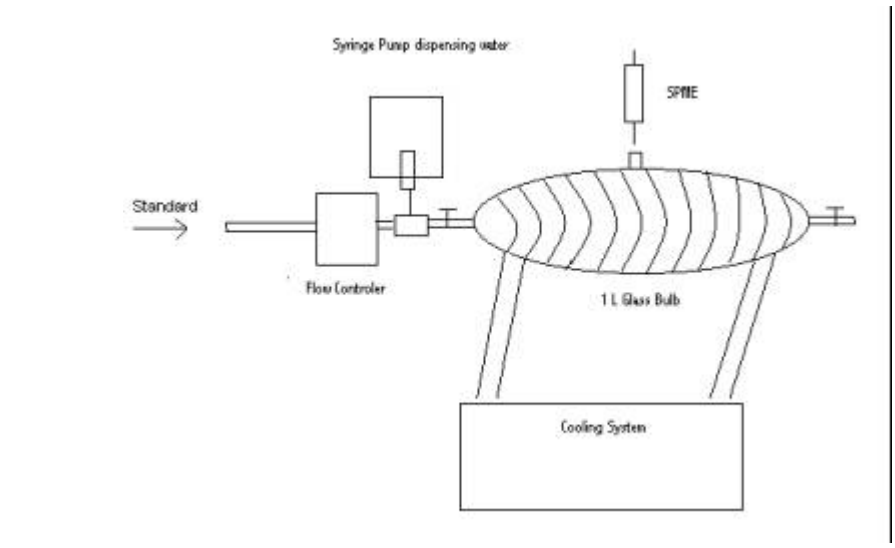
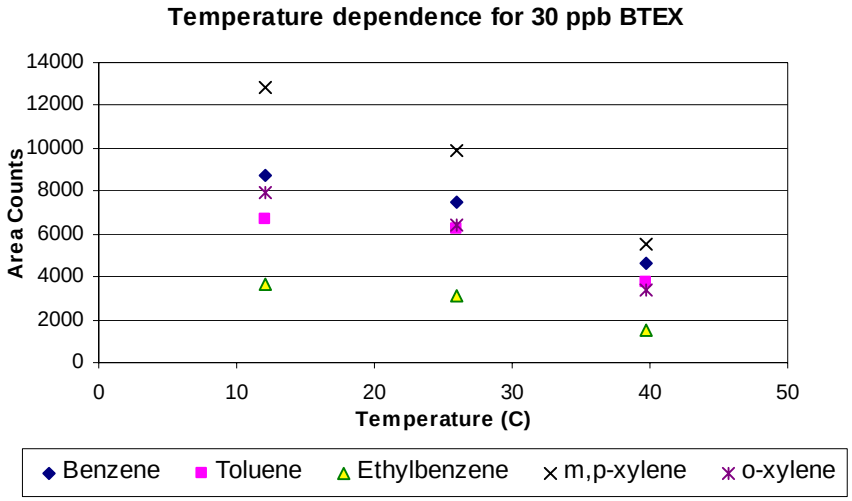


Figure 2.3-1. Set-up for tem perature (upper pane l) and relative hum idity (lower panel) dependence measurements

2.3.2.2 SPME Temperature Dependence

PDMS coating has a small decrease in the response of organics for samples with relative humidity close to 100%. The primary experimental parameter that control the response is temperature. In theory, the effect of temperature on the distribution constant can be predicted, since log(Kfg) is linear with 1/T and the heat of vaporization of the pure solvent (Kfg – partition coefficient). In other words, Kfg can be calculated for the given sampling conditions (Pawliszyn, 2002). This theoretical approach is based on the liquid properties of the PDMS coating in the fiber. However, in practice the theory doesn't satisfactorily match the experimental values. Therefore, we performed more experiments and utilized the experimental approach.

Standards were measured at different temperatures using the dynamic system described above and results were compared to those obtained in a room temperature static calibration. The experiments were performed at different BTEX concentration levels, as shown in figure 2.3-2.



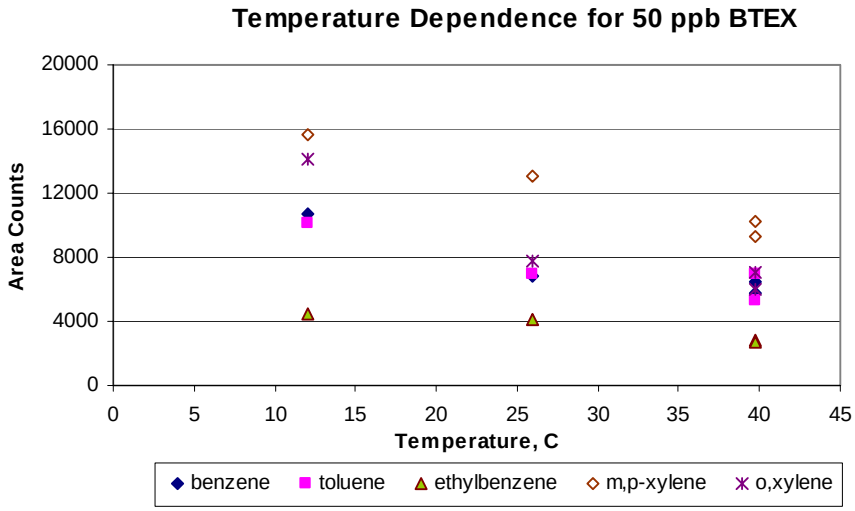


Figure 2.3-2. Temperature Dependence for 30, 50, and 100 ppb BTEX Concentrations.

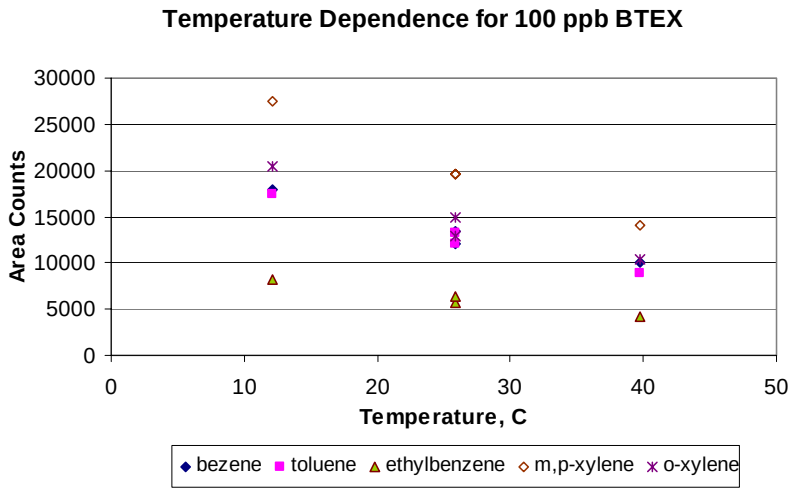


Figure 2.3-2–cont'd. Tem perature De pendence for 30, 50, and 100 ppb BTEX Concentrations.

These data can be plo tted by tem perature in order to obtain a li near relationship with concentration as in Figure 2.3-3.

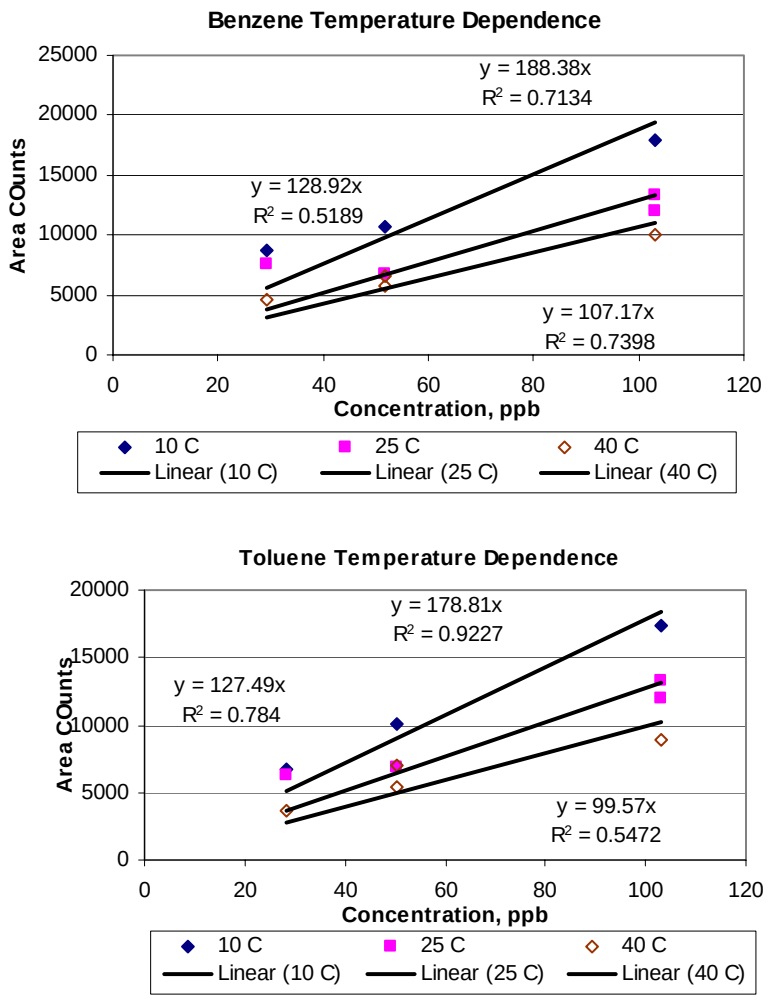
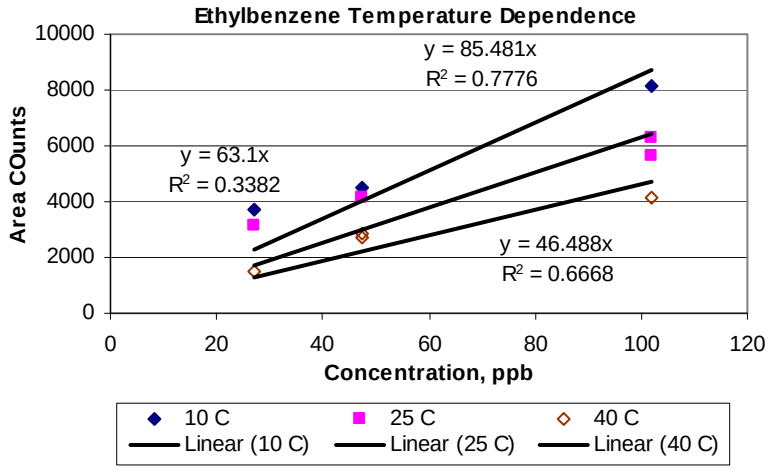
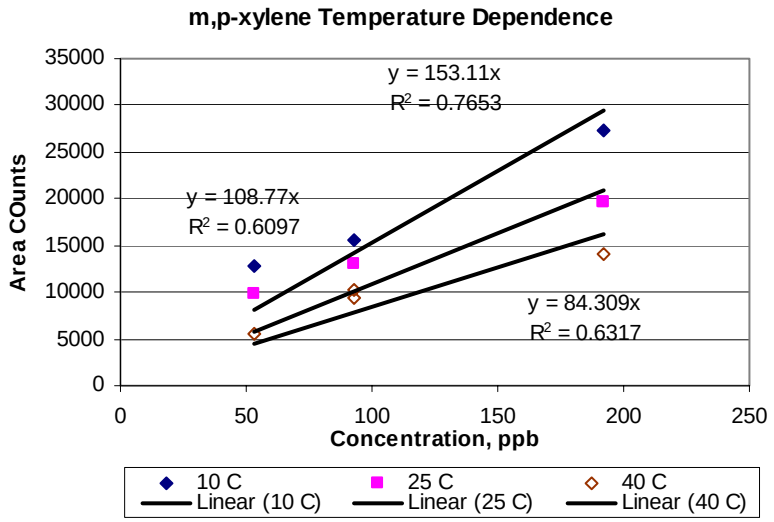


Figure 2.3-3. Concentration calibration at a given temperature for the BTEX compounds.





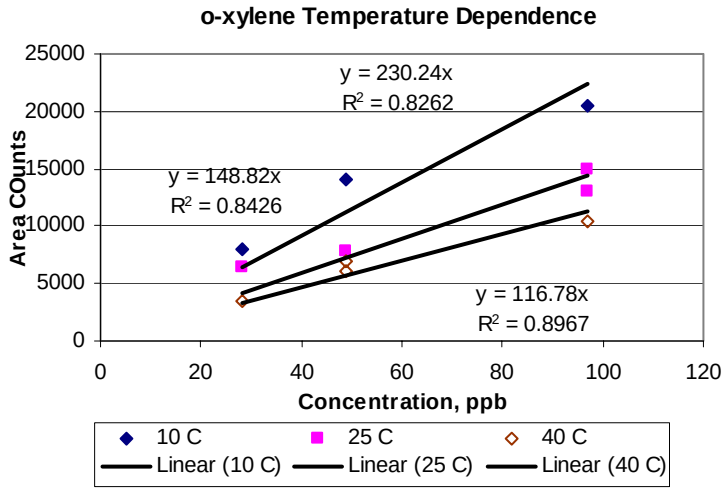


Figure 2.3-3-cont'd. Concentration calibration at a given temperature for the BTEX compounds.

Furthermore, we plotted the slopes from this linear relationship vs. temperature in order to analyze the SPME response for a given temperature. Figure 2.3-4 shows the linear relationship between the slopes at different temperatures.

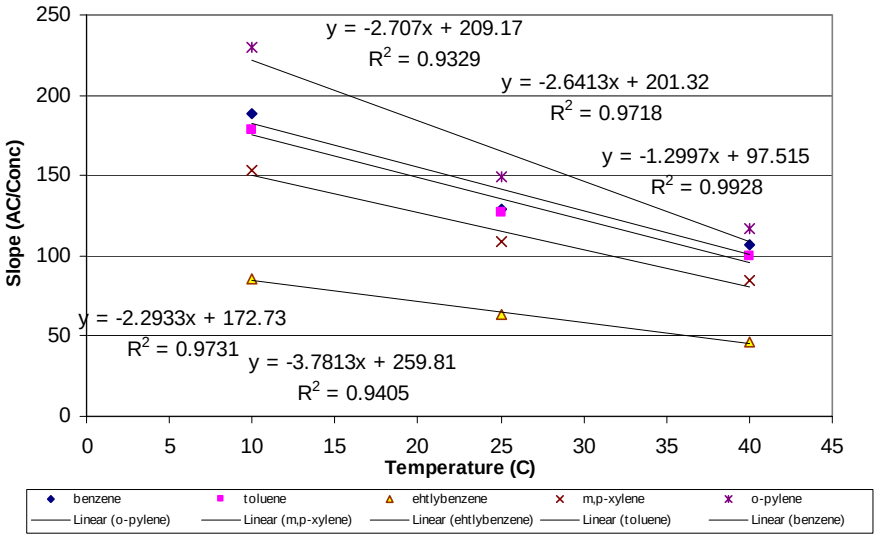


Figure 2.3-4. Dynamic Calibration Temperature Dependence

From this dynamic temperature calibration we correlated the three variables analyzed (such as area counts, temperature, and concentration) and calculated the concentration of the sample by the area counts from the analysis and the sampling temperature. Furthermore, we compared the 25C dynamic and static calibrations and extrapolated the other temperature GC/PID responses in obtaining figure 2.3-5.

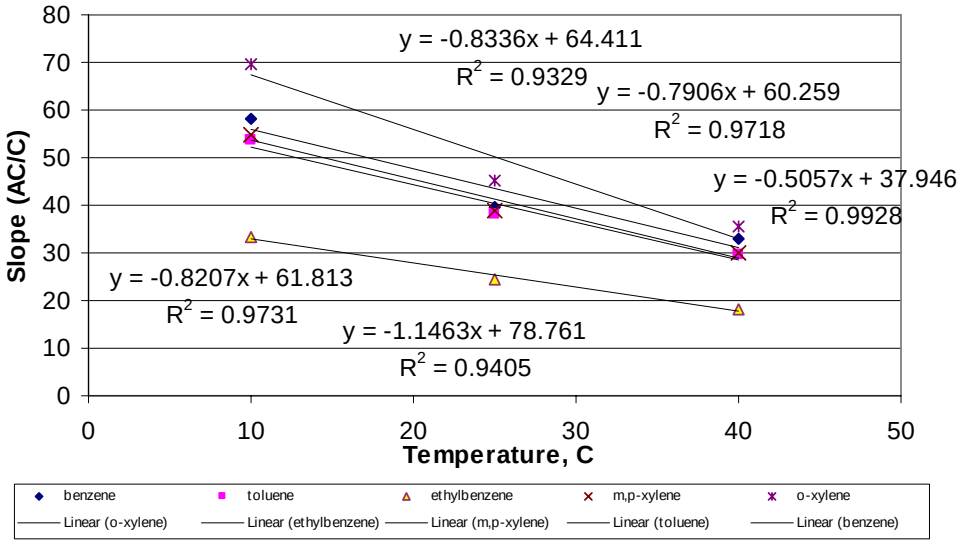


Figure 2.3-5. Static Calibration Temperature Dependence (By interpolation from dynamic system)

The equations that result from these extrapolations are the following:

STATIC SYSTEM (INTERPOLATED FROM DYNAMIC SYSTEM)

Component	equation	correl	Concentration
benzene	y = -0.8336x + 64.411	R2 = 0.9329	AC/(-0.8336T+64.411)
toluene	y = -0.7906x + 60.259	R2 = 0.9718	AC/(-0.7906T+60.259)
EtBenzene	y = -0.5057x + 37.946	R2 = 0.9928	AC/(-0.5057T+37.946)
m/p-xylene	y = -0.8207x + 61.813	R2 = 0.9731	AC/(-0.8207T+61.813)
o-xylene	y = -1.1463x + 78.761	R2 = 0.9405	AC/(-1.1463T+78.761)

AC/C=aT+c
C=AC/(aT+c)

2.3.2.3 SPME Humidity Dependence

Chai and Pawliszyn, 1995, performed several experiments in order to determine the influence of humidity for the 100 µm PDMS response factor. Humidity usually decreases the response factor of each individual compound. The lower response depends on temperature. At lower temperatures, the humidity has a larger decrease in the response factor of a compound. Some compounds are not greatly affected by humidity. The highest effect of humidity seems to be an approximately 25% decrease when going from dry air at 0C-10C into 25% relative humidity. Changes of the area counts at ranges of temperature of 0C-25C for changes in relative humidity from 25%-75% are almost negligible (also discussed by Parreira et al, 2002).

It is understood that humidity affects the fiber response because water at high concentrations is completely adsorbed into the coating of the fiber.

Initial data from the experimental set up described earlier is shown below:

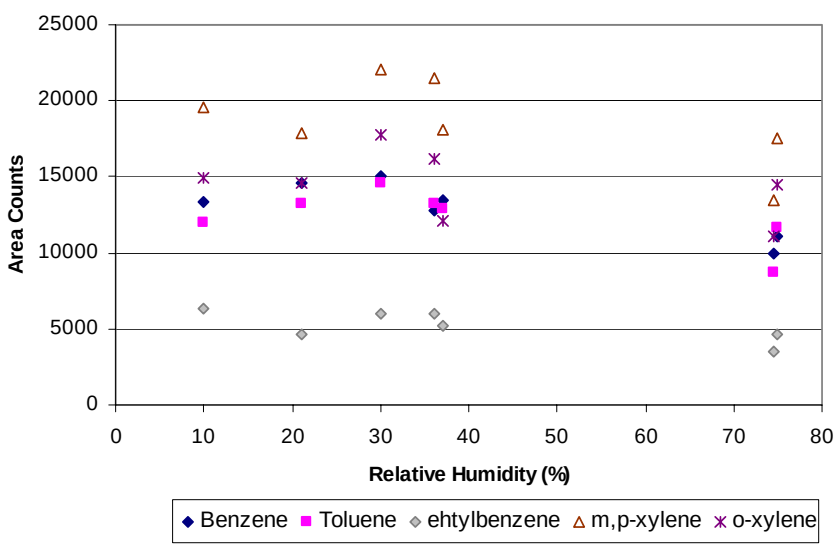


Figure 2.3-6. Humidity Dependence on SPME response for a 100ppb BTEX standard at 25C.

Current experiments at 25C determined that humidity in the BTEX compounds does not affect the GC/PID response significantly, although is lowers the response slightly at RH > 75% .

2.4 Data Capture

The overall data capture rate for all the 2nd Reno Pilot Study measurements is provided in Table 2.4-1, with the complete details for each ME presented in Appendix A. Overall the data capture for the integrated methods was nearly complete . Only one solid adorbent tube was lost to breakage. The "Refuel Can" in Table 2.4-1 refers to the 5-minute integrated canister collected during the actual refueling event. One canister could not be sampled because it was at atmospheric pressure when opened in the field, and the data obtained from the other one were invalidated, thus leading to a 80% capture rate for this category. The "Breath Can" refers to the breath canisters (2 or 3 per ME) which were all collected. For the continuous and semi-continuous methods, we had very good data capture with only one run missing for the Outside PID (the one measuring outside the vehicle cabin during the freeway ME). This was due to a software difference between this and our older instrument that resulted in the data logging function being accidentally turned off. The NDIR instrument lost some data due to insufficient power in a few early runs; fortunately the T-15 CO functioned perfectly for these runs. For the few runs where the T-15 CO data logging had problems, we have the NDIR data thus at least one instrument was functioning for CO during all MEs. The MS200 worked very well during most of the early runs, but some detector sensitivity problems and other undiagnosed problems resulted in complete loss of data for the last four runs. One freeway run had mostly good data with 5 minutes out of the 40 minute total being lost due to electrical noise of undetermined origin. This is a similar problem we had during the San Antonio study and may be related to the van's electrical system since proximity to the other instruments in the refueling MEs did not cause similar noise.

The formaldehyde instrument showed some good data but overall data capture rate was low , mostly due to an electrical shortage in the thermocouple that controls the heated reaction cell. This problem was not identified and fixed until the afternoon of May 2, 2003. Without adequate control of the temperature of the heated reaction cell, there is little certainty that the formaldehyde collected was actually derivatized in a consistent manner. This malfunction was diagnosed and fixed prior to the parking garage sample ME2-4, and did not reoccur. Another major source of malfunction was the presence of air in the sample stream reaching the detector. Although an in-line debubbler worked well for removing air bubbles from the sample stream, air may still have reached the detector if pump flow rates were not properly balanced among the 4 pumps and air was accidentally pumped into the detector. This occurred during the freeway (ME1-5) and refueling without vapor recovery (ME4-4) tests on May 5, 03. Another limitation of this continuous instrument was the long stabilization time required for the fluorescence detector upon instrument start-up. In some cases, response at the detector was still stabilizing when the sampling period began. One of the most significant limitations of the formaldehyde monitor was an apparent sensitivity to moving environments. It has been observed that when the formaldehyde instrument was warmed up and operated in a stationary environment, such as a parking garage, and then subjected to transport while still operating, response at the detector oscillated and increased in overall.

Figure 2.4-1 shows the response of the continuous formaldehyde analyzer, stabilized and "zeroed" with a DNPH cartridge at the inlet, when stationary and following startup and driving of the sampling van where the response of the detector increases and oscillates.

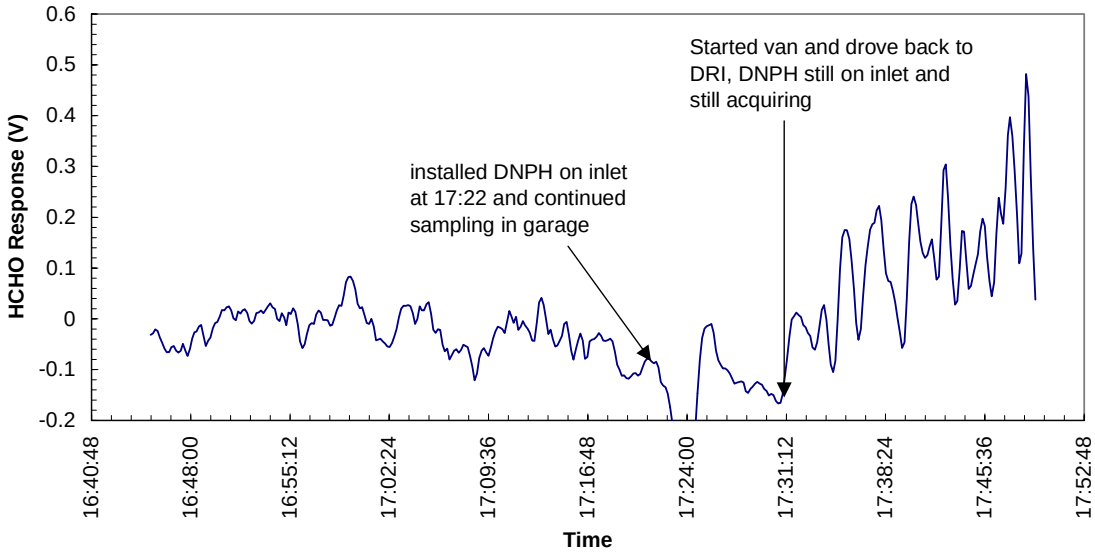


Figure 2.4-1. Effect of driving on continuous formaldehyde analyzer, during and after sampling in ME2-5.

The environmental conditions (temperature, relative humidity, position, speed and other parameters) had one run where the logging system apparently locked up about 6 min into the run and gave no further data. This was a 20 min refueling run and does not represent a significant loss in data since the temperatures and humidity probably did not change appreciably.

Table 2.4-1. Data Capture Summary

Parameter	Data Capture
Ambient Can	100%
Refuel Can	80%
Breath Can	100%
DNPH	100%
Solid Ads.	95%
SPME	100%
PID In (1)	100%
PID Out (2)	80%
NDIR CO	85%
T-15 CO	85%
MS200	70%
Formaldehyde	10%
Env. Cond.	95%

3. RESULTS

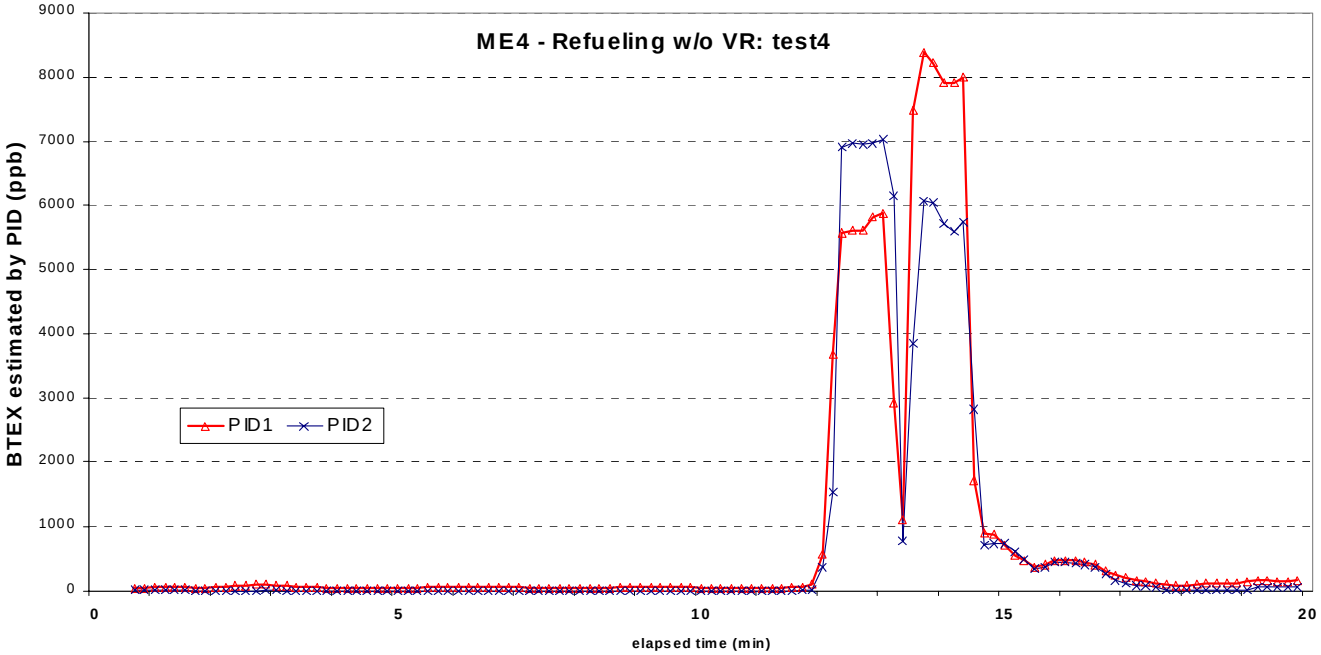
The main goal of the 2nd Reno Pilot Study was to demonstrate proper operation and reliability of analytical instrumentation and comparability of time-integrated, semi-continuous and continuous methods for compounds of interest. The results section examines the consistency between redundant measurements and co-pollutants, evaluates temporal and spatial variations, and correlations among the various data sets for measured parameters that we expect will be correlated. One key aspect of the study design was the built-in redundancy between the continuous methods and the time-integrated methods. For example, CO was measured from the time-integrated canister samples and from the T-15 and NDIR instruments. We measured BTEX from canisters, continuous MS-200 and semi- continuous SPME as well as a surrogate measure in the PID signal. Formaldehyde was measured by the continuous HCHO instrument and by the DNPH cartridges. In addition, we measured PID signal from two independent ppbRAE units positioned in-cabin and outside the cabin, or collocated in outdoor microenvironments.

3.1 Method Comparison of Redundant Data

3.1.1 PID versus PID

Two identical ppbRAE continuous PID monitors were used to estimate total VOC concentrations, ionizable at 10.6 eV, inside and outside the vehicle cabin. Prior to and after the pilot study, both units were calibrated using an activated carbon inlet filter for the zero point and a certified BTEX mixture (total concentration 3700 ppb) for span.

During several tests, the second unit was collocated with its inlet within 10 cm of the inlet of the primary unit for quality assurance purposes. The resulting data is shown in Figure 3.1-1a,b. While the two units track each other accurately, after adjusting for differences in inlet transit time, the absolute concentrations recorded differ significantly. The primary unit (PID1) demonstrated a positive offset of 40-50 ppb, which was expected since it would not read below ~40 ppb even when the carbon inlet filter was in place. This behavior is evident in the tests shown in Figure 3.1-1b. No consistent bias was observed at the high peak concentrations shown in Figure 3.1-1a, with both units reading higher at times. Since this time a difference in software was identified, and they have been harmonized for future studies.



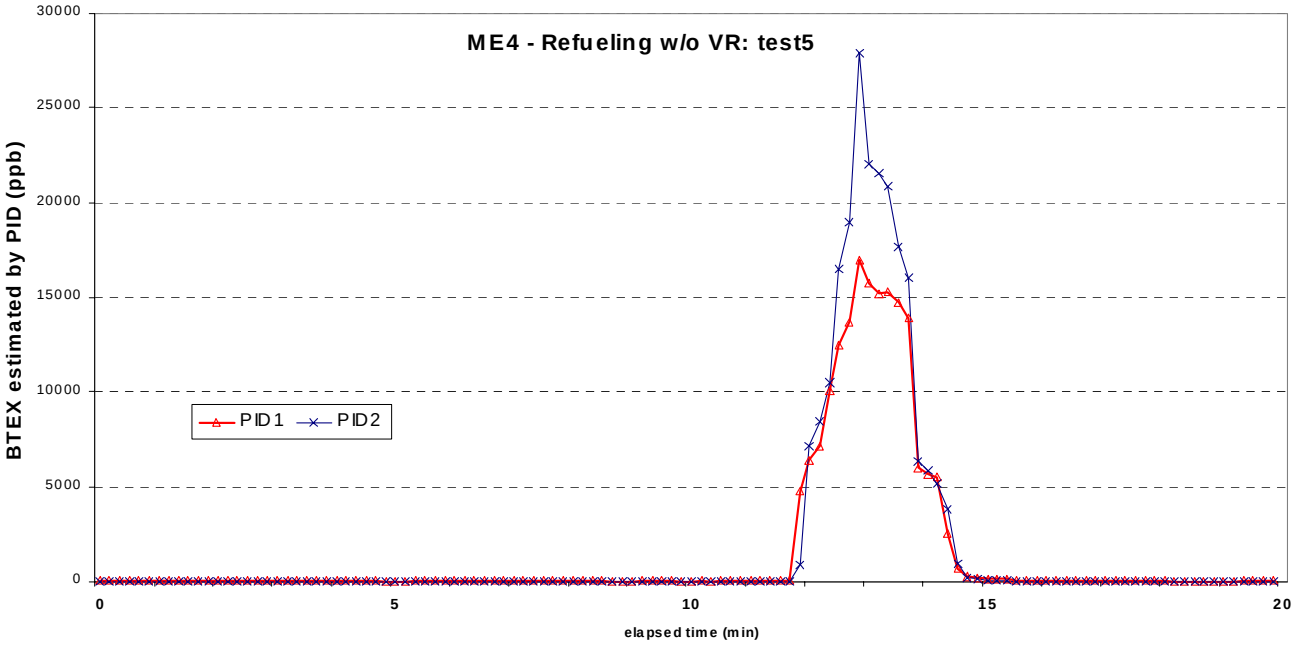
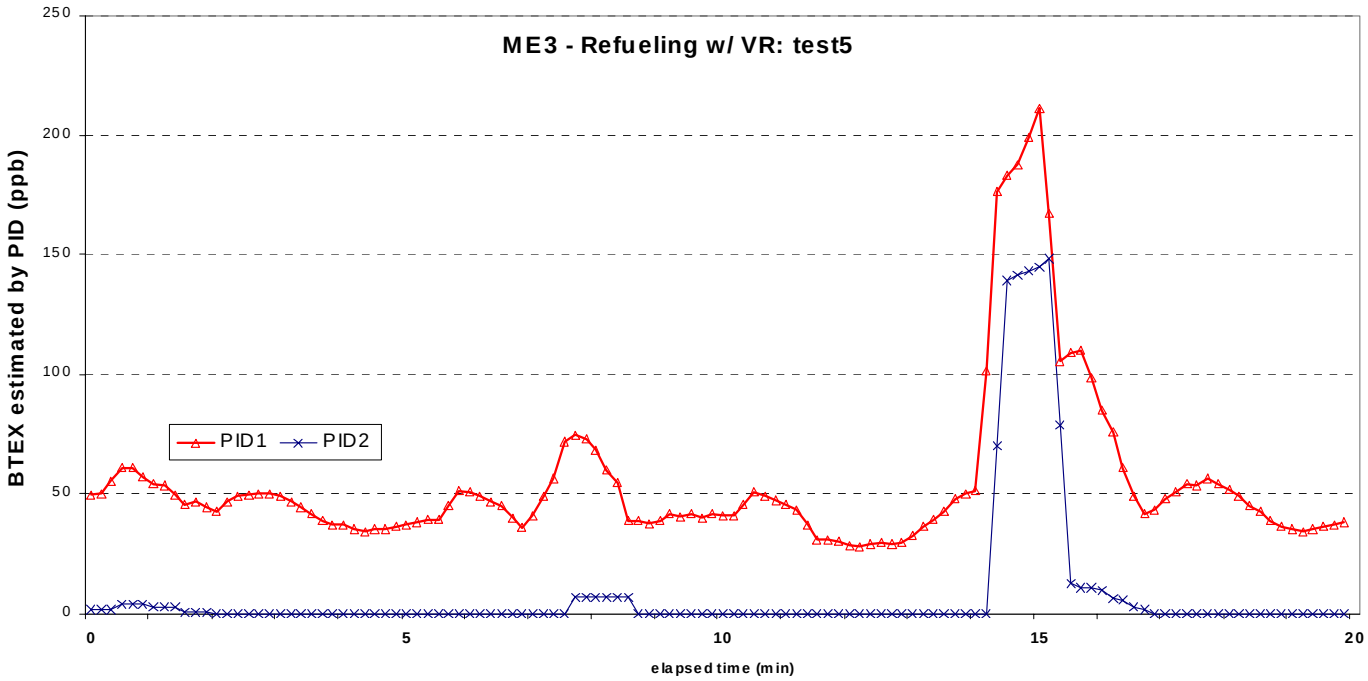


Figure 3.1-1a. Comparison of estimated BTEX concentrations measured by PID instruments with inlets collocated within 10 cm. Data are running 1 minute averages. VR = nozzle vapor recovery.



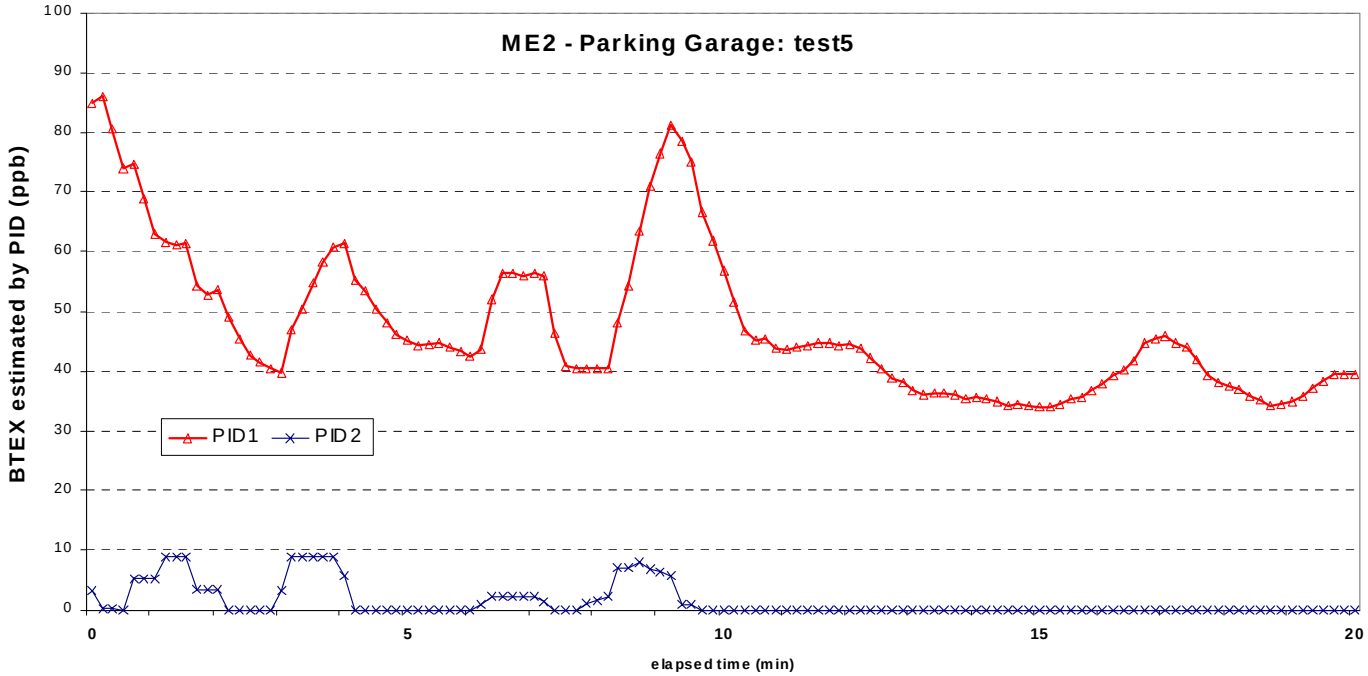
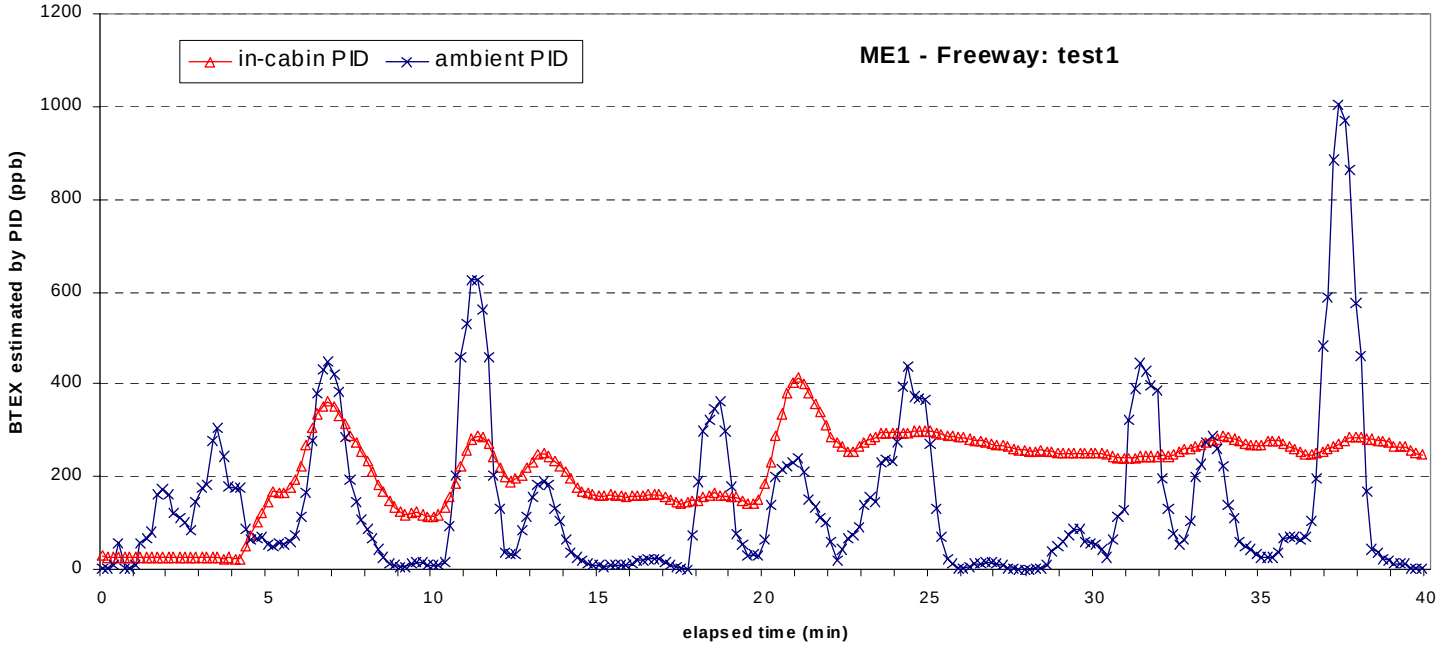


Figure 3.1-1b – cont'd. Comparison of estimated BTEX concentrations measured by PID instruments with inlets collocated within 10 cm. Data are running 1 minute averages. VR = nozzle vapor recovery.

Figure 3.1-2 shows the corresponding total VOC concentrations, ionizable at 10.6 eV, recorded by the two pbRAE monitors during four freeway driving tests (data for the ambient unit during test 2 was lost due to a data logger configuration error) where the second unit measured ambient VOC concentrations outside the vehicle. As in the collocated unit tests, the two monitors track each other well during the high ventilation segment of the test (first 20 minutes). The less dynamic variations in concentration recorded by the in-cabin unit are consistent with expectations.

After the switch to low ventilation conditions at 20 minutes elapsed time, the in-cabin unit shows very little correlation to the ambient unit and, while not always stable, shows no accumulating drift evidence of interior sources or interferences.



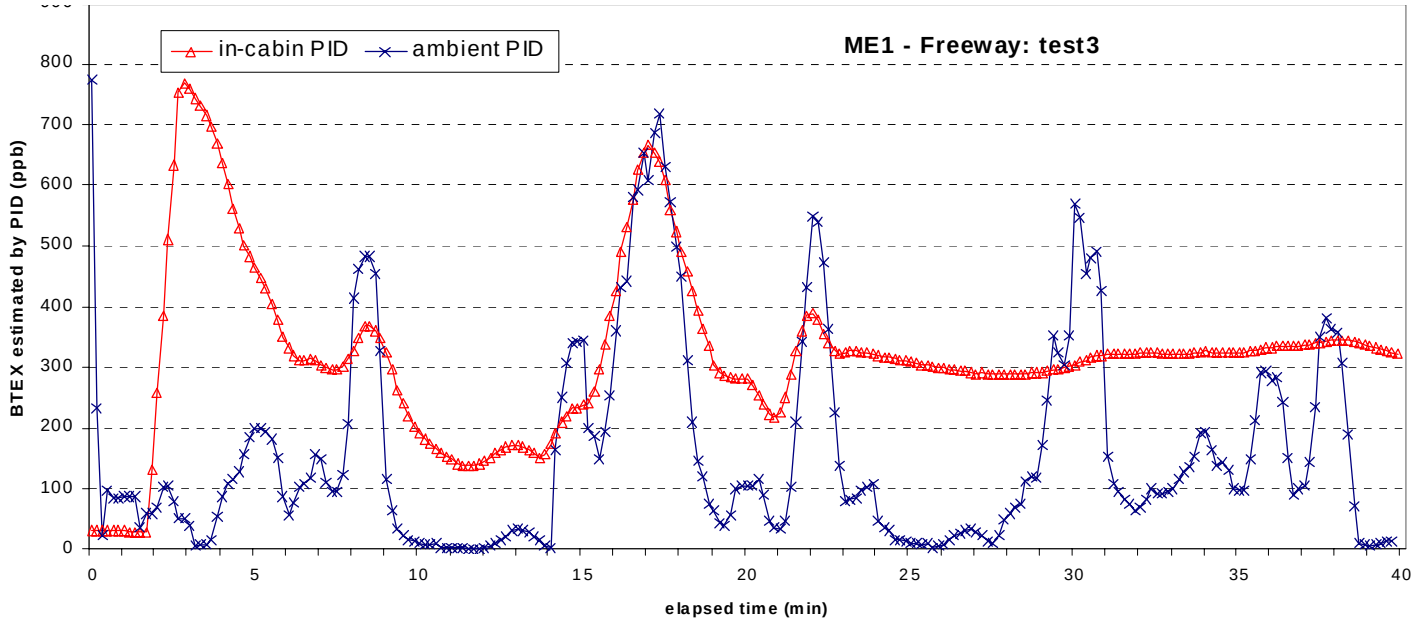
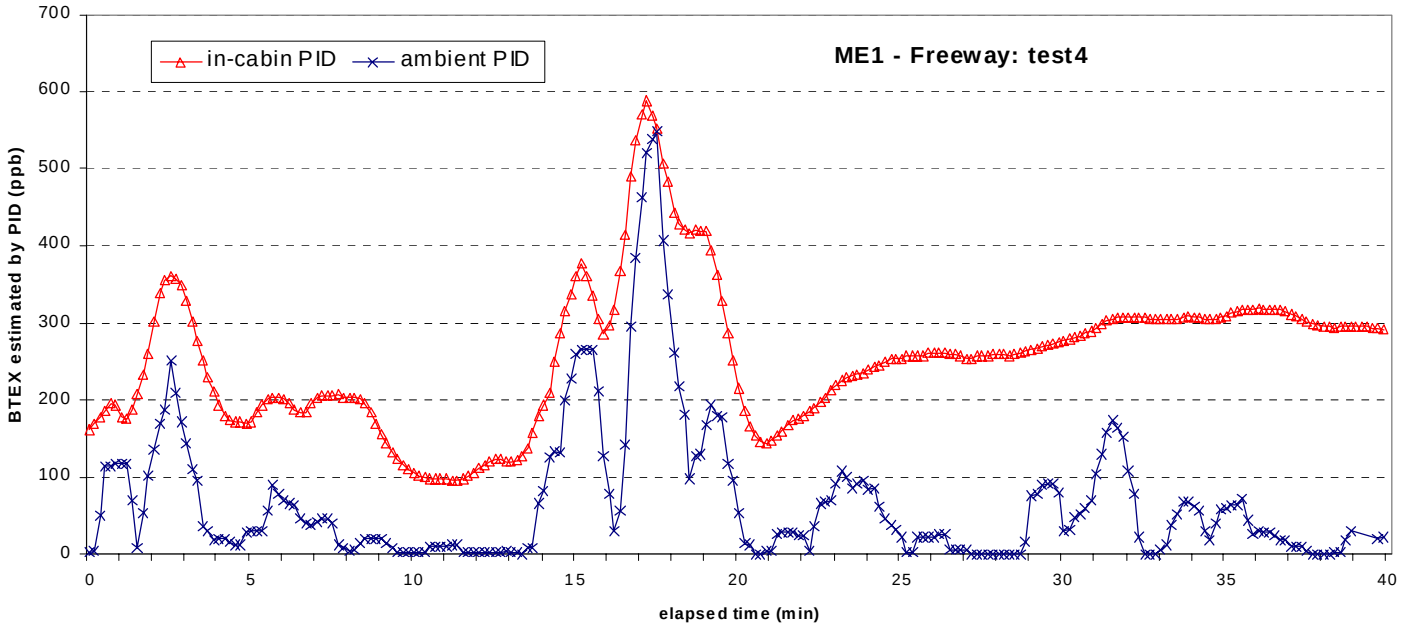


Figure 3.1-2. Comparison of estimated BTEX concentrations measured by PID instruments during freeway driving tests. Data are running 1 minute averages.



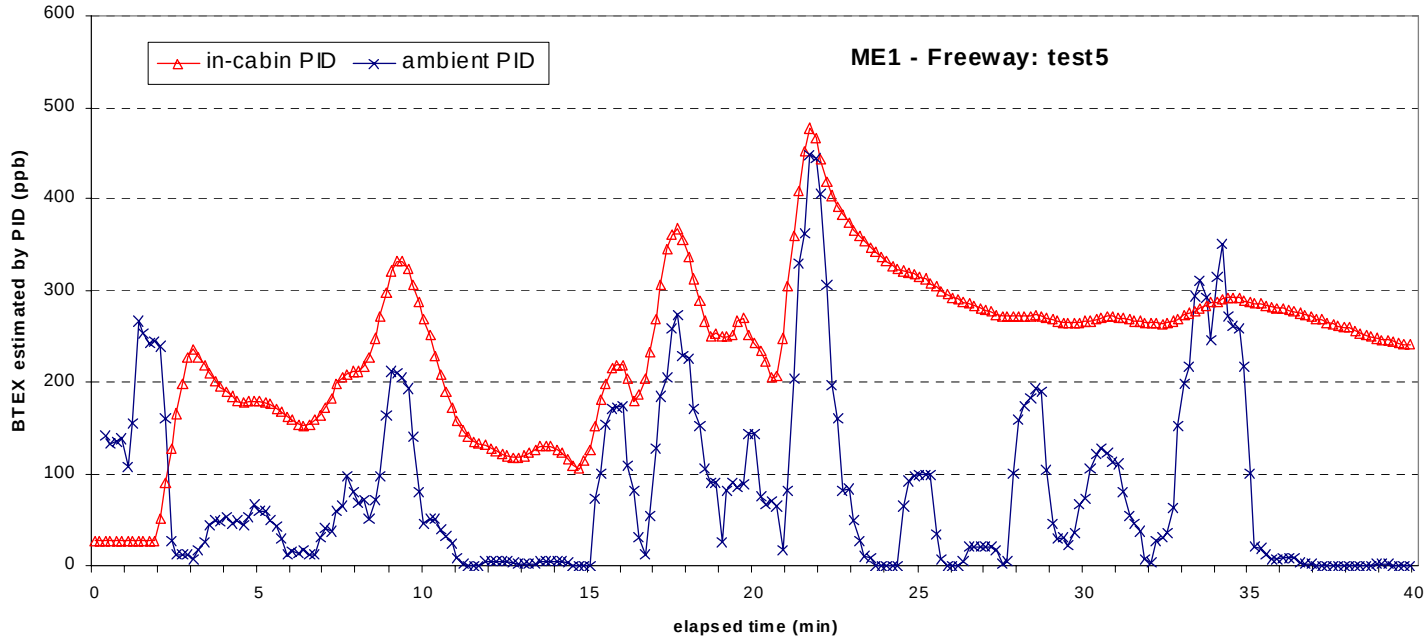


Figure 3.1-2 –cont'd. Com parison of estim ated BTEX concentrations m easured by PID instruments during freeway driving tests. Data are running 1 minute averages.

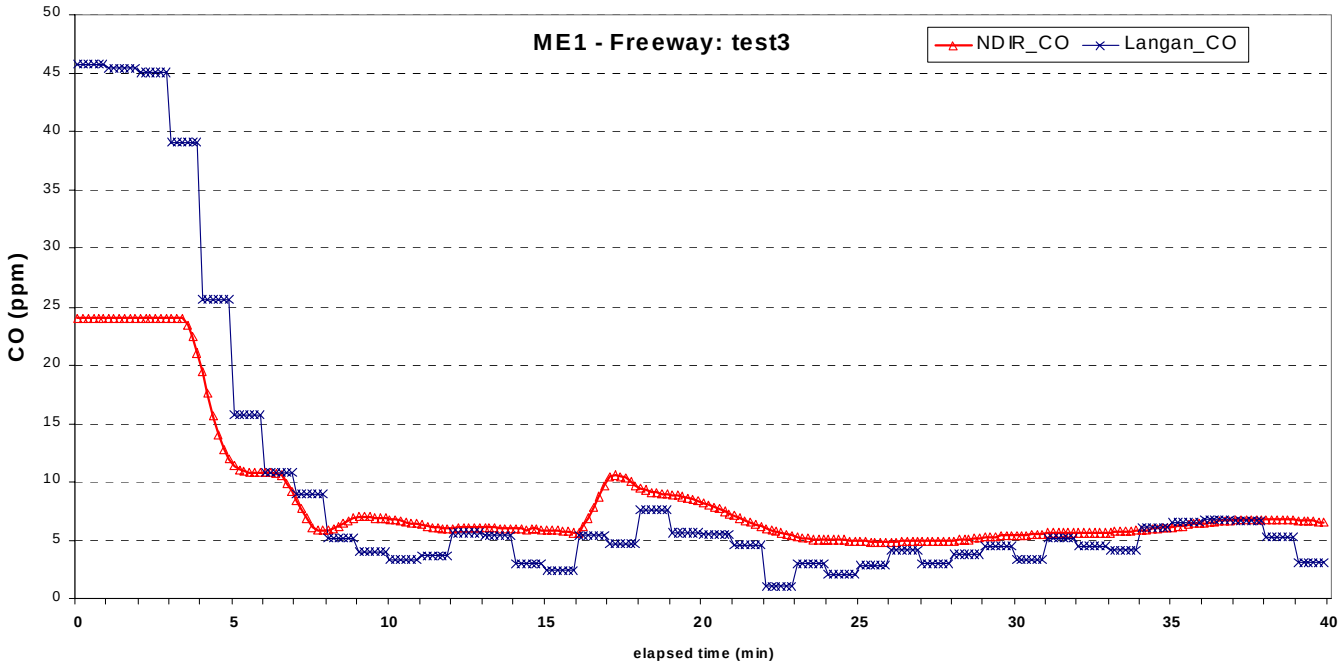
3.1.2 NDIR vs. Electrochemical CO

Both an EPA-certified gas-filter correlation NDIR optical CO analyzer (API model 300) and a portable battery-operated passive electrochemical cell instrument (Langan T-15) were operated during all tests to measure CO. Although data recovery was less than 100% for each method, and the electrochemical instrument was not equipped to sample outside the in-cabin breathing zone during the refueling and garage tests, collocated measurements were collected during the two tests shown in Figure 3.1-3.

Although the NDIR instrument recorded higher peak values, due to its faster reponse time, the measurements are generally consistent to within about 1 ppm. During the low-ventilation, half of the tests shown the CO concentrations remain at or decrease towards the lowest level measured during the high-vent phase. This behavior suggests that no in-cabin sources or interferences are present.

There was good agreement between the two types of CO analyzers, due to the NDIR instrument's internal adaptive filtering. This filter, which is required for EPA certification, is intended to adjust the response rate of the instrument with respect to the stability of the raw detector signal during a preceding time period, to reduce noise. The length of the 'filtering' period can range from 10 seconds up to 2 minutes, according to the manufacturer. In practice, the adaptive filter effectively averages the output data over a variable time period, resulting in concentration fluctuations that are broader and have a peak that occurs later in time and a lower maximum height. This effect can be seen in Figure 3.1-4, which shows the measured CO concentrations from two similar instruments drawing air from the same inlet inside the cabin of the test van while driving on freeway and surface streets with windows open (this test was performed later in the day than the ME1 tests, concentrations are lower). The API300 was the same instrument used in the pilot study, while the ML9830 (Monitor Labs) was an equivalent EPA-certified gas-filter correlation NDIR instrument that was operated with the adaptive filter turned off (a fixed 10 second filtering period was selected). Both instruments have the same performance specifications and were calibrated just prior to the test using zero air and a 10.0 ppm CO standard, yet the ML9830 time series is much more dynamic and shows higher peak concentrations. Figure 3.1-4 also shows a time series of the ML9830 data in which the four minutes preceding each data point were averaged. This series matches the API300 data almost exactly, except for the first large peak which was apparently steep enough to trigger the API300's adaptive filter into fast response mode.

Despite the differences in response rate, the overall average concentrations recorded for the test period shown were very comparable: 1.26 ppm from the ML9830 versus 1.31 ppm from the API300. Fast response is desired in order to better characterize the variability of pollutant concentrations in a microenvironment, so the ML9830 is preferable for the field study. In addition to the convenience of front panel configuration of the data filter, the ML9830 also uses about 50% less power and has an internal zero air generator to allow automatic baseline checks.



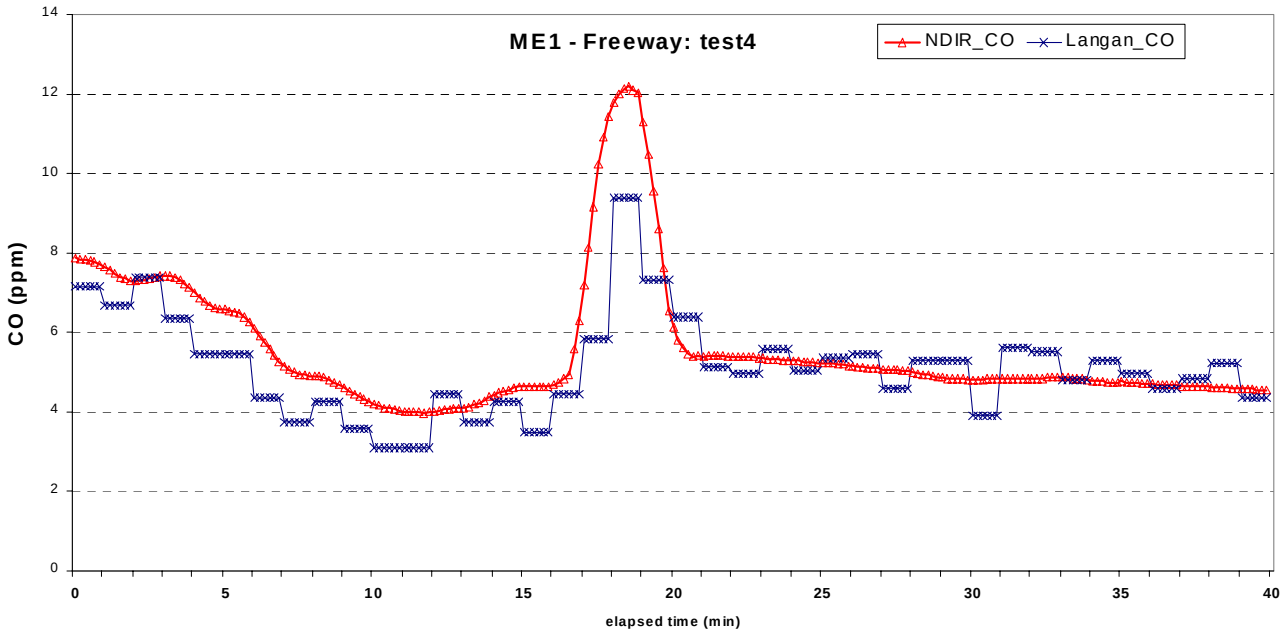


Figure 3.1-3. Comparison of NDIR (API model 300) and electrochemical (Langan T15v) CO monitors during two freeway driving tests.

The NDIR CO data are running 1 minute averages, while the electrochemical instrument recorded data is in discrete 1 minute averages. In test 3, the NDIR instrument's analog output range (0-20 ppm) was exceeded during the first 4 minutes.

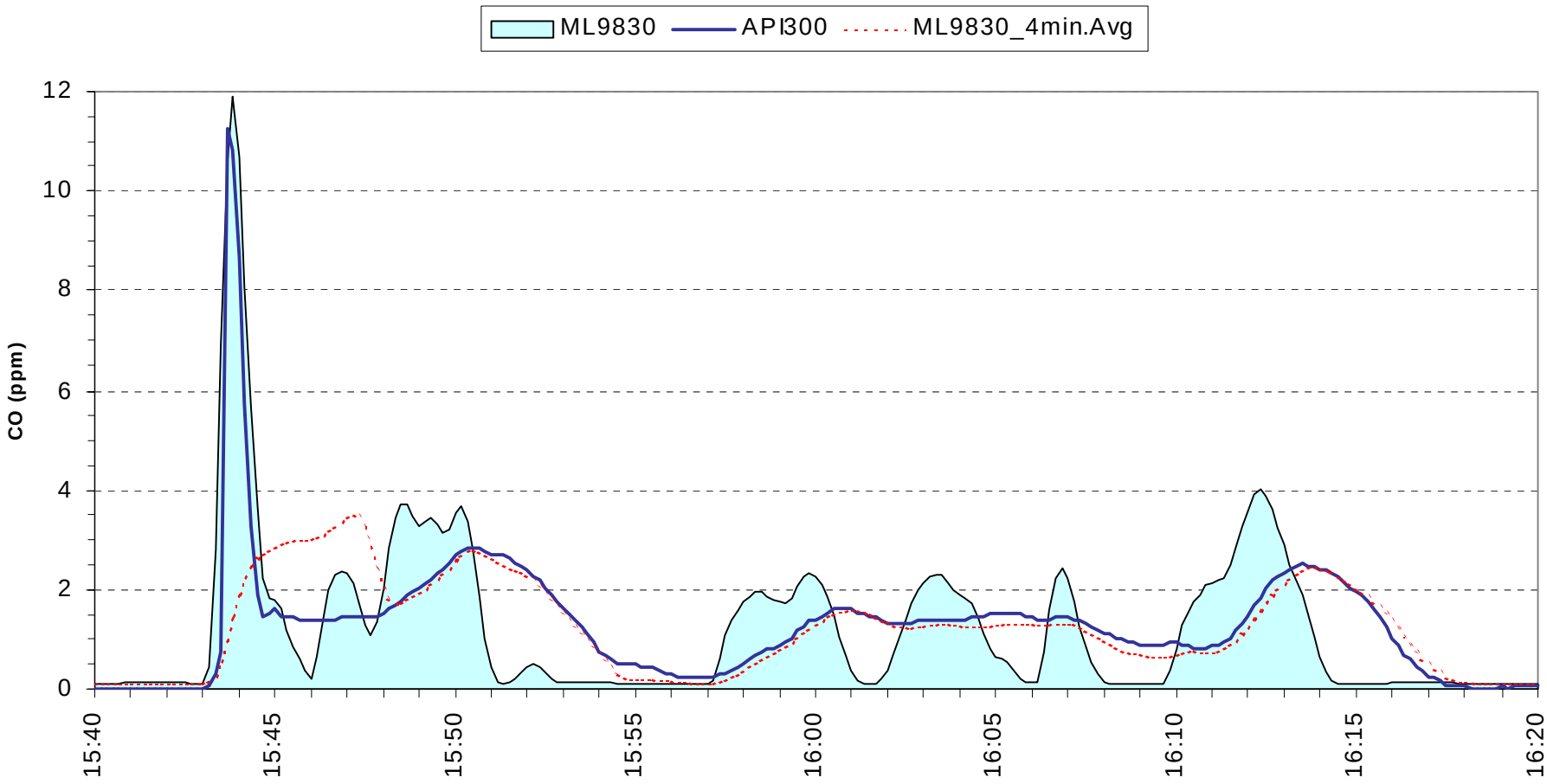
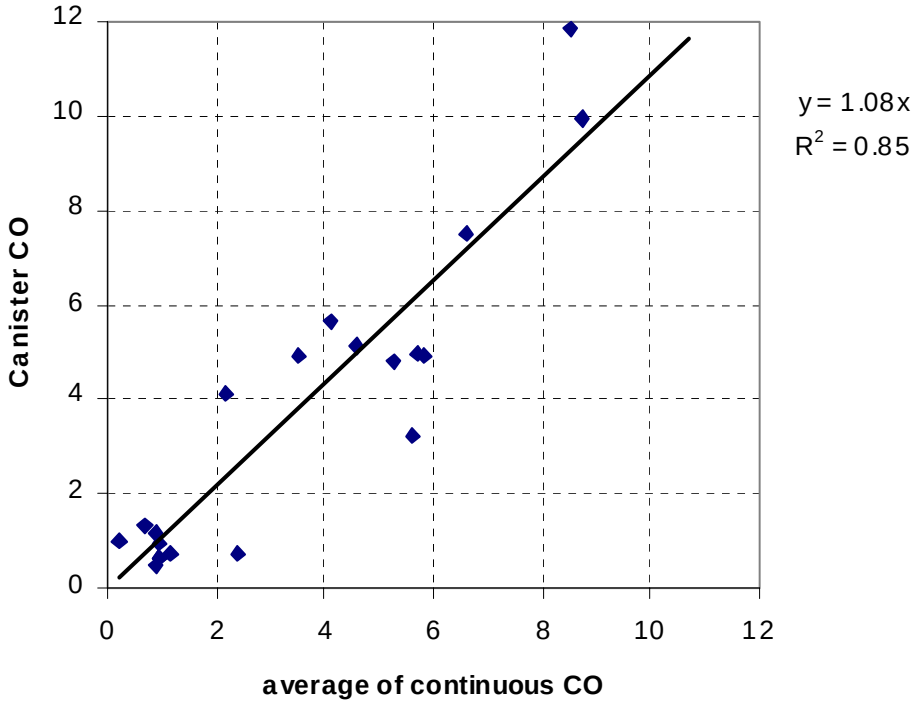


Figure 3.1-4. Comparison of two gas-filter correlation NDIR CO analyzers during on-road sampling.

Data from the ML9830 instrument are shown as recorded (10 second averages) and as 4 minute running averages.

3.1.3 CO versus Canister CO

Average CO concentrations were also measured by GC analysis of the integrated canister samples that were collected for the duration of each test. Figure 3.1-5 shows a scatter plot of the average continuous data from the NDIR or electrochemical CO instruments versus the CO from the corresponding canister. The canister CO is generally about 8% higher, but there is no consistent bias. The comparison is also made on a test-by-test basis in the second chart of this figure, showing that discrepancies between the two methods occur in all microenvironments and at both high and low concentrations. The underestimation of CO by the NDIR instrument in the two tests with the highest average concentration (ME1- test 3 and ME2 – test 2) is due, at least in part, to exceedences of the instruments output range which resulted in truncation of peak concentrations above about 23 ppm. This over-ranging problem was identified and corrected before the end of the pilot study.



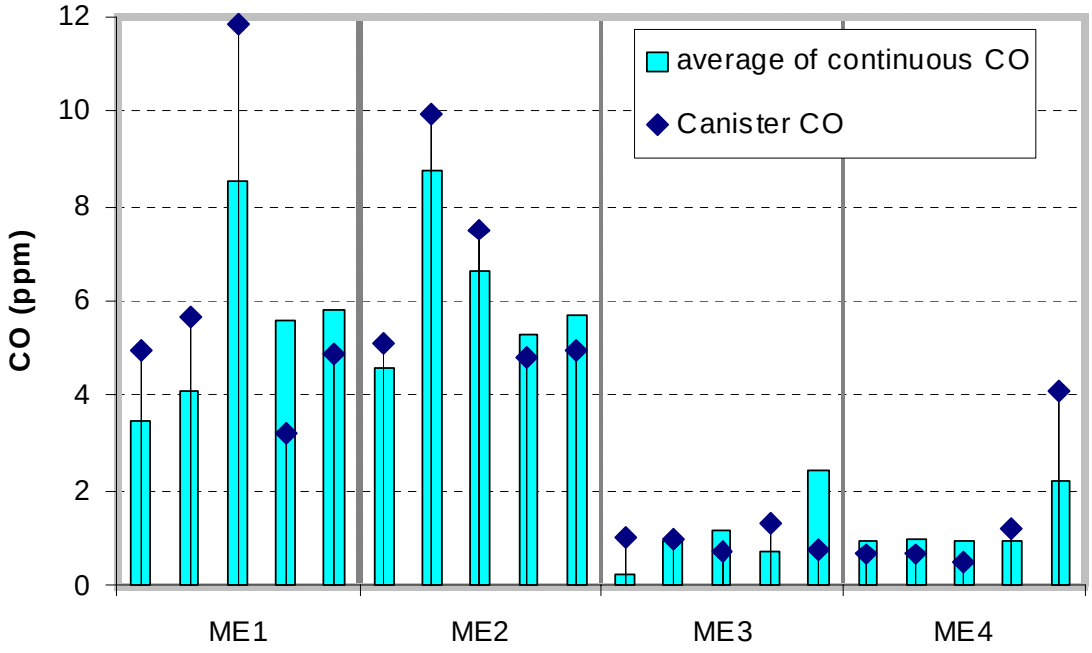


Figure 3.1-5. Average CO concentration for each test measured by continuous monitor and GC analysis of integrated canister sample. ME1= morning rush hour commute; ME2=parking garage; ME3= refueling with vapor recovery; ME4= refueling without vapor recovery.

3.1.4 MS vs. Canister

The MS200 performed well in 16 of the 20 ME tests. For all of those runs we can compare the integrated MS200 response to the canister data. Figure 3.1-6 shows the correlation for benzene, toluene and the sum of the C8 benzenes (ethylbenzene, o, m, & p-xylene). The C8 benzenes are presented together because we cannot separate them using the MS 200. The correlations are all very good, with > 0.9 R-square. The correlation for toluene is the best with a 0.99 R-square. Both toluene and the C8 benzenes show a close 1:1 correlation, but benzene seems to be overpredicted by the MS200.

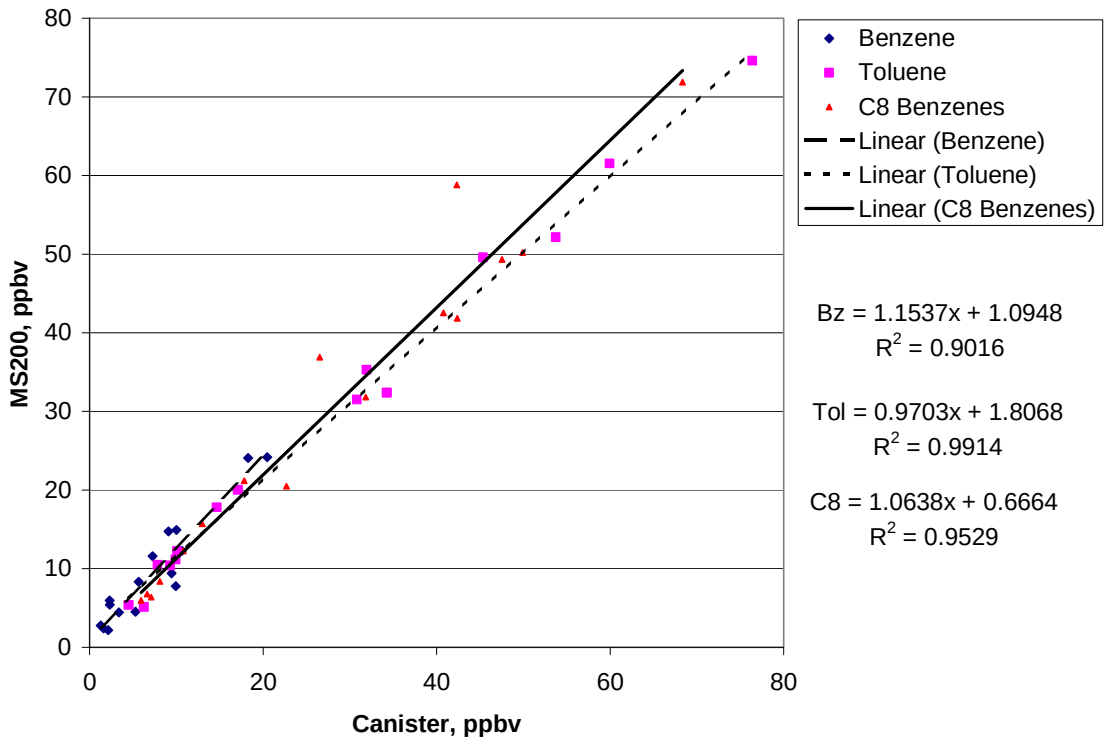


Figure 3.1-6 Comparison of canister and MS200 data for all measured species.

To further investigate the comparison for benzene, we plotted the benzene concentrations in Figure 3.1-7. This figure shows random scatter around the trend line over the range of 25 ppbv down to less than 2 ppbv. Overall the MS200 performed very well for runs with valid data. We are still investigating the causes of the failures of this instrument and feel that it provides excellent supplemental data but should not be relied upon as a primary method.

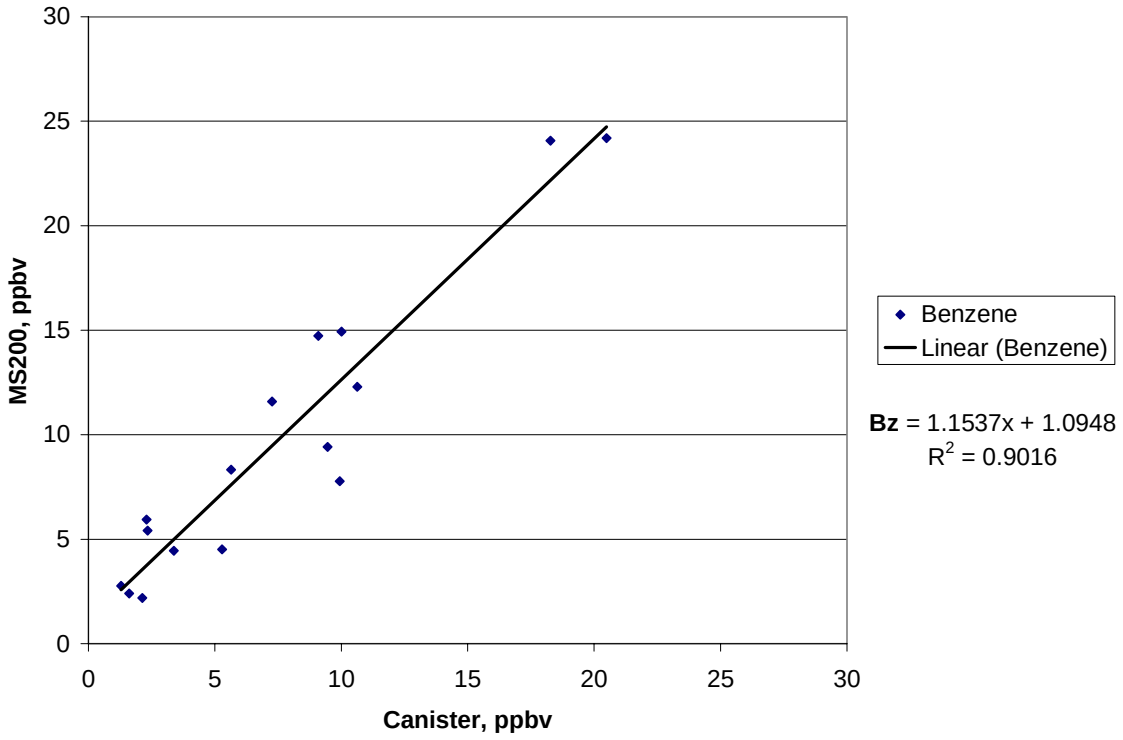


Figure 3.1-7. Comparison of MS200 and canister for benzene only.

3.1.5 SPME vs. Canisters

Table 3.1-1 shows the comparison of canister BTEX data with averaged and temperature corrected SPME data. In general, SPME BTEX concentrations are higher than canister concentrations. This is most probably due to the temperature differences between the static calibration and sampling conditions and inadequate correction for temperature. However, the passive SPME sampling rate could also be affected by the local wind speed, especially if the local gusts are close to 5 mph threshold. We observed higher SPME uptake of analytes in the dynamic system, if the flow rate of a standard gas mixture was higher than 100 ml/min.

After cleaning and conditioning, the SPME fibers were stored in the freezer and taken to sampling sites in a cooler with dry ice. Although the fibers were taken out of the cooler prior to sampling, we are not certain if sufficient time was allowed for fiber equilibrations to ambient temperature. In retrospect, it was an error, since we determined later that the fiber uptake is highly dependent on temperature (see Section 2.3.2). For the primary study we will change the SPME fiber storage conditions and will store them in metal cans with activated charcoal at the bottom (similar to Tenax tubes) at ambient temperature.

Table 3.1-1. Data comparison between SPME and Canister

site	date	strthhmm	can benze	spme benze	can tolue	spme tolue	can etbz	spme etbz	can mp_xyl	spme mp_xyl	can o_xyl	spme o_xyl
Freeway	4/29/03	742-822	9.10	15.03	45.35	87.42	7.48	18.37	24.92	50.53	9.94	15.96
Refueling W/Vapor Recovery	4/29/03	1200-1220	3.38	11.94	9.91	52.85	1.43	10.70	4.82	27.04	1.85	10.03
Garage	4/29/03	1642-1712	5.65	19.00	14.67	56.49	3.10	16.11	10.52	43.12	4.20	14.04
Freeway	4/30/03	739-819	10.01	24.01	53.75	127.78	8.69	25.11	29.48	72.93	11.74	23.15
Refueling W/O Vapor Recovery	4/30/03	921-941	9.46	29.04	34.27	112.88	5.50	18.02	19.02	66.76	7.31	19.75
Refueling W/Vapor Recovery	4/30/03	1045-1105	1.30	4.66	4.53	20.46	0.97	6.93	3.50	19.48	1.47	5.00
Refueling W/O Vapor Recovery	4/30/03	1205-1245	2.13	11.02	7.85	51.68	1.15	14.11	3.96	31.28	1.52	7.29
Garage	4/30/03	1645-1715	9.94	37.25	31.92	110.84	6.98	26.43	24.06	87.42	9.75	31.54
Freeway	5/1/03	720-800	18.13	32.60	75.57	146.83	12.28	26.77	40.13	84.28	15.46	28.29
Refueling W/O Vapor Recovery	5/1/03	1106-1126	2.34	6.80	10.10	49.24	1.83	14.57	6.48	39.62	2.51	10.41
Refueling W/Vapor Recovery	5/1/03	1225-1245	1.61	5.61	6.28	17.02	1.20	4.60	4.21	13.58	1.68	3.23
Garage	5/1/03	1642-1717	10.63	20.33	34.25	71.17	7.23	13.91	25.35	45.99	9.81	15.34
Freeway	5/2/03	735-815	7.27	22.62	30.81	114.78	4.77	24.76	15.66	67.07	6.09	21.03
Refueling W/O Vapor Recovery	5/2/03	918-938	20.49	44.77	59.93	154.25	8.13	31.25	28.70	92.90	10.71	29.19
Refueling W/Vapor Recovery	5/2/03	1036-1056	2.30	20.44	9.28	67.20	2.10	12.17	7.83	42.82	3.06	12.74
Garage	5/2/03	1645-1715	5.29	6.07	17.10	22.80	3.79	5.55	13.53	15.84	5.36	4.58
Freeway	5/5/03	750-830	9.60	19.25	44.69	108.01	8.31	18.21	28.76	63.52	11.35	20.17
Refueling W/O Vapor Recovery	5/5/03	923-943	66.93	52.76	142.14	198.26	11.17	18.30	36.03	63.81	11.75	16.26
Refueling W/Vapor Recovery	5/5/03	1045-1105	1.55	5.75	7.23	18.13	1.39	2.49	4.96	9.74	1.91	2.09
Garage	5/6/03	1645-1715	4.86	6.29	14.16	22.39	3.25	5.82	11.75	20.92	4.55	6.85

Figure 3.1-8 shows the scatter plots for canis ter and S PME data before temperature corrections.

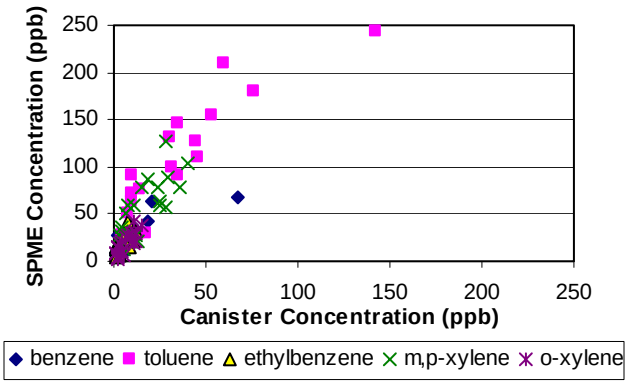


Figure 3.1-8. Scatter Plots for raw data from SPME vs canister for the Pilot Study 2003

Scatter plots after temperature correction.

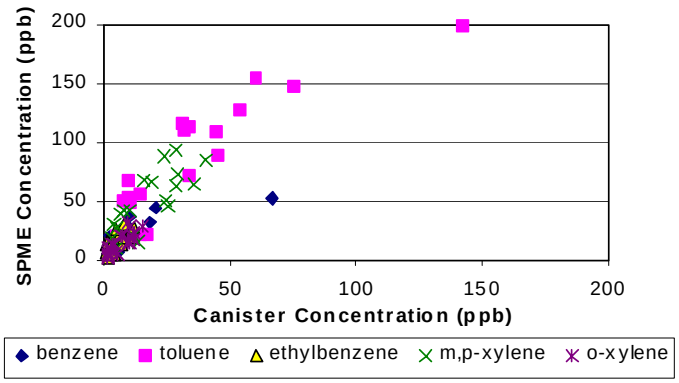


Figure 3.1-9. Scatter Plots for temperature corrected SPME vs canister data for the Pilot Study 2003

Figure 3.1-10 and Table 3.1-2 show s the correla tions after rem oving the two visible outliers (benzene and toluene from refueling w/o vapor recovery May 5th at 923-943):

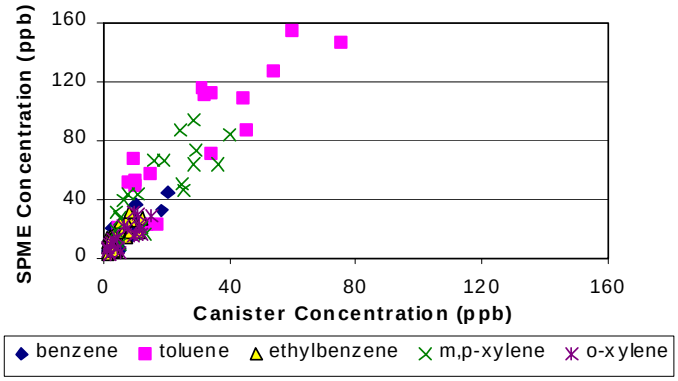


Figure 3.1-10. Scatter plots from SPME vs Canister for the Pilot Study 2003 with two outliers removed.

Table 3.1-2. Correlation of Scatter Plots from SPME and Canister Comparison

Compound	Equation	Correlation
Benzene	y = 1.8365x + 4.9732	R^2 = 0.7291
Toluene	y = 1.9202x + 22.617	R^2 = 0.7936
Ethylbenzene	y = 1.6894x + 7.1997	R^2 = 0.5255
m,p-xylene	y = 1.7814x + 17.323	R^2 = 0.6452
o-xylene	y = 1.6367x + 4.0433	R^2 = 0.6526

The scatter plots show linearity of the SPME data compared to canister data but the relatively low correlation values and the slope in the range of 1.6 – 1.9 can be associated with the differences in storage of the conditioned fibers before sampling. As noted above, most fibers were not probably stabilized to ambient temperature before sampling. Since the fibers were colder than the environment, some variability of the data is expected. This problem will be corrected in the primary study.

Sampled fibers were stored an average of 5 hours and all samples were analyzed the same sampling day.

3.1.6 SPME vs. MS

Data from SPME semi-continuous samples compared satisfactorily with continuous data obtained from the MS 200. In general concentrations are within the same ranges and changes in concentration levels track each other most of the time. However, the SPME concentrations are higher in most cases. As explained before, this may be due to the inadequate correction for temperature and humidity differences as compared with static calibration conditions and cold fiber storage conditions prior to sampling.

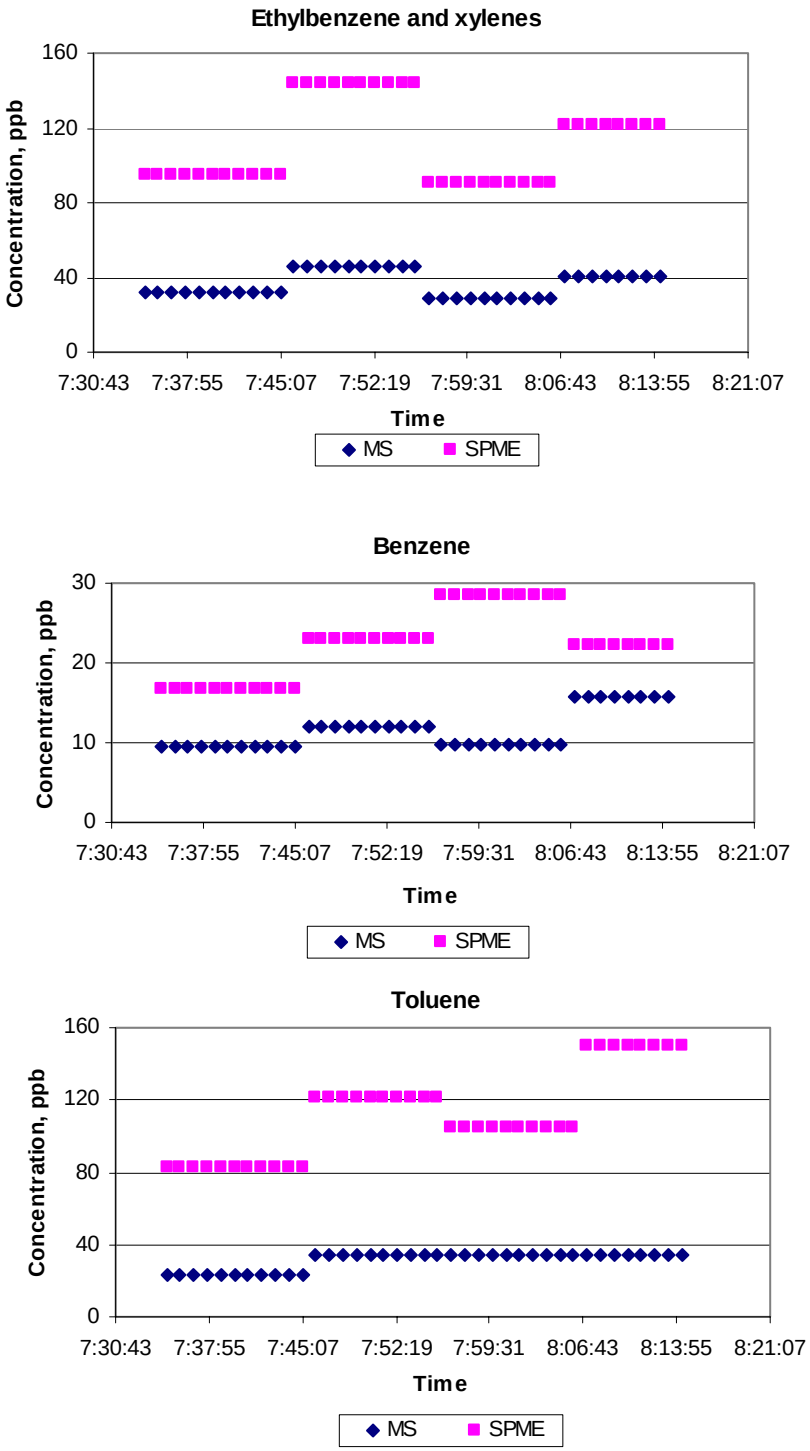


Figure 3.1-11. 10 m inutes average MS data vs SPME benzene and toluene concentrations: Freeway 5/02 7:35-8:15 am

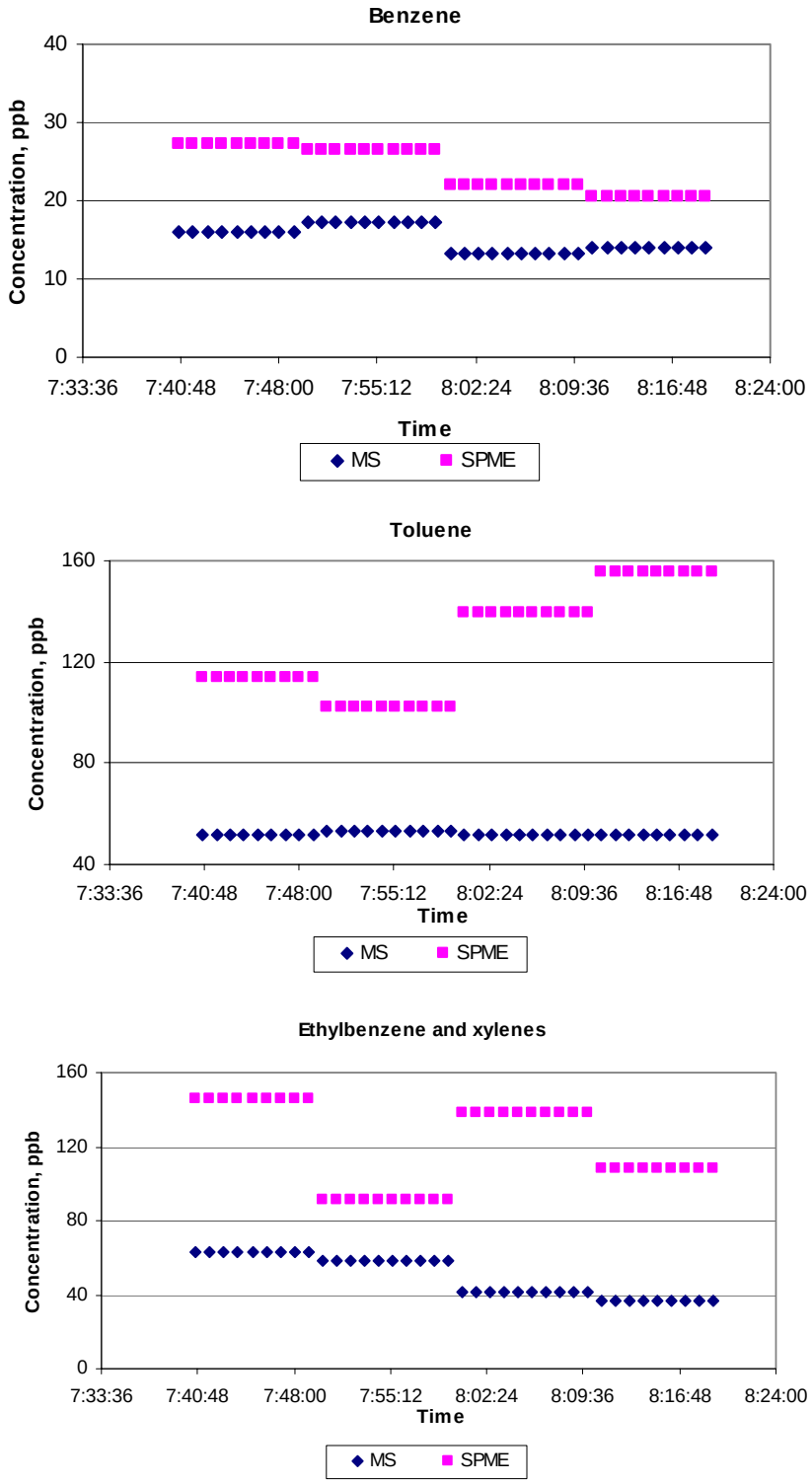


Figure 3.1-12. 10 minutes average MS data vs SPME benzene and toluene concentrations: Freeway 4/30, 7:35 am

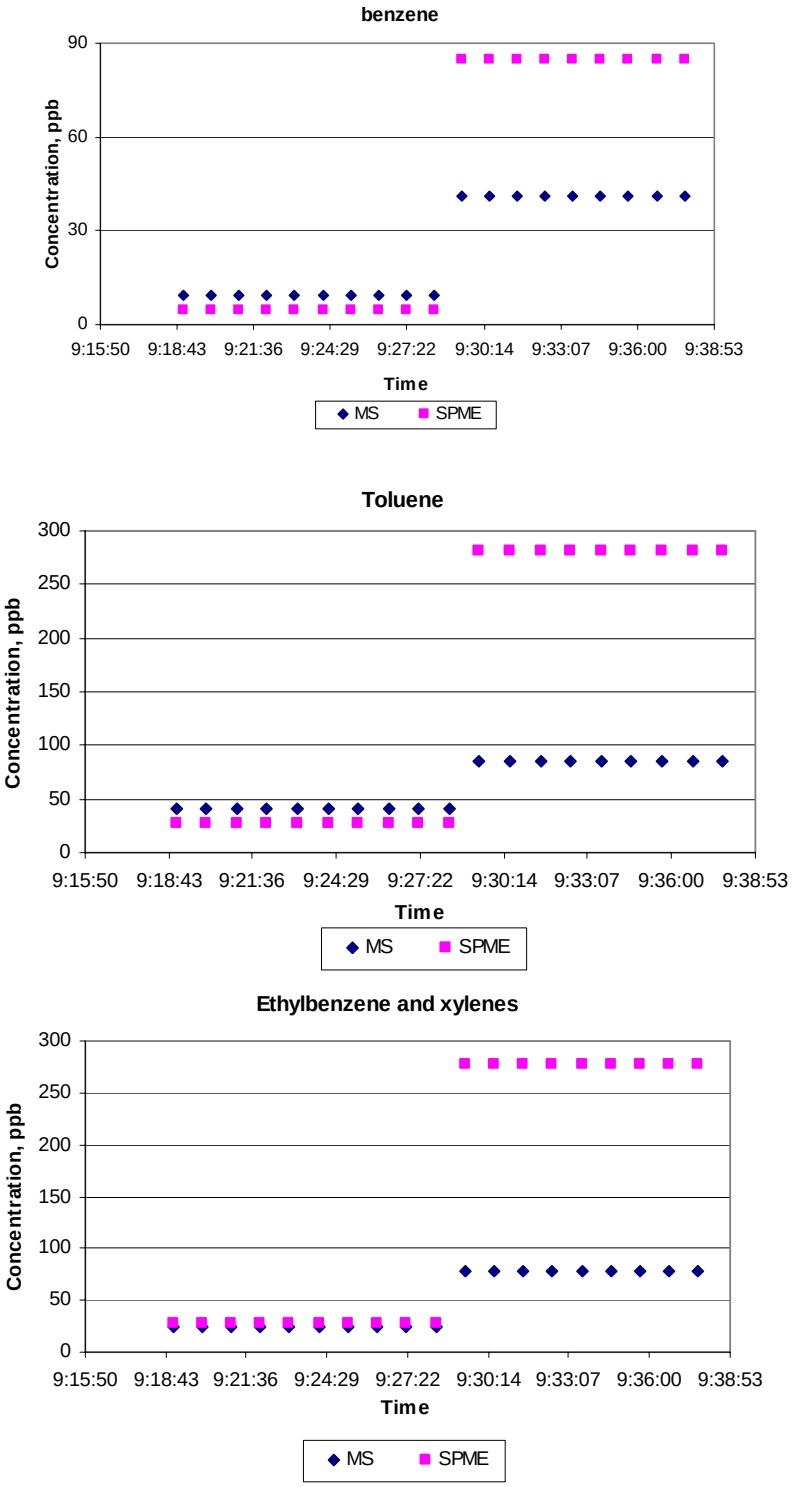


Figure 3.1-13. 10 m inutes average MS data vs SPME benzene and toluene concentrations: Refueling w/o VR 5/02 9:18 am

3.1.7 DNPH vs. Formaldehyde

Comparisons of formaldehyde data are few since the supplemental continuous analyzer provided little reliable data due to flow fluxuation and unstability during movement Comparison of formaldehyde data from DNPH with the final garage sampling event (ME2-5) shows that average concentration of formaldehyde detected by the continuous instrument was 11.5 ppb, and the time integrated DNPH sample for the same event was only 5.41 ppb. If data from the continuous CO monitor from the same experiment is used to reconstruct concentrations of formaldehyde for the earlier portions of the run, the average formaldehyde concentration may be estimated and compared to the DNPH time-integrated formaldehyde data (described in 3.2.2.).

The continuous formaldehyde detector is designed for stationary laboratory use, which accounts for its poor performance on a mobile platform. Based on these pilot study results, continuous formaldehyde measurements will only be made for stationary measurements in the 3 city field studies.

3.1.8 Tenax vs. Canisters

Appendix B list the full data sets for canister and Tenax samples. Since Tenax and canister samples overlap at C8-C12 carbon numbers, it is possible to compare concentrations for toluene, ethylbenzene, m/p-xylene and o-xylene obtained from both methods. Figure 3.1-14 shows that the correlations between both methods are good. The scatterplots exclude the 5/5/03 refueling without vapor recovery (ME4) samples. For this one ME4 replicate, the canister value was much higher than the Tenax sample, suggestive of a Tenax tube breakthrough. for this ME. This could be due to the extremely high gasoline concentrations encountered in this ME. It is possible that the breakthrough occurred for Tenax sample. One issue with the Tenax samples is the accurate determination of the volume sampled. Since the flow rate is measured at the beginning and at the end of all sampling periods, and the average flow is used for volume calculation, it is possible that the volume is not very precise, if the flow drop over the sampling period is substantial and non-linear. We are currently improving on the standard method by adding the data logger to the canister-Tenax-DNPH cartridge sampling system that will allow us to continuously monitor flow rates, thus allowing for accurate volume determination.

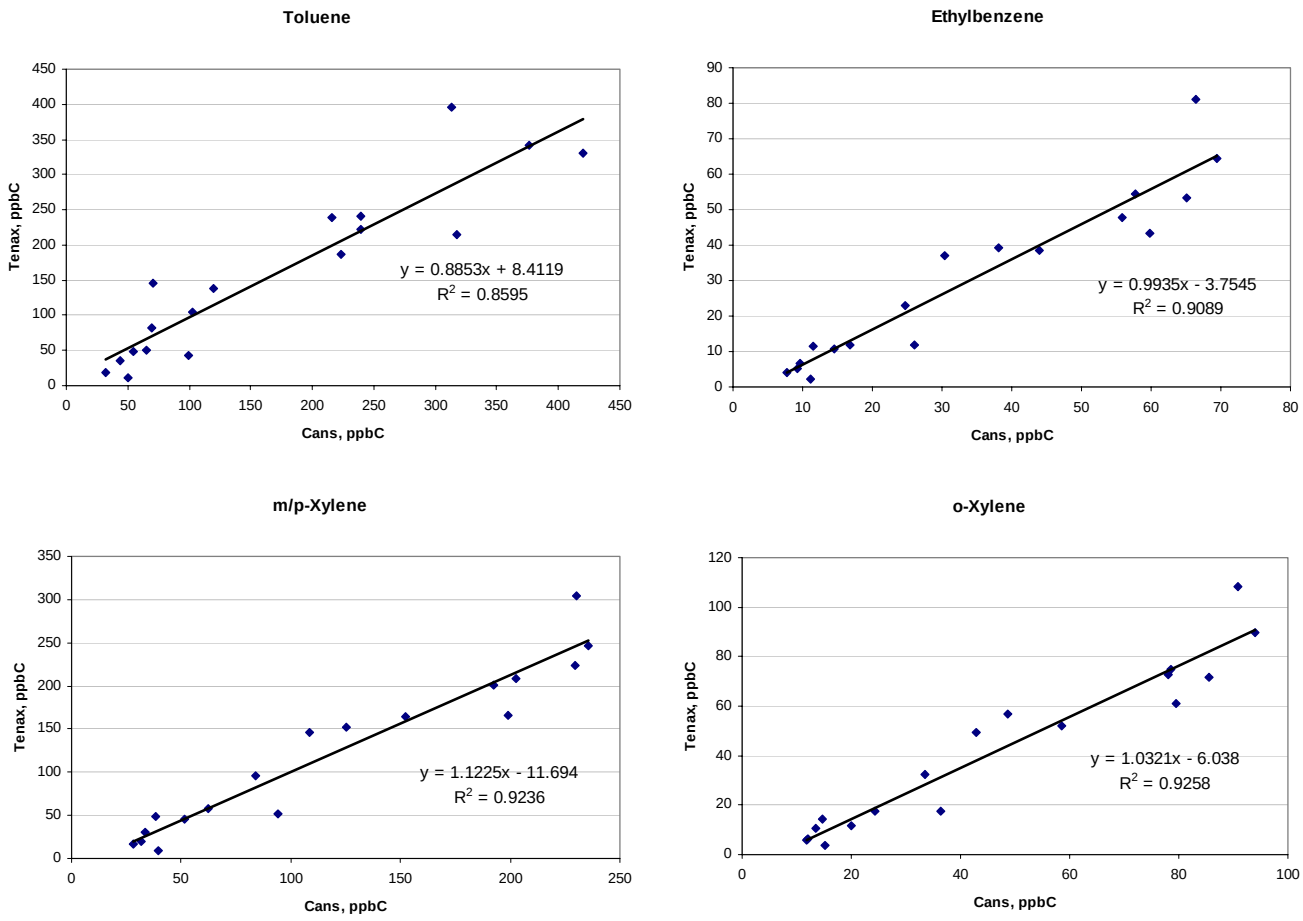


Figure 3.1-14 Comparison of canister and Tenax data for all ME

3.2 Comparisons of Correlated Data

3.2.1 PID vs. CO

Since both carbon monoxide and BTEX are produced by gasoline combustion, they are expected to track each other in an automobile exhaust dominated environments. Figure 3.2-1 shows the two measurements track well during the parking garage tests that are focused on cold-start emissions, although the ratio is variable as indicated by the scatter in Figure 3.2-3. The apparent time lag for the smaller peaks is an artifact of the API NDIR CO instrument's adaptive filtering, described in the previous section, and subsequent averaging of the data.

During the freeway driving tests, shown in Figure 3.2-4, the correlation between CO and VOC is good, but not as high as the parking garage data.

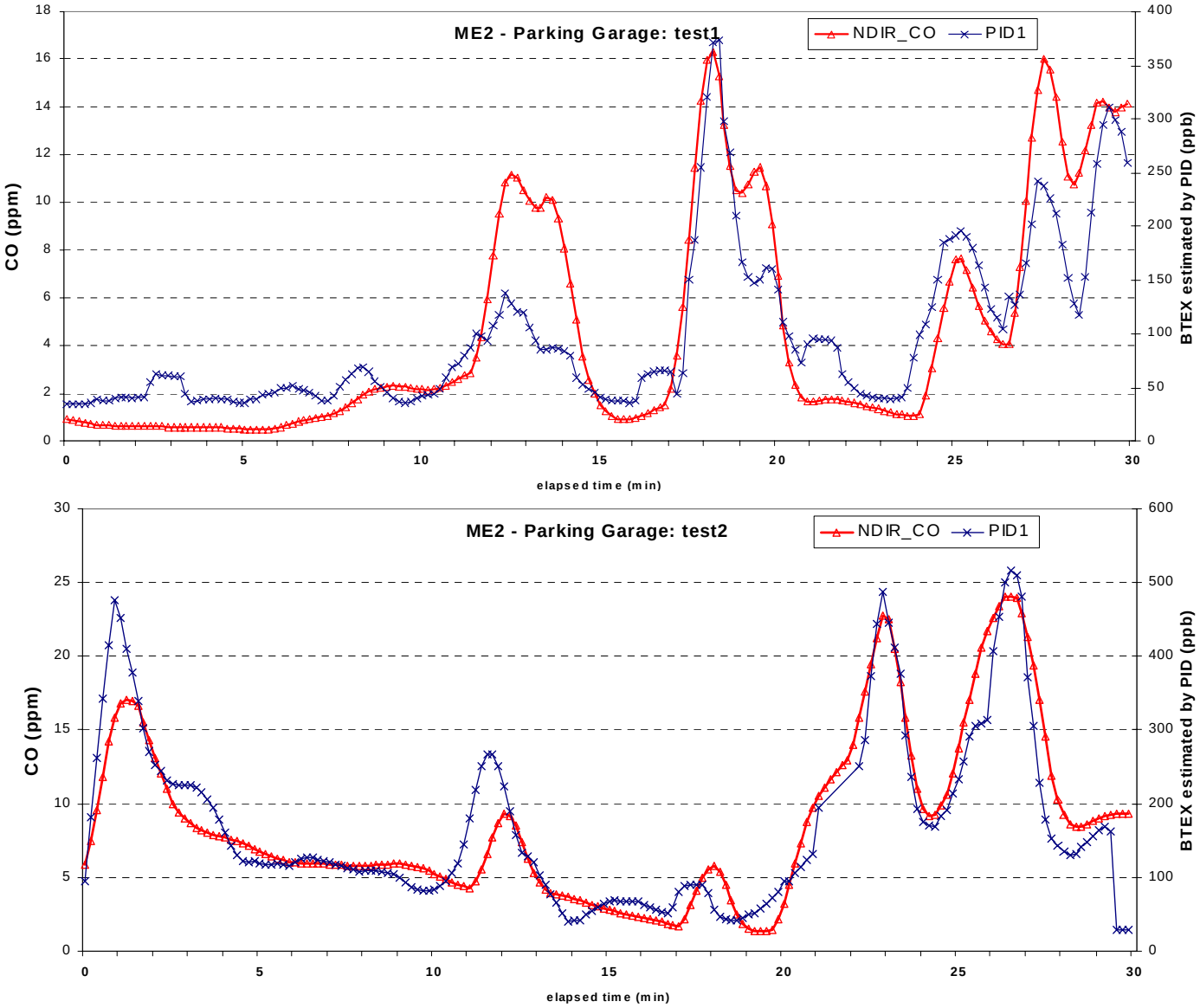


Figure 3.2-1. Comparison of CO and BTEX by PID during parking garage tests.

Data are running 1 m inute averages. The CO instrument's analog out put range (0-20 ppm) was exceeded briefly during the two large peaks near the end of test 2.

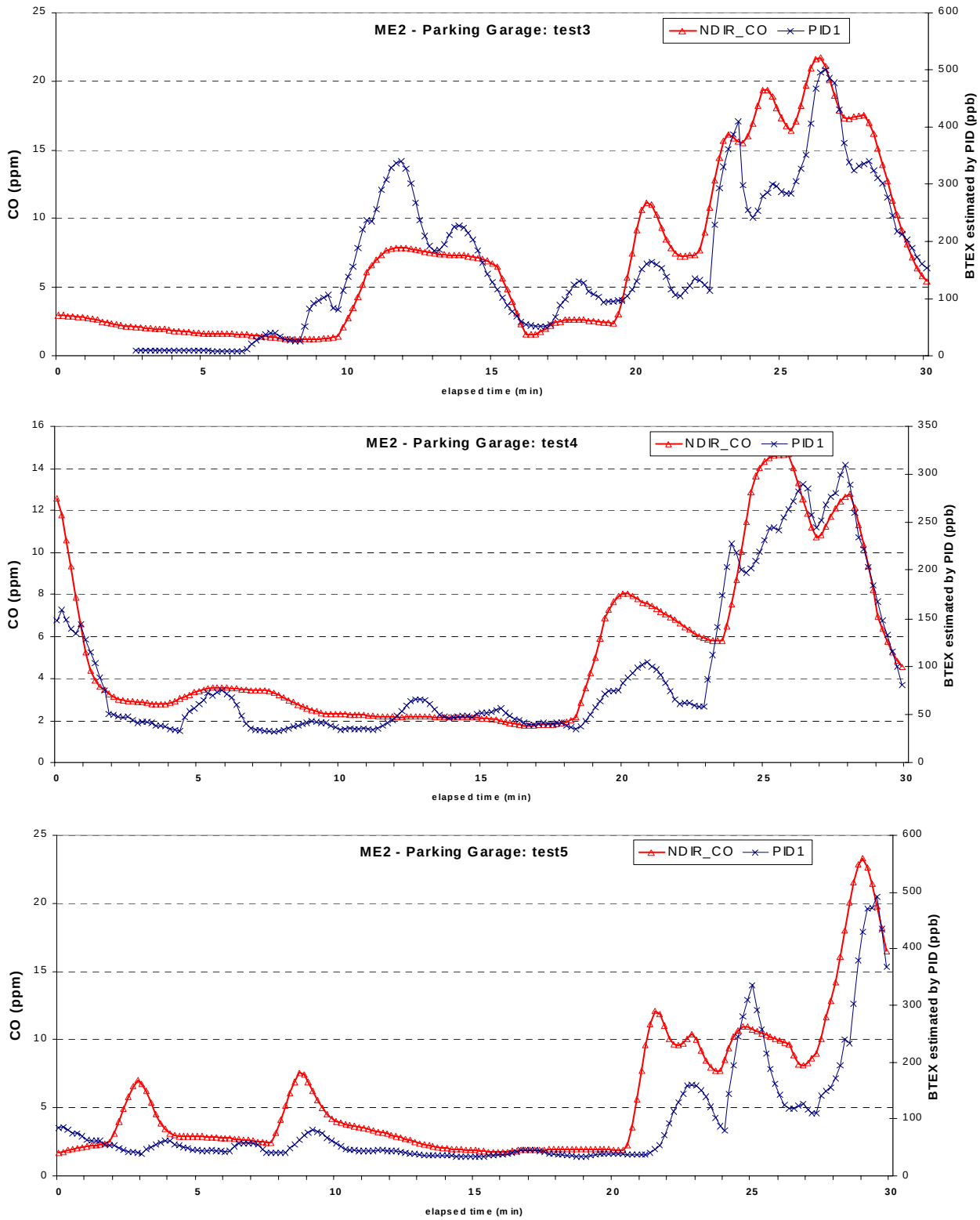


Figure 3.2-1 – cont'd. Comparison of CO and BTEX by PID during parking garage tests. Data are running 1 minute averages.

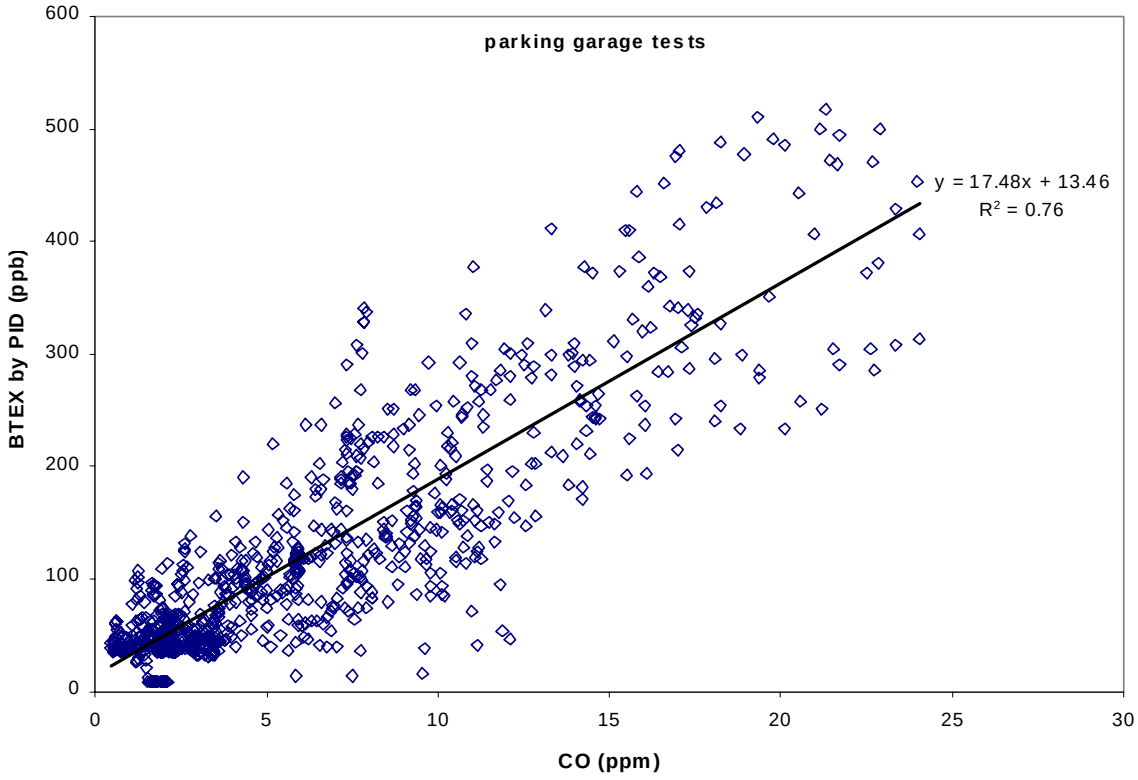


Figure 3.2-3. Scatter plot of CO vs BTEX by PID during parking gara ge tests. Data are running 1 minute averages.

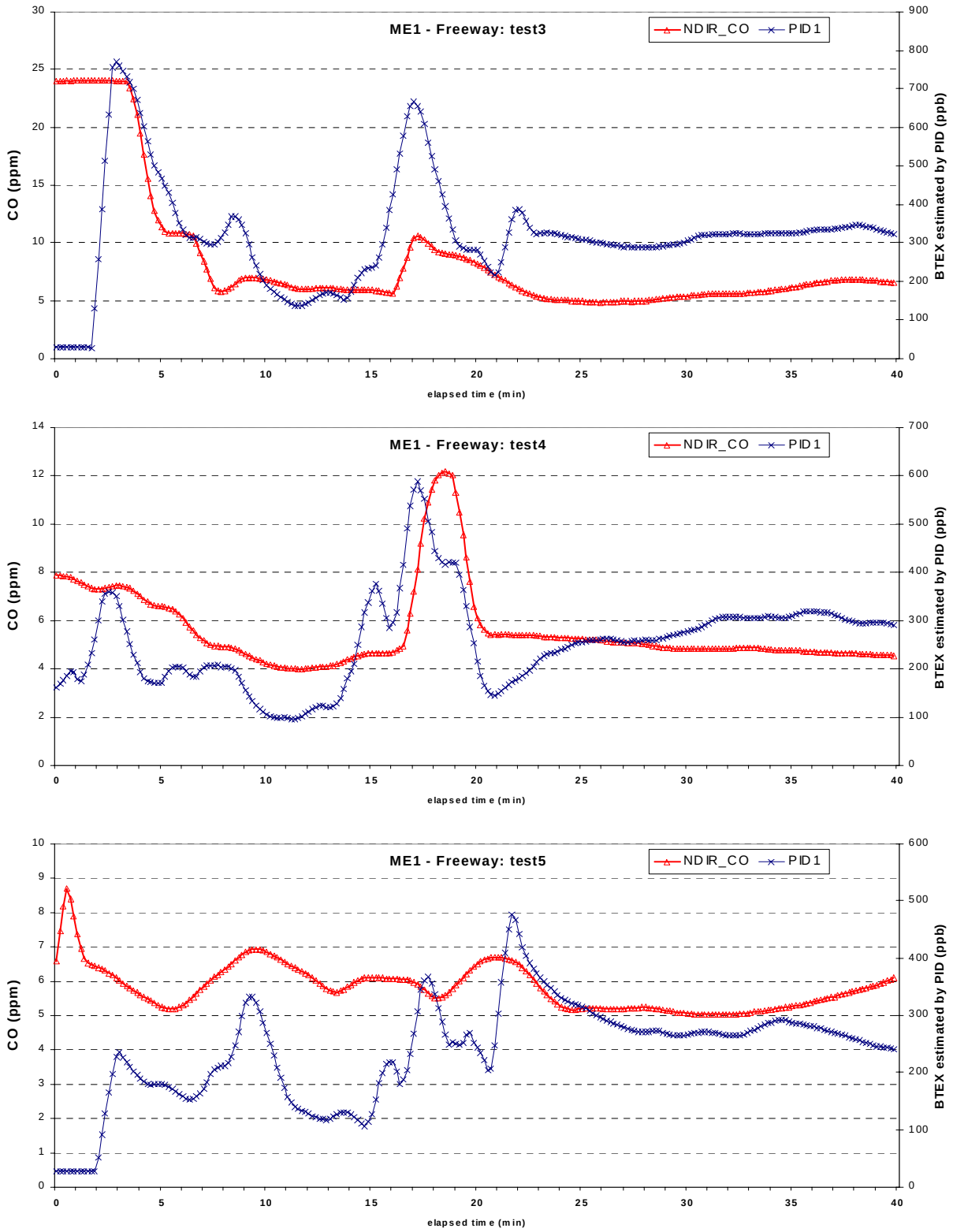


Figure 3.2-4. Comparison of CO and BTEX by PID during freeway driving tests.

Data are running 1 minute averages. In test 3, the CO instrument's analog output range (0-20 ppm) was exceeded during the first 4 minutes.

3.2.2 CO vs. Formaldehyde

For the last two garage sampling events (ME2-4 and ME2-5), time series for continuous formaldehyde and CO show inconclusive results. Figure 3.2-5 shows time series data for CO and formaldehyde for ME2-4. During the ME2-4 period in which formaldehyde data was above the detection limit, both the CO and formaldehyde appear to respond to the same event, but the peaks are not in phase with each other.

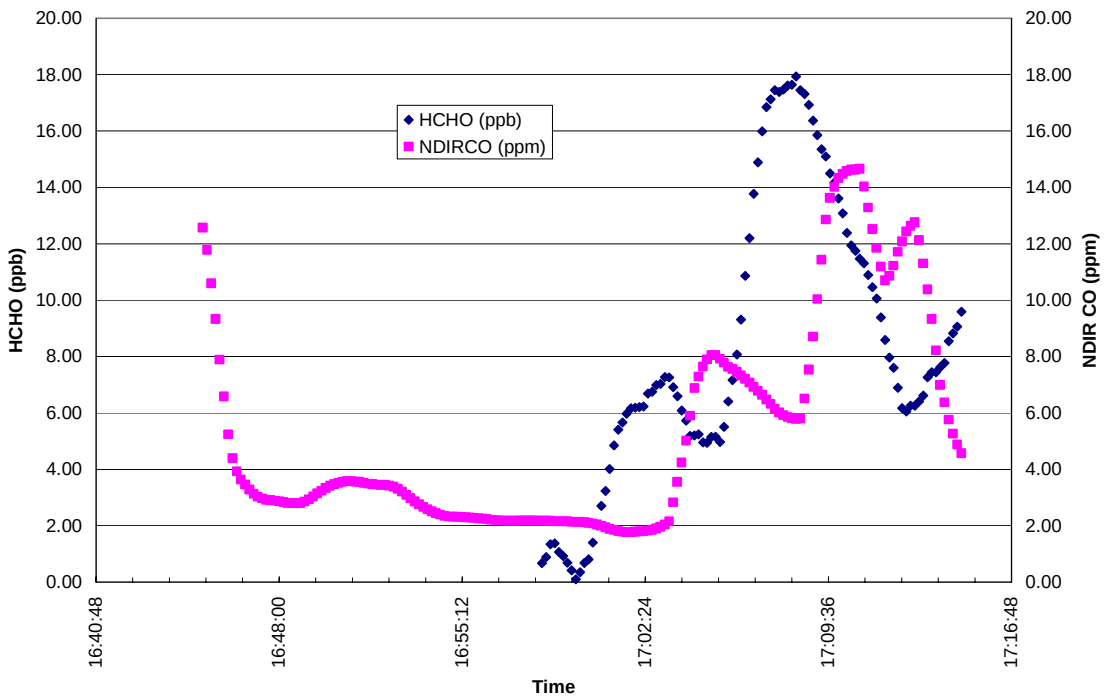


Figure 3.2-5 ME2-4 continuous HCHO and CO time series with unexplained difference in lag between the two instruments.

Approximately 2.5 minutes separate the instrument responses. This indicates that either the time lag correction of 6 minutes is not accurate for this test, or the adaptive smoothing feature of the CO instrument is causing a delayed peak rise in CO. Figure 3.2-6 shows the same time series data following adjustment of the formaldehyde data by 2.5 minutes to compensate for the undetermined source of error. The data track each other very well.

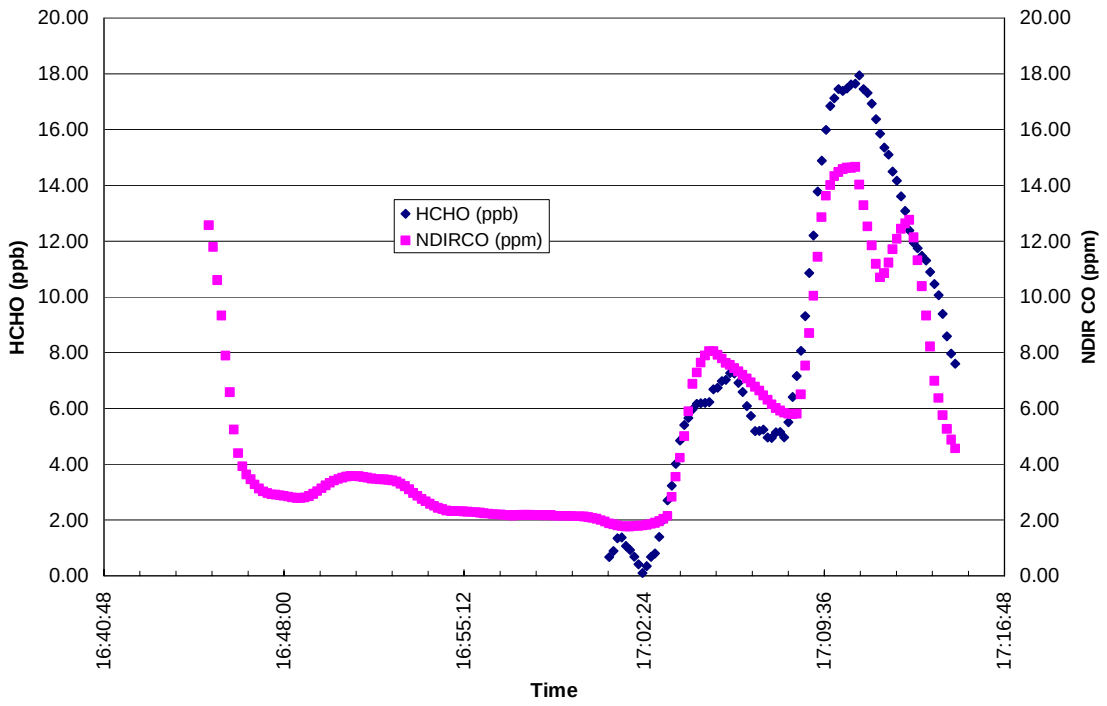


Figure 3.2-6. ME2-4 continuous HCHO time series shifted back 2.5 minutes to match CO time series.

Once this time adjustment was made, CO and HCHO concentrations were compared by regression, and the resulting equation ([HCHO] = [CO]*1.2996-1.14587, $R^2 = 0.91$) was used to estimate HCHO concentrations for the period prior to successful data capture for this experiment. The resulting average concentration for the estimated formaldehyde data combined with the actual formaldehyde data was 5.414 ppb. The time integrated formaldehyde data from the DNPH for the ME2-4 experiment was 7.348 ppb. The estimated value is 74 % of the observed time integrated sample. Despite the discrepancy in phase between the continuous CO and formaldehyde analyzers, this experiment is the best indication that the continuous formaldehyde analyzer may work well if properly tuned and operated in a suitable environment. It also indicates that CO may serve as a useful surrogate for formaldehyde. To explore this relationship further, formaldehyde results from the DNPH cartridges were plotted in a scatter plot against CO from time integrated canister samples for each microenvironment. Figure 3.2-7 shows the plot with different microenvironments having unique symbols on the plot. Formaldehyde from the Freeway microenvironment does not correlate with CO samples from the same environment. The garage and refueling microenvironments appear to have a positive correlation with CO but cluster for each microenvironment. Fitting a linear regression through data points for the Garage and Refueling microenvironments, neglecting the Freeway microenvironment, gives a good correlation ([HCHO] = 0.594*[CO] + 0.397, $R^2 = 0.793$).

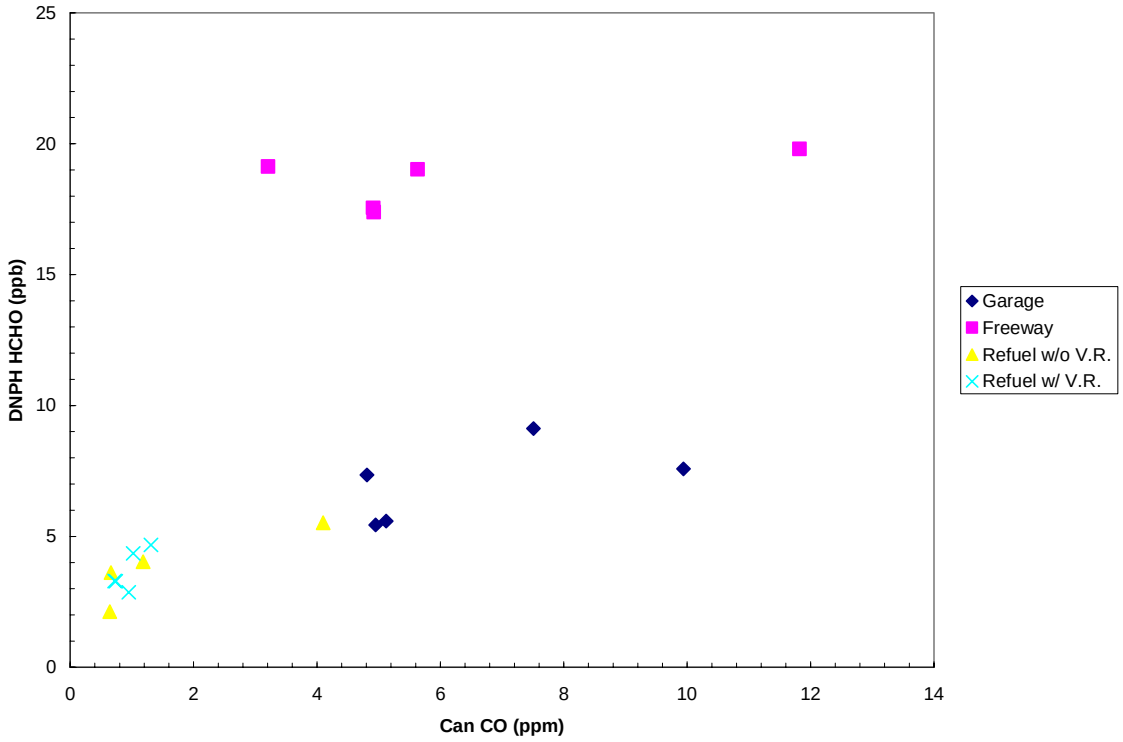


Figure 3.2-7. Scatter plot of formaldehyde (from DNPH) and CO for all microenvironments.

Finally, comparison of continuous for maldehyde and CO m easurements for the last garage sampling event (ME2-5) shows poor correlation in phase and tim ing (Figure 3.2-8). The unexplained 2.5 m inute lag that resolved peak s in the ME2-4, did little to help this comparison.

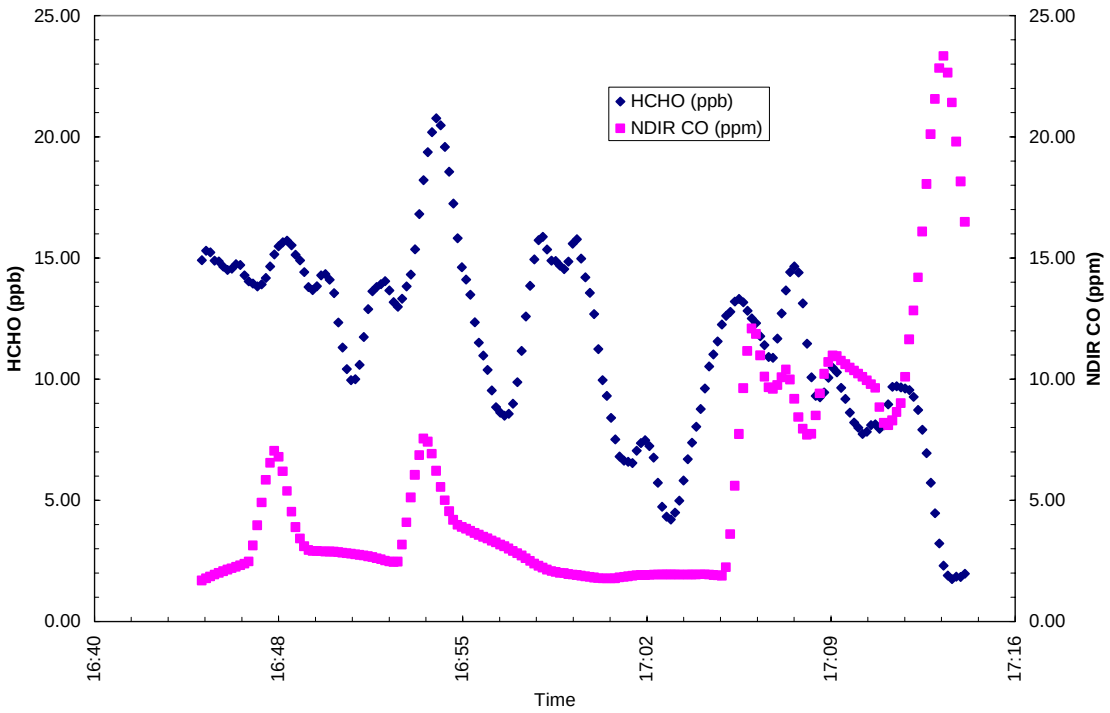


Figure 3.2-8. Formaldehyde and CO time series for ME2-5.

3.2.3 SPME vs. PID

SPME total BTEX se mi-continuous data com pares reasonably with the continuous signal obtained from the interior PID situated righ t next to the fiber while sampling. The SPME concentrations are with in the rang e of the PID signal and follow the changes in PI D concentrations.

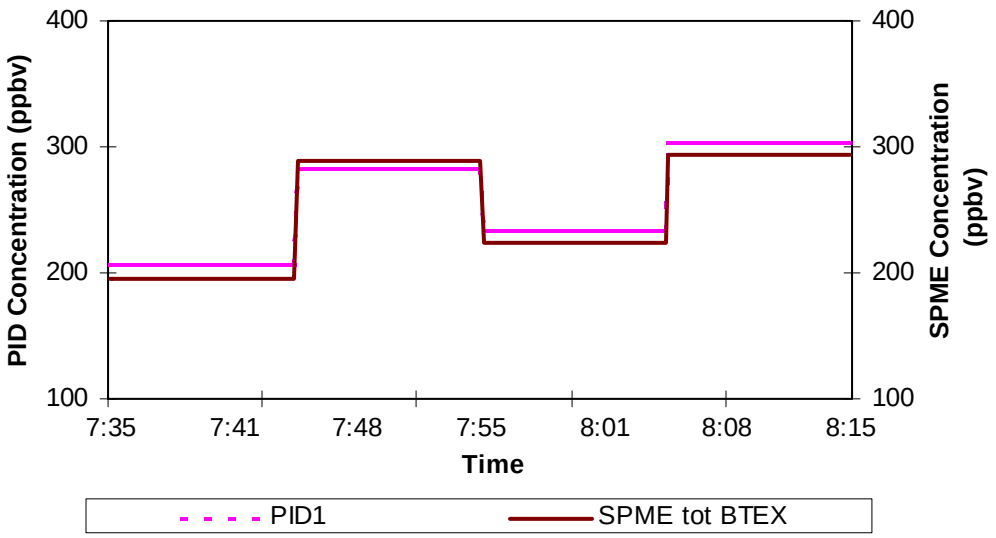


Figure 3.2-9. SPME 10 min total BTEX vs. PID 10 min averages, Freeway, 5/02, 7:35 am

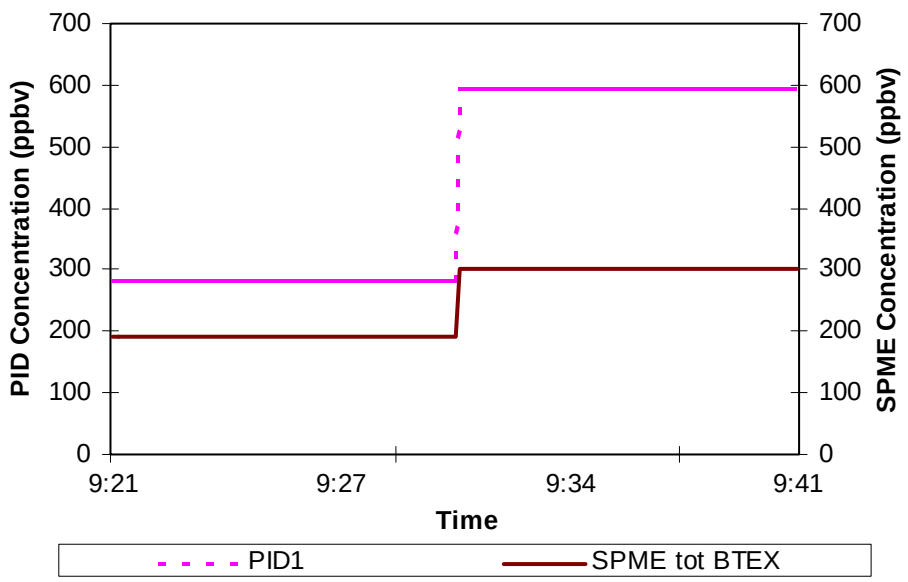


Figure 3.2-10. SPME 10 m in total BTEX vs. PI D 10 m in averages, Refueling w/o VR 4/30 9:21am.

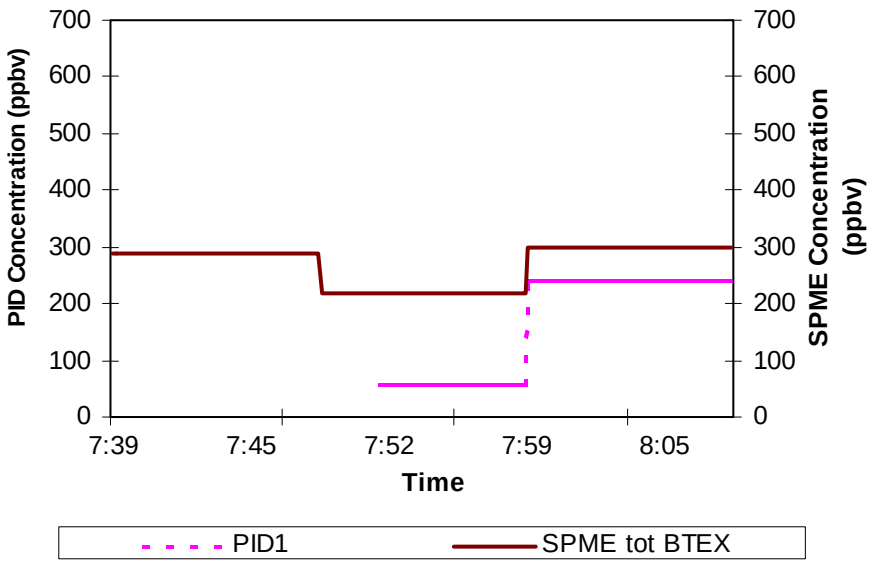


Figure 3.2-11. SPME 10 min total BTEX vs. PID 10 min averages, Freeway 4/30, 7:35 am.

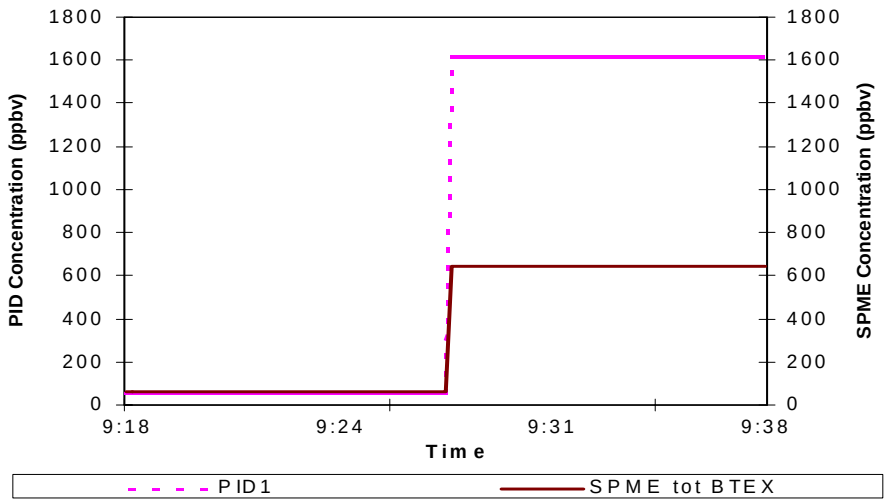


Figure 3.2-12. SPME 10 m in total BTEX vs. PI D 10 m in averages, Refueling w/o VR 5/02 9:18 am.

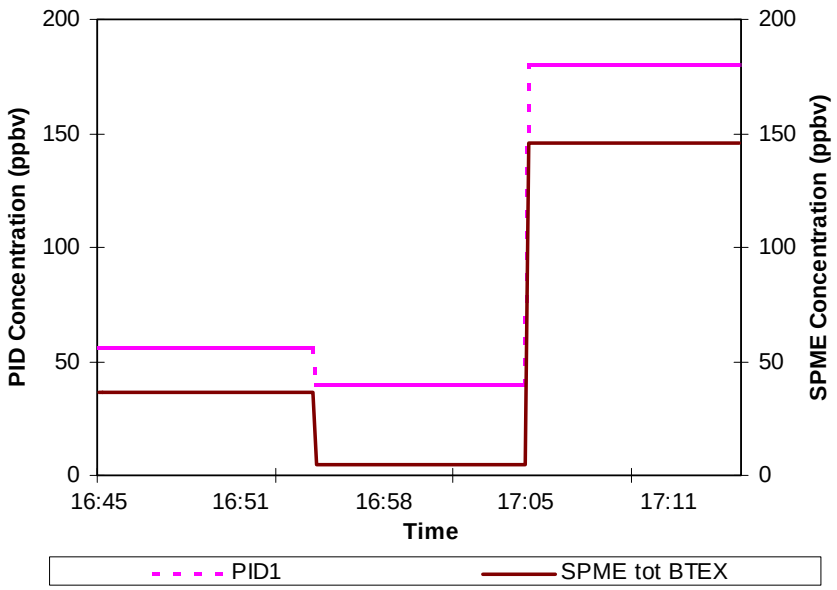


Figure 3.2-13. SPME 10 m in total BTEX vs. PID 10 m in averages, Parking Garage 5/06, 16:45 pm.

Continuous estimates of total VOC by a PID ppbRAE monitor compared reasonably to the semi-continuous measurements of BTEX obtained from analysis of SPME fibers.

3.3 Environmental Factors

The various environmental conditions monitored during this study are presented in this section by microenvironment. These data were collected once every 10 seconds, to simplify the presentation, we present the average for each 10 min segment (to correspond with the SPME time interval) and the overall average value In addition, we present temperature and wind data collected at a weather station on top of DRI's building. These data are useful as a general reference for local conditions, however, it is important to point out that DRI's building is on top of a hill with nothing to block winds for approximately 270 degrees around and is noted as being one of the windiest spots in the area. This is important since we selected the refueling stations in a location at the bottom of a nearby valley approximately 250 feet lower in elevation with a large ridge blocking the prevailing winds. For all stationary MEs we monitored wind with a hand-held anemometer that had a lower-limit of detection of approximately 1 mph.

For the freeway microenvironment (ME1), we measured temperature and relative humidity at the driver's breathing zone which was also the sample inlet location for all equipment except the second PID which was monitoring the air outside the van. The outside PID inlet was located on the radio antenna on the right front corner of the van. Since the sampling location was inside the van, the temperature is typically higher than the ambient. We also monitored the temperature on the outside surface of the fuel tank. These data are presented in Table 3.3-1 along with the average conditions for the DRI weather station. The average temperature in the van climbed during the runs partially due to the fact that we started low ventilation conditions halfway through the run. Relative humidities were relatively constant. The fuel tank temperature climbed steadily during the run, which was interesting considering the ambient temperatures did not. This was due to the recirculation of fuel after is passes the fuel injectors and picks up heat from the engine. The 10 second data of fuel tank temperatures for an example run are presented in Figure 3.3-1.

Table 3.3-1. Environmental Conditions for Freeway Driving MEs.

ME	Date	Start	End	Data Set	Sampling Point Measures Temp, C	Sampling Point Measures Humidity, %	Fuel Tank Temp, C	Ambient Conditions (DRI Weather Station) Wind, mph	Ambient Conditions (DRI Weather Station) Temp, C
ME1 - Freeway 4/29	04/29/03	7:42	8:22	avg. of 1st 10 minutes:	12	37	5		
				avg. of 2nd10 minutes:	12	32	7		
				avg. of 3rd 10 minutes:	16	32	11		
				avg. of 4th 10 minutes:	21	32	13		
				Average of all	15	33	9	1.8	4.4
ME1 - Freeway 4/30	04/30/03	7:39	8:19	avg. of 1st 10 minutes:	10	42	4		
				avg. of 2nd10 minutes:	13	34	7		
				avg. of 3rd 10 minutes:	21	28	11		
				avg. of 4th 10 minutes:	25	26	14		
				Average of all	17	33	9	3.0	1.5
ME1 - Freeway 5/01	05/01/03	7:20	8:00	avg. of 1st 10 minutes:	11	44	7		
				avg. of 2nd10 minutes:	16	31	8		
				avg. of 3rd 10 minutes:	20	30	10		
				avg. of 4th 10 minutes:	21	34	12		
				Average of all	17	35	9	1.2	4.4
ME1 - Freeway 5/02	05/02/03	7:35	8:15	avg. of 1st 10 minutes:	16	36	11		
				avg. of 2nd10 minutes:	20	30	12		
				avg. of 3rd 10 minutes:	23	30	15		
				avg. of 4th 10 minutes:	23	33	16		
				Average of all	20	32	14	4.5	7.8
ME1 - Freeway 5/05	05/05/03	7:50	8:30	avg. of 1st 10 minutes:	15	39	7		
				avg. of 2nd10 minutes:	17	33	9		
				avg. of 3rd 10 minutes:	20	36	12		
				avg. of 4th 10 minutes:	22	39	16		
				Average of all	18	37	11	1.8	5.4

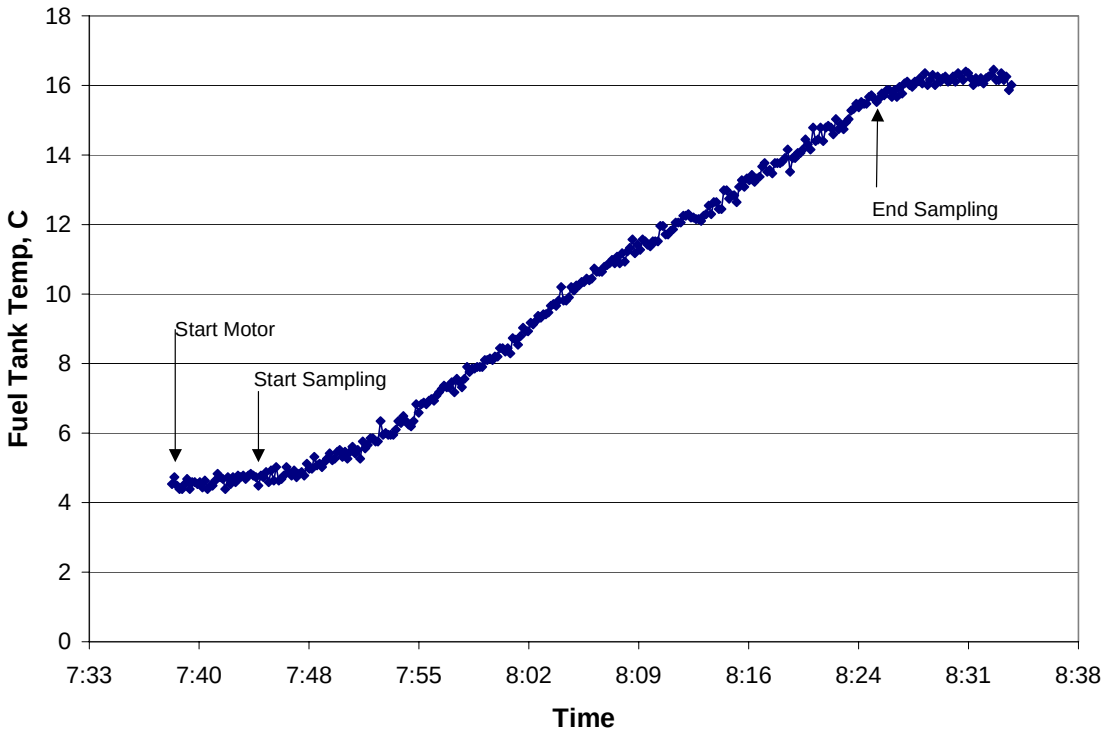


Figure 3.3-1. Fuel tank temperatures during freeway ME on 4/29/03. Ambient temperature was 4.4 C during this time.

For the garage microenvironment (ME2) we measured temperature and relative humidity at the sampling point, which was also the sample inlet location for all equipment located on the tripod near the van. These data are presented in Table 3.3-2 along with the average conditions for the DRI weather station. The average temperature and relative humidities were relatively constant, as was the fuel tank temperature as might be expected for this stationary and mostly indoor ME. While the average winds at DRI were quite high (twice in excess of 10 mph) inside the garage the winds were calm and undetectable by the hand-held anemometer. The above-ground garage is also approximately 3.5 miles south and slightly west of the DRI building (measured in a straight line).

Table 3.3-2. Environmental Conditions for Garage MEs.

ME	Date	Start	End	Data Set	Sampling Point Measures Temp, C	Sampling Point Measures Humidity, %	Fuel Tank Temp, C	Ambient Conditions (DRI Weather Station) Wind, mph	Ambient Conditions (DRI Weather Station) Temp, C	Local Winds
ME2 - Parking Garage 4/29	04/29/03	16:42	17:12	avg. of 1st 10 minutes:	11	35	15			
				avg. of 2nd10 minutes:	10	35	15			
				avg. of 3rd 10 minutes:	10	36	15			
				Average of all	10	35	15	8.3	9	Calm, not measureabl
ME2 - Parking Garage 4/30	04/30/03	16:45	17:15	avg. of 1st 10 minutes:	12	33	14			
				avg. of 2nd10 minutes:	11	33	14			
				avg. of 3rd 10 minutes:	11	33	14			
				Average of all	11	33	14	10.4	10	Calm, not measureabl
ME2 - Parking Garage 5/01	05/01/03	16:42	17:17	avg. of 1st 10 minutes:	16	24	16			
				avg. of 2nd10 minutes:	14	25	16			
				avg. of 3rd 10 minutes:	14	26	16			
				Average of all	15	26	16	4.9	14	Calm, not measureabl
ME2 - Parking Garage 5/02	05/02/03	16:45	17:15	avg. of 1st 10 minutes:	14	46	15			
				avg. of 2nd10 minutes:	14	48	15			
				avg. of 3rd 10 minutes:	14	47	15			
				Average of all	14	47	15	4.5	12	Calm, not measureabl
ME2 - Parking Garage 5/06	05/06/03	16:45	17:15	avg. of 1st 10 minutes:	14	34	16			
				avg. of 2nd10 minutes:	13	34	16			
				avg. of 3rd 10 minutes:	14	35	15			
				Average of all	14	34	16	11.7	11	Calm, not measureabl

For the refueling microenvironments (ME3 was with vapor recovery, ME4 was without vapor recovery), we measured temperature and relative humidity at the sampling point which was also the sample inlet location for all equipment. This was located on the tripod between the van and the fuel pump to allow us to assess the conditions at the breathing zone of the person refueling the van. These data are presented in Table 3.3-3 along with the average conditions for the DRI weather station. The average temperature and relative humidities were relatively constant, as was the fuel tank temperature as might be expected for this 20 minute stationary ME. While the average winds at DRI did go above the 5 mph threshold for three of the MEs, the winds at the refueling stations were much lower as monitored by the hand-held anemometer. The stations are 1.3 and 1.9 miles from the DRI building (measured in a straight line). Also presented in Table 3.3-3 are the maximum numbers of cars seen in the station, the amount of fuel dispensed and the amount dropped on the ground following refueling. The station with the vapor recovery was a much busier station with more than twice the number of cars as the other station. The station used for refueling without vapor recovery (ME4) could refuel a maximum of four vehicles at one time, as it had two pumps and each pump could be used from either side. The station used for refueling with vapor recovery (ME3) could refuel a maximum of 8 vehicles at once, as it had two islands with two pumps each and each pump could be approached from either side. For all MEs we managed a relatively consistent number of gallons dispensed which was possible since we could unload fuel from the van to a nearly constant level. For each refueling ME, we filled up until the automatic shutoff stopped the filling process. The number of drops spilled was not as consistent partially due to the difficulty in precisely dropping a fixed amount of fuel out of the nozzle. The number in Table 3.3-3 is the number of drops spilled which was an approximate count of the number of wet spots noted on the pavement. The exception is the first ME where a large amount of fuel unexpectedly came out of the nozzle and left a single spot approximately 5 cm in diameter.

Table 3.3-3. Environmental Conditions for Refueling MEs.

ME	Date	Start	End	Data Set	Sampling Point Measures Temp, C	Sampling Point Measures Humidity, %	Fuel Tank Temp, C	Max. Cars In Station	Gallons Dispensed	Drops of Fuel Spilled	Ambient Conditions (DRI Weather Station) Wind, mph	Ambient Conditions (DRI Weather Station) Temp, C	Local Winds
ME3 - Refueling w/ VR 4/29	04/29/03	12:00	12:20	avg. of 1st 10 minutes:	11	28	12						
				avg. of 2nd10 minutes:	11	28	13						
				Average of all	11	28	13	6	16.50	5 cm pool	5.9	7.4	1 - 2 mph
ME3 - Refueling w/ VR 4/30	04/30/03	10:45	11:05	avg. of 1st 10 minutes:	9	37	14						
				avg. of 2nd10 minutes:	9	36	15						
				Average of all	9	36	15	4	16.25	25	3.8	6.5	2 mph from SE
ME3 - Refueling w/ VR 5/01	05/01/03	12:25	12:45	avg. of 1st 10 minutes:	14	24	16						
				avg. of 2nd10 minutes:	14	24	16						
				Average of all	14	24	16	3	16.42	5	7.6	11.9	2 - 4 mph from SE var
ME3 - Refueling w/ VR 5/02	05/02/03	10:36	10:56	avg. of 1st 10 minutes:	11	53	15						
				avg. of 2nd10 minutes:	10	54	14						
				Average of all	11	53	15	5	15.40	10	2.5	8.5	< 1 mph, some drizzle
ME3 - Refueling w/ VR 5/05	05/05/03	10:45	11:05	avg. of 1st 10 minutes:	12	35	17						
				avg. of 2nd10 minutes:	12	35	16						
				Average of all	12	35	17	6	17.50	12	3.9	9.0	<1 mph from SSE
ME4 - Refueling w/o VR 4/3	04/30/03	9:21	9:41	avg. of 1st 10 minutes:	14	28	14						
				avg. of 2nd10 minutes:	14	28	14						
				Average of all	14	28	14	3	15.80	6	2.9	3.6	1 - 2 mph from NNW
ME4 - Refueling w/o VR 4/3	04/30/03	12:01	12:21	avg. of 1st 10 minutes:	12	30	16						
				avg. of 2nd10 minutes:	13	28	16						
				Average of all	13	29	16	1	15.40	12	3.2	7.9	2 - 4 mph variable dir.
ME4 - Refueling w/o VR 5/0	05/01/03	11:06	11:26	avg. of 1st 10 minutes:	15	22	14						
				avg. of 2nd10 minutes:	14	22	14						
				Average of all	14	22	14	1	14.18	3	6.6	9.8	2 - 3 mph from SSE
ME4 - Refueling w/o VR 5/0	05/02/03	9:18	9:38	avg. of 1st 10 minutes:	11	42	18						
				avg. of 2nd10 minutes:	10	44	17						
				Average of all	11	43	18	2	17.31	12	3.5	8.7	1 - 2 mph, overcast
ME4 - Refueling w/o VR 5/0	05/05/03	9:23	9:43	avg. of 1st 10 minutes:	17	28	18						
				avg. of 2nd10 minutes:	17	30	18						
				Average of all	17	29	18	1	14.50	20	3.9	8.3	< 1 mph from W

3.4 Reconstructed Data

One of the objectives of this study was to determine if the original objective of using surrogate measures to determine the time series of compounds of interest was valid. To answer this question, this section details the reconstruction of the time series for benzene and BTEX from the PID data and the comparison of this to the benzene and BTEX determined by the MS200 portable mass spectrometer.

The procedure is first to average the 10 second data that is recorded by the PID instrument up to 1 minute data for comparison with the MS200 data set (1 minute increments). This time series is then used along with the integrated canister value to reconstruct a time series of the canister concentrations. To accomplish this, a ratio is taken between the PID value at each point and the average PID value for the time series. This number is multiplied by the integrated canister value to give a reconstructed value for that data point and is compared to the time-corresponding data point from the MS200.

The first example presented is for the freeway driving (ME1) on 4/29/03. Figure 3.4-1 shows the time series for benzene in this ME. A few data points are missing from the MS data where some electrical noise rendered those data points invalid. The general trend of the peaks is reproduced by both the MS200 and the PID reconstructed data, however, the peak values are much higher in the MS200. This is confirmed by the comparison of the integrated values, where the MS200 showed 14.7 ppb and the canister 9.1. ppb. This ratio (1.6) nearly accounts for the differences and may be due to offset (zero point) or calibration differences in the MS200. Comparing the time series for the sum of the BTEX species, we obtain the plot in Figure 3.4-2. In this figure, the structure of the time series and the magnitude of the peaks are both much more precisely reproduced than is the case with just benzene. Due to both the higher concentrations of toluene and the C8 benzenes, and the better performance of the MS200 with these species. Section 3.1.9 details the performance of the MS200 versus the canisters and shows that benzene is consistently the most difficult species to measure, especially at the lower levels. The integrated canister measurement for this sample was 97 ppb for the sum of the BTEX species while the MS200 reported 123 ppb. Looking at the two highest peaks in this time series (8:01 and 8:03 am) it appears that the timing is slightly off with the MS200 lagging the PID reconstructed data.

To further investigate the timing between these two instruments, we looked at a higher concentration sample with a significant spike in the concentration (ME4 refueling without vapor recovery from 5/2/03). Figure 3.4-3 shows the reconstructed time series for benzene along with the MS200 values for benzene. Figure 3.4-4 presents the same data for BTEX. In both figures, the series is well reproduced however the peak values recorded by the MS200 are much lower than the reconstructed. During the "non-peak" part of the ME, the MS200 appears to be reading consistently higher than the reconstructed values. Overall, however, the values match quite well with the ratio of MS200/canister of 1.05 for the BTEX species and 1.18 for benzene. As with the previous example, it appears that the timing of the peak concentration is out of phase by one minute. To look more closely at the peak concentration, we used the original 10 second data from the PID to reconstruct a 10 second time series for the BTEX species and plotted that along with the 1 minute data in Figure 3.4-5. This figure

does not show the entire time series; rather it focuses on the period of the peak exposure from 9:27 to 9:33 am. In this figure, the 10-second reconstructed data shows two peaks where the 1-minute reconstructed and the MS200 data show one peak. The 1-minute time averaged data may better represent what the MS200 is measuring, since the MS200 does not integrate samples over the 1-minute period. Rather, the nature of the flow-through system smears the peaks out over a longer time due to the time it takes analytes to diffuse through the inlet system and into the mass analyzer. The flow-through system also means that some very short duration high peaks may not be seen at all.

Overall the comparison of the reconstructed BTEX and MS200 BTEX values substantially agree and this provides added confidence that we can represent the peak exposures well by using the PID values to reconstruct time series for the BTEX species. While we do not have a direct measure for 1,3-butadiene, we would suggest that it could also be adequately represented by the PID values, especially for exhaust-dominated MEs.

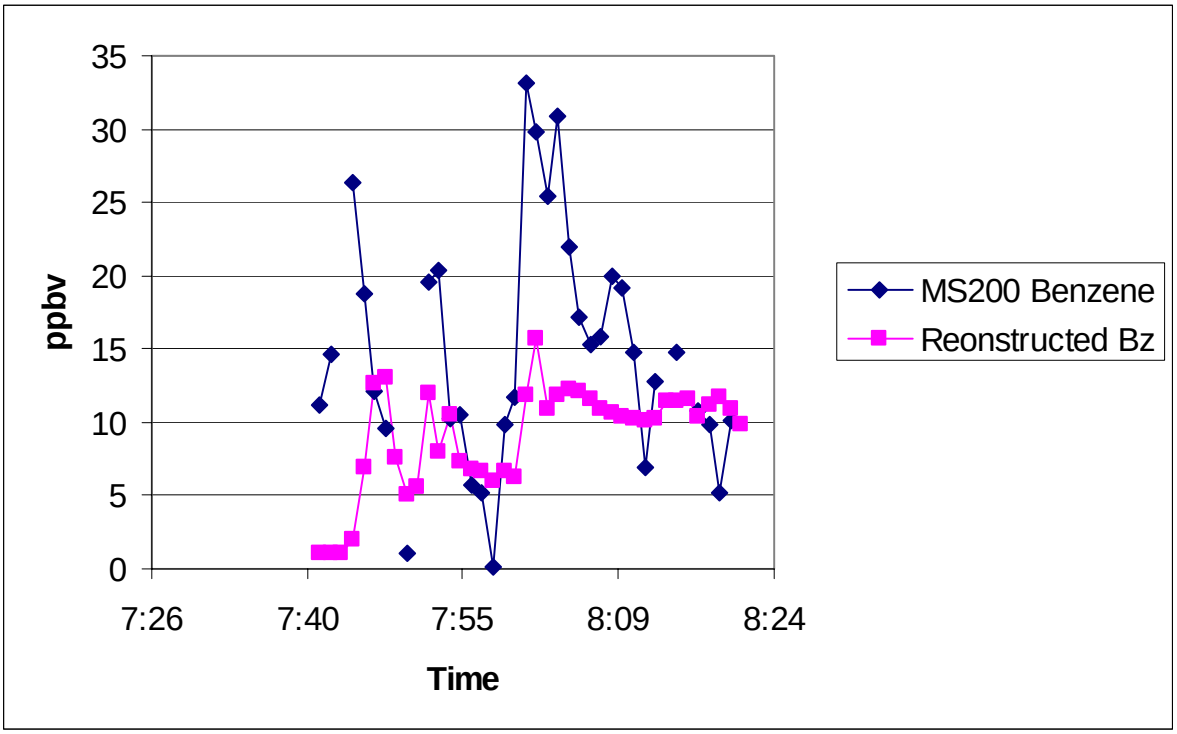


Figure 3.4-1. ME1 (freeway driving) on 4/29/03: Time series of benzene from the MS200 and reconstructed benzene concentrations from the PID and canister measurements.

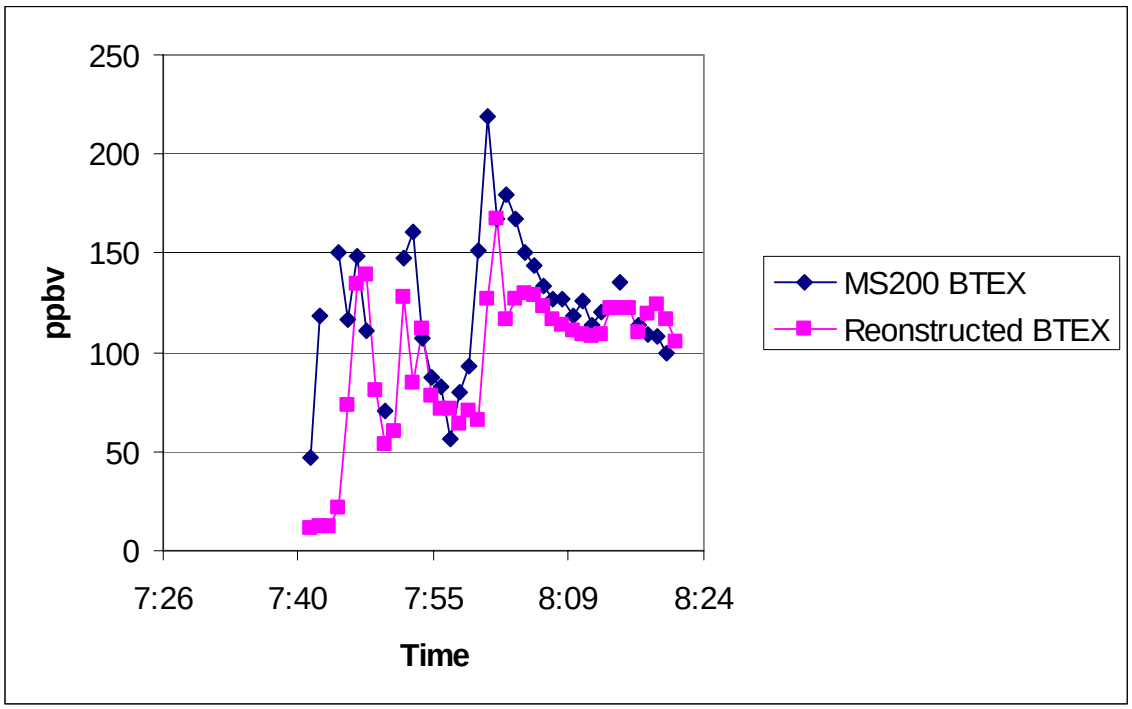


Figure 3.4-2. ME1 (freeway driving) on 4/29/03 : Time series of BTEX from the MS200 and reconstructed BTEX concentrations from the PID and canister measurements.

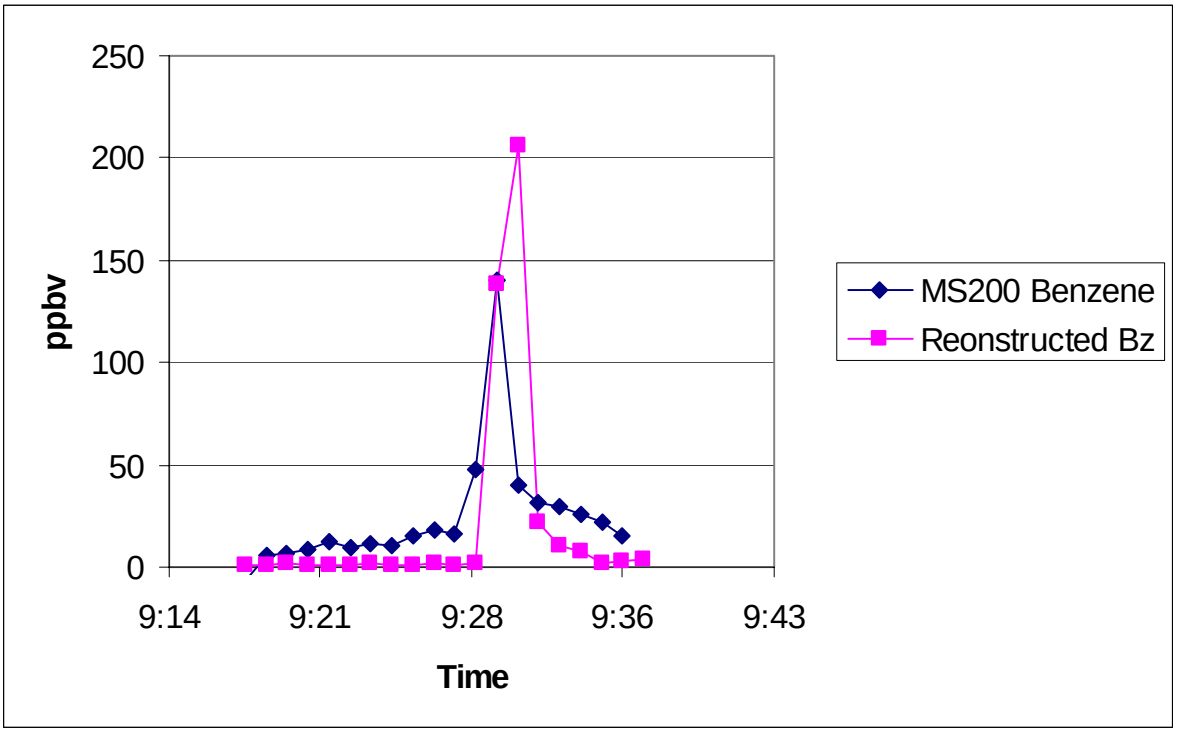


Figure 3.4-3. ME4 (refueling without vapor recovery) on 5/2/03: Time series of benzene from the MS200 and reconstructed benzene concentrations from the PID and canister measurements.

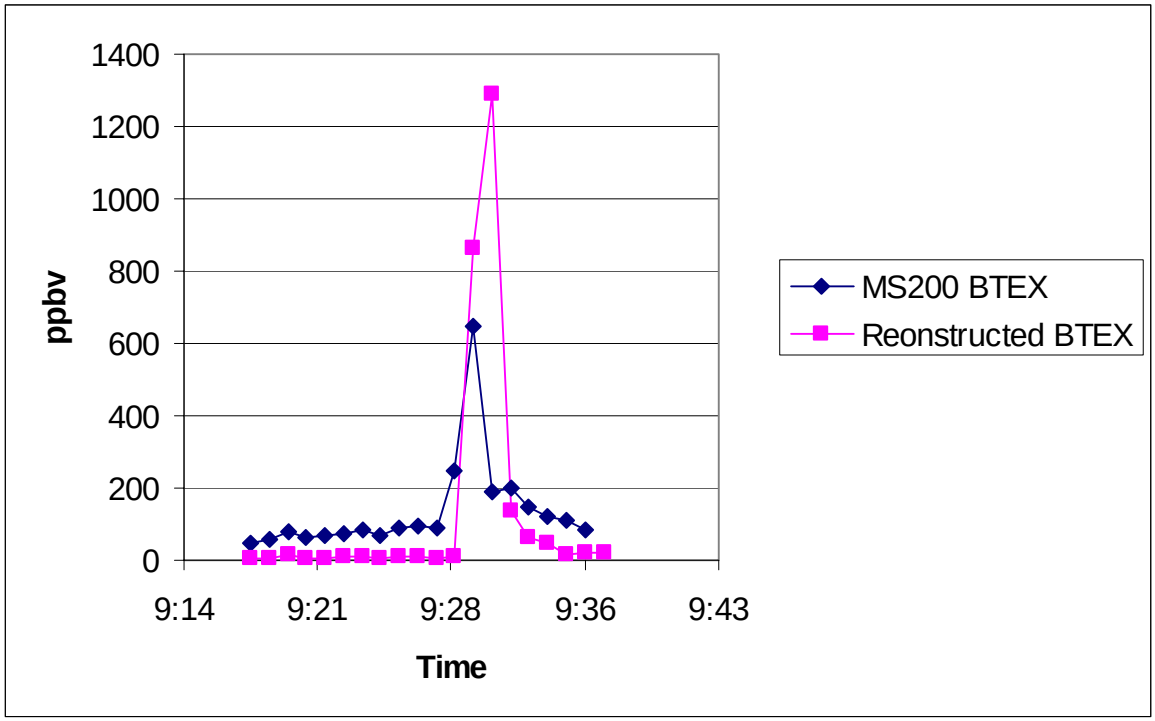


Figure 3.4-4. ME4 (refueling without vapor recove ry) on 5/2/03: Tim e series of BTEX from the MS200 and reconstructed BTEX concentrations from the PID and canister measurements.

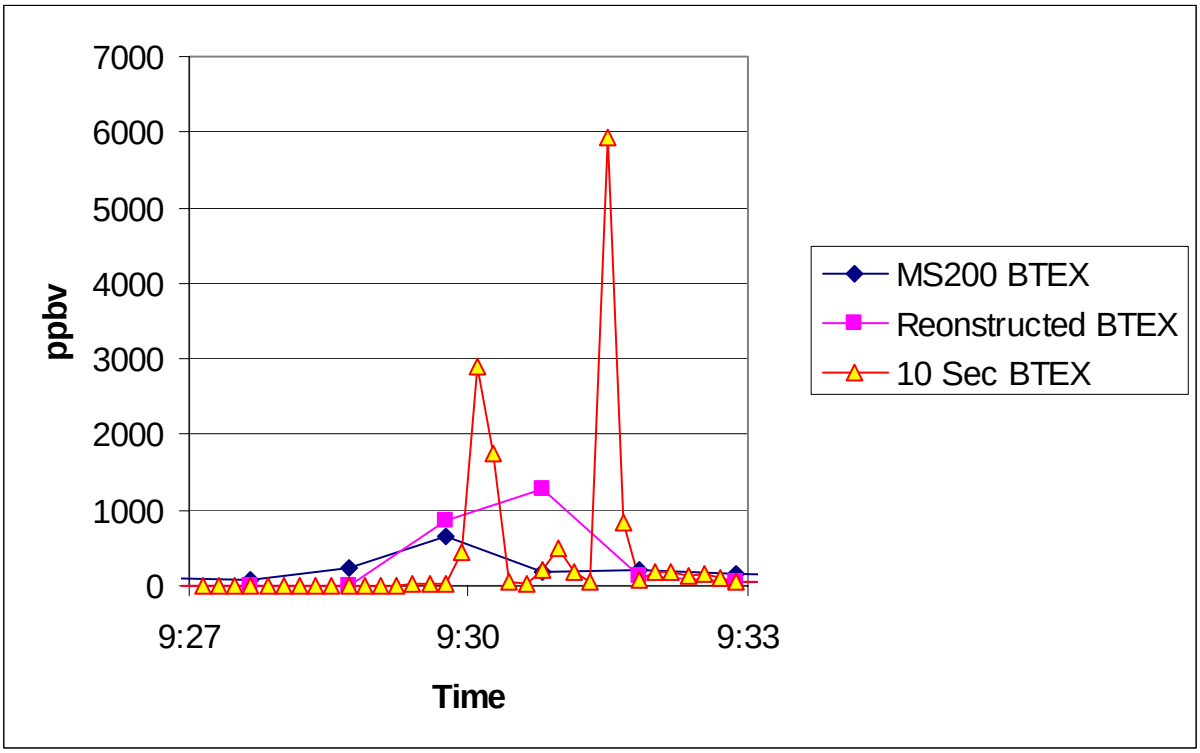


Figure 3.4-5. ME4 (refueling without vapor recove ry) on 5/2/03: Tim e series of BTEX from the MS200 and reconstructed BTEX concentra tions at both 1 m inute and 10 second time resolution.

3.5 Breath Data

Two subjects, labeled "B" and "J", performed breath sample collections. The CO2 level in their breath samples was measured prior to the commencement of the pilot study, and averaged 5.4% for B and 6% for J. As described in Section 2.1, two breath samples were collected at refueling ME (prior to refueling and 10 sec after refueling), and three during each commuter traffic and garage test (before, after a peak exposure, and at the end of the ME sampling time). All breath samples were analyzed for CO2, BTEX, 1,3-butadiene, ethanol and MTBE as described in Section 2.3. The whole data set is presented in Appendix C.

Figure 3.5–1 shows the CO2 values in the breath samples of subjects B and J collected in all ME, organized by the subject and by the microenvironment. It is clear that one pre- test freeway sample collected by J is invalid, since CO2 value is below 1%. Excluding this one sample, the mean CO2 value for subject B averages at 5.4%, and for subject J at 6.07% for all ME.

Figure 3.5-2A shows the concentrations of 1,3-butadiene, benzene, ethylbenzene, m/p- and o-xylenes in the breath samples for all freeway tests (organized in the chronological order) and Figure 3.5-2B shows the concentrations of toluene and ethanol for the same ME. Figures 3.5-3 A and B and Figure 3.5-4 A and B shows the same compound concentrations for the garage and refueling ME, respectively. The range of concentrations for 1,3-butadiene, benzene, ethylbenzene, m/p- and o-xylenes agree reasonably well for both subjects, there is clearly a large difference in the toluene concentrations. Subject B contains much higher toluene concentrations in the breath – it looks like the toluene is present in the breath of this subject, regardless of the exposure. The reason of this phenomenon is unknown to us. Ethanol concentrations are rather high and variable, not dependant on the exposure. MTBE concentrations are very low and are not shown on these figures. Neither MTBE nor ethanol are present in the Reno fuel at this time of the year.

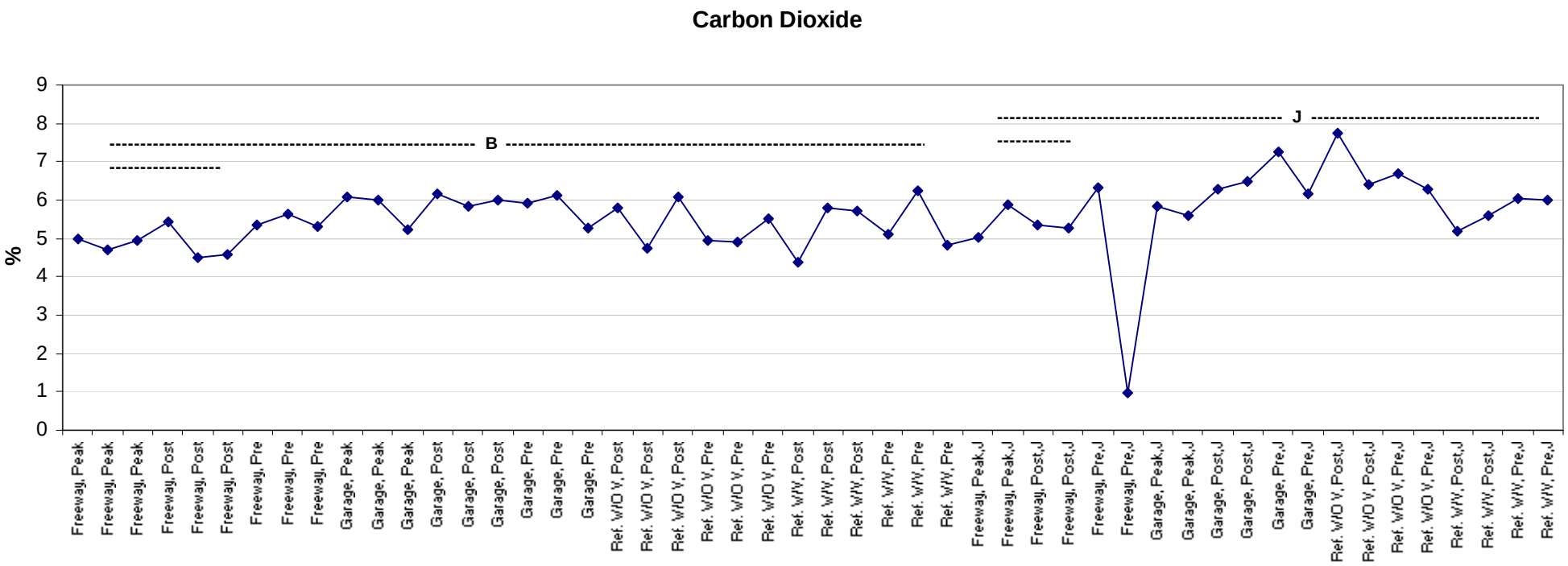


Figure 3.5–1. CO2 values in the breath samples of subjects B and J collected in all ME, organized by the subject and by microenvironment.

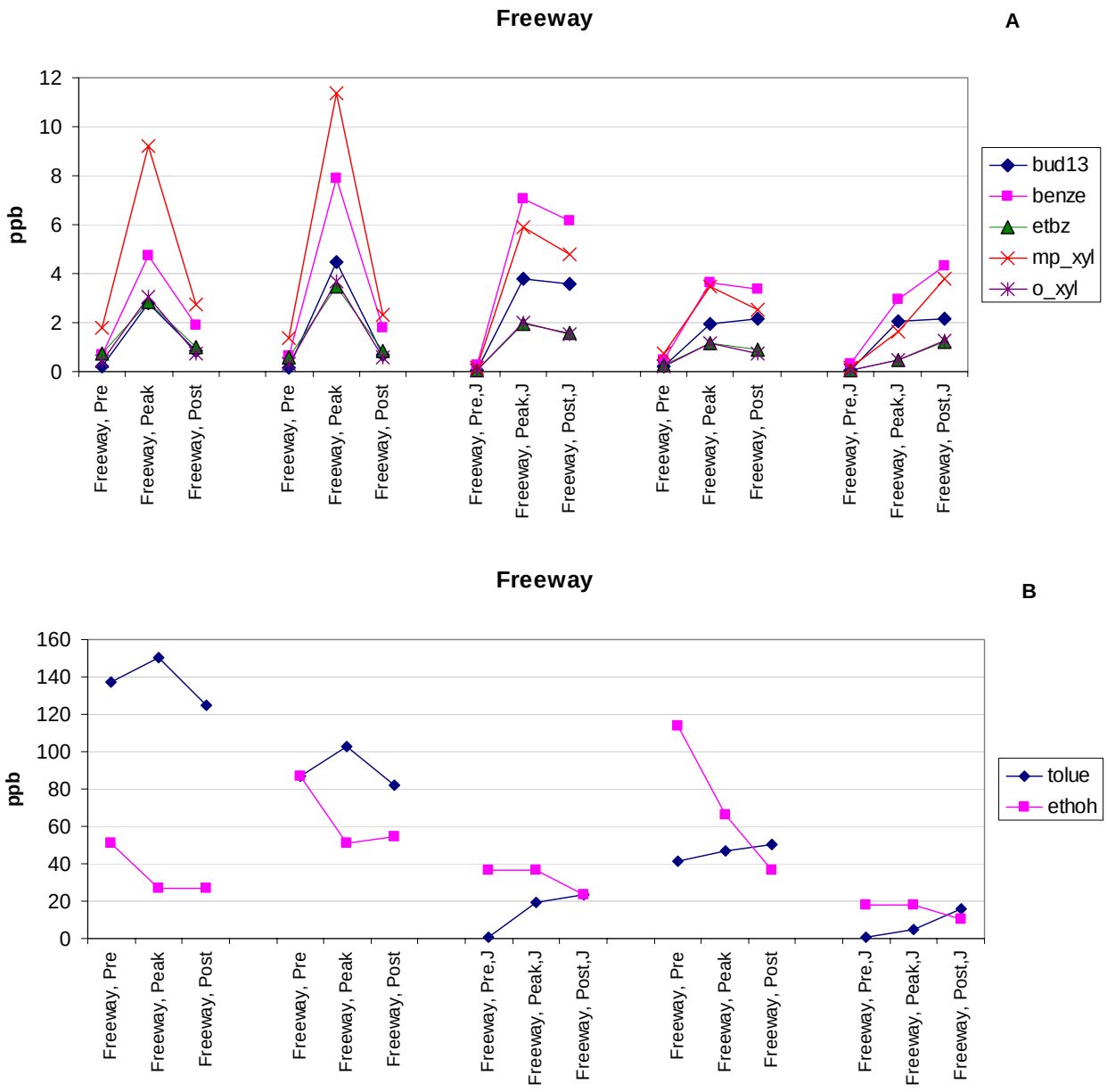


Figure 3.5-2. The concentrations of 1,3-butadie ne, benzene, ethylbenzene, m /p- and o-xylenes (A) and tolu ene and ethanol (B) in the breath samples of subject B (not labeled) and J in the freeway driving ME. The runs are shown in chronological order

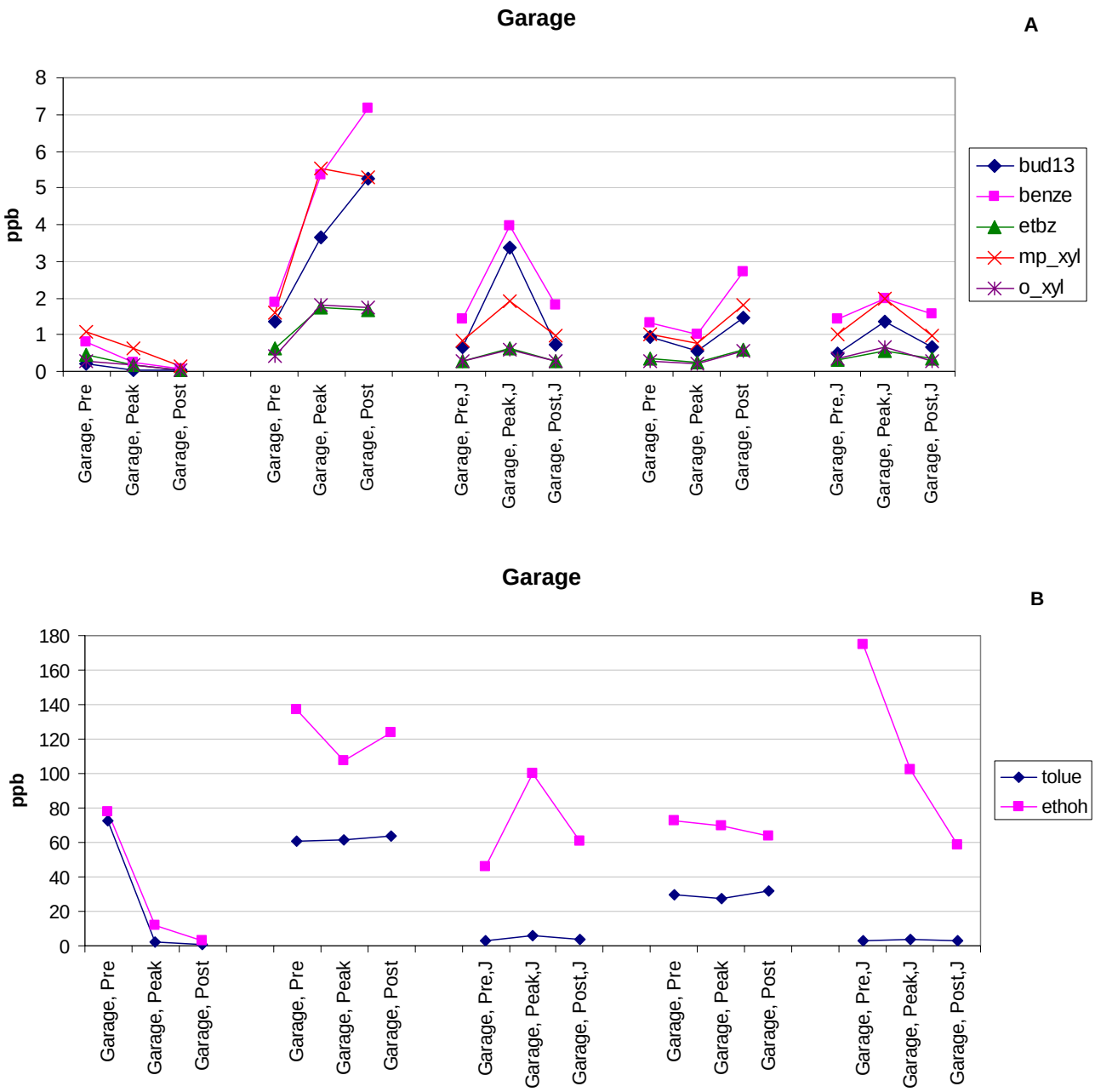


Figure 3.5-3. The concentrations of 1,3-butadie ne, benzene, ethylbenzene, m /p- and o-xylenes (A) and tolu ene and ethanol (B) in the breath samples of subject B (not labeled) and J in the garage ME. The runs are shown in chronological order

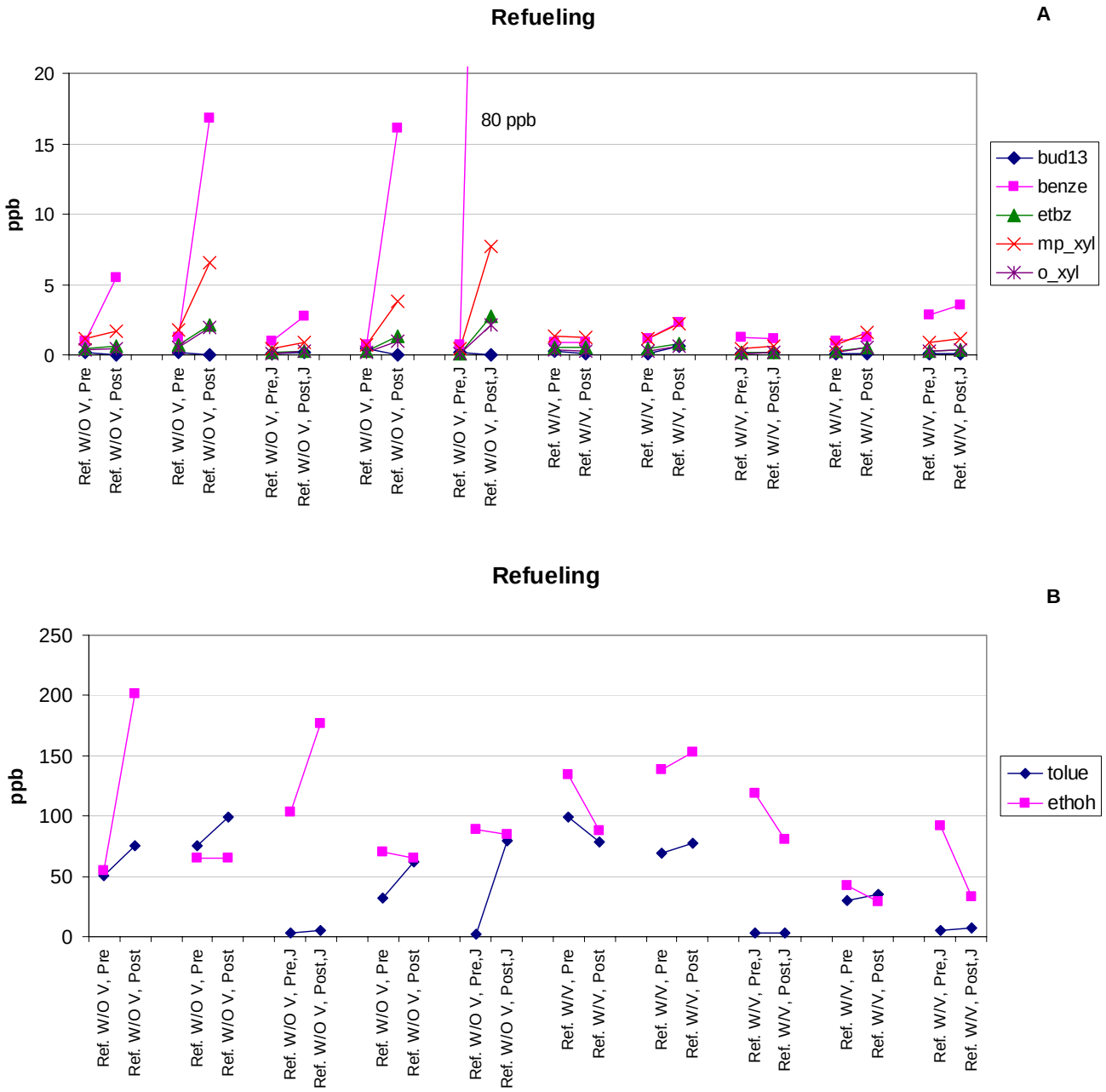


Figure 3.5-4. The concentrations of 1,3-butadie ne, benzene, ethylbenzene, m /p- and o-xylenes (A) and tolu ene and ethanol (B) in the breath samples of subject B (not labeled) and J during refueling. The runs are shown in chronological order

3.6 Consistency of Microenvironment Conditions

Each of the four microenvironments included in this pilot study was repeated 5 times to assess the variability of the environmental conditions and precision of the characterization methods. During the testing periods there were no significant variations in meteorological conditions and the same protocols were observed, so it is reasonable to attribute any variations in the range or magnitude of measurements to differences in activity in the microenvironment, daily variations in background concentrations, or measurement uncertainty. Statistical summaries of the continuous CO and BTEX by PID data are presented in this section to examine this variability. The statistics represented are the maximum and mean of the running 1 minute averages of the continuous concentration measurements recorded every 10 seconds during each test. The 10th and 90th percentile values for each test are also represented to give a better representation of the range of concentrations observed. Charts of the average for each microenvironment and standard deviation of the average among the 5 replicates are also included in Figure 3.6-3.

3.6.1 CO

Figure 3.6-1 shows the API NDIR CO data except for the first two repetitions of ME1 and the first ME3 for which the NDIR data was invalid because of insufficient battery. For those three tests discrete 1 minute averages from the electrochemical CO instrument are summarized in the chart.

The range of concentrations is large for all tests, with the exception of several of the refueling tests (ME3 and ME4) where CO concentrations were near background throughout the tests. Despite the large range, the differences between microenvironments are clearly evident. The parking garage tests, ME 2, had higher maximum and 90th percentile concentrations than all but one of the freeway tests even though the average concentrations are similar. The two refueling MEs are consistently lower than the freeway or garage in both the mean and maximum values. The third freeway (ME1) test appears to be an outlier due to a high initial level of CO (see Figure 3.2-4), possibly a result of capturing exhaust from the van in the cabin prior to the start of the driving cycle.

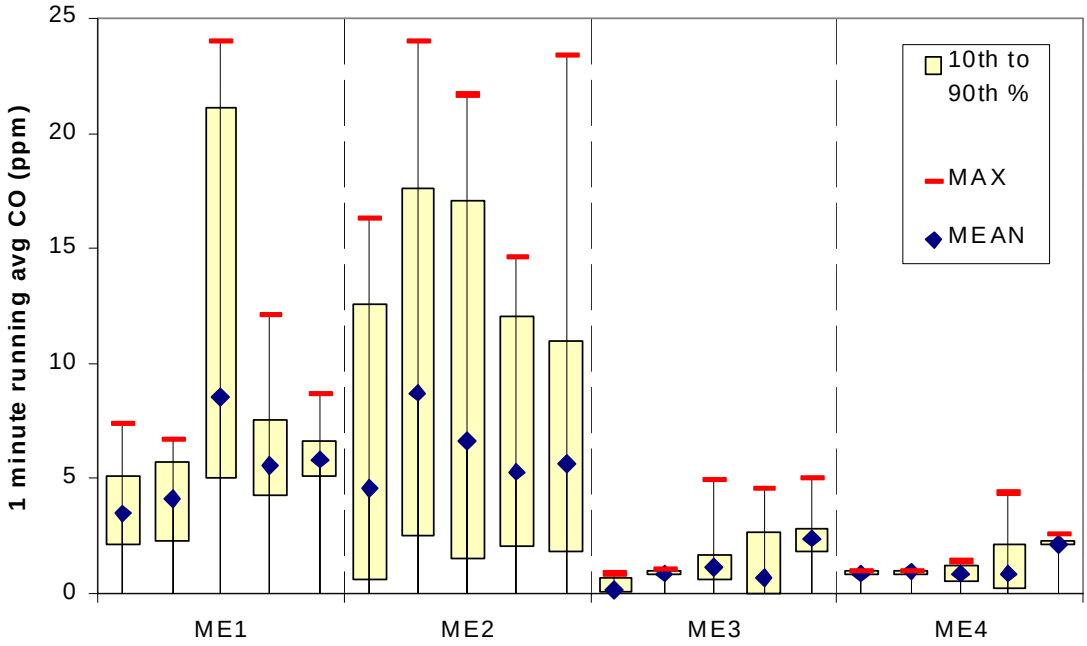


Figure 3.6-1. Range and variability of CO concentration during tests. Statistics for each of the five replicate tests are shown for each microenvironment.

Data summarized are running 1-minute averages (at 10 second intervals) of NDIR CO data, except for the first two ME1s and first ME3 which are discrete 1 minute averages from the electrochemical CO instrument. The shaded bars indicate the range from the 10th to 90th percentile. Microenvironments are: freeway driving (ME1), parking garage (ME2), refueling with vapor recovery (ME3), and refueling without vapor recovery (ME4).

3.6.2 PID

The range and variability of BTEX concentrations estimated by the primary ppbRAE VOC monitor (PID1) are summarized in Figure 3.6-2. As with CO, the range of the mean and maximum values is large for all tests, but still smaller than the overall difference between microenvironments. The largest range occurred for refueling without vapor recovery (ME4), which is to be expected since very high VOC levels occurred during the refueling process. In all cases, the 10th percentile values were near the lower limit of detection (they appear to be zero in the chart due to scale) suggesting that background levels of BTEX were very low.

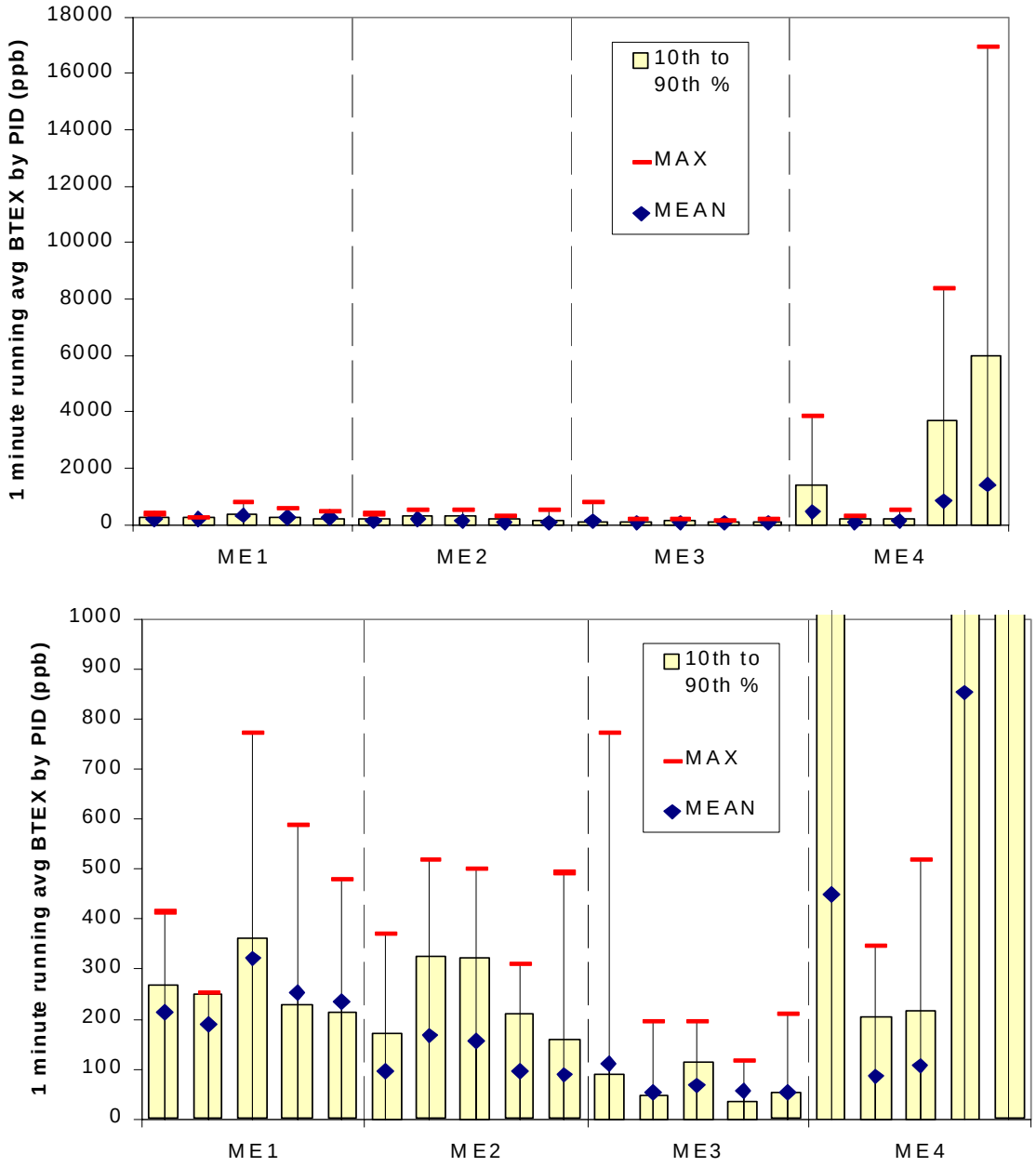


Figure 3.6-2. Range and variability of BTEX by PID concentration during tests.

Statistics for each of th e five rep licate te sts are shown for each m icroenvironment. Data summarized are running 1-minute averages (at 10 second intervals) The shaded bars indicate the range from the 10th to 90th percentile. The lower chart shows the sam e dat a on an expanded s cale. M icroenvironments are: free way driving (ME1), parking garage (ME2), refueling with vapor recovery (ME3), and refueling without vapor recovery (ME4).

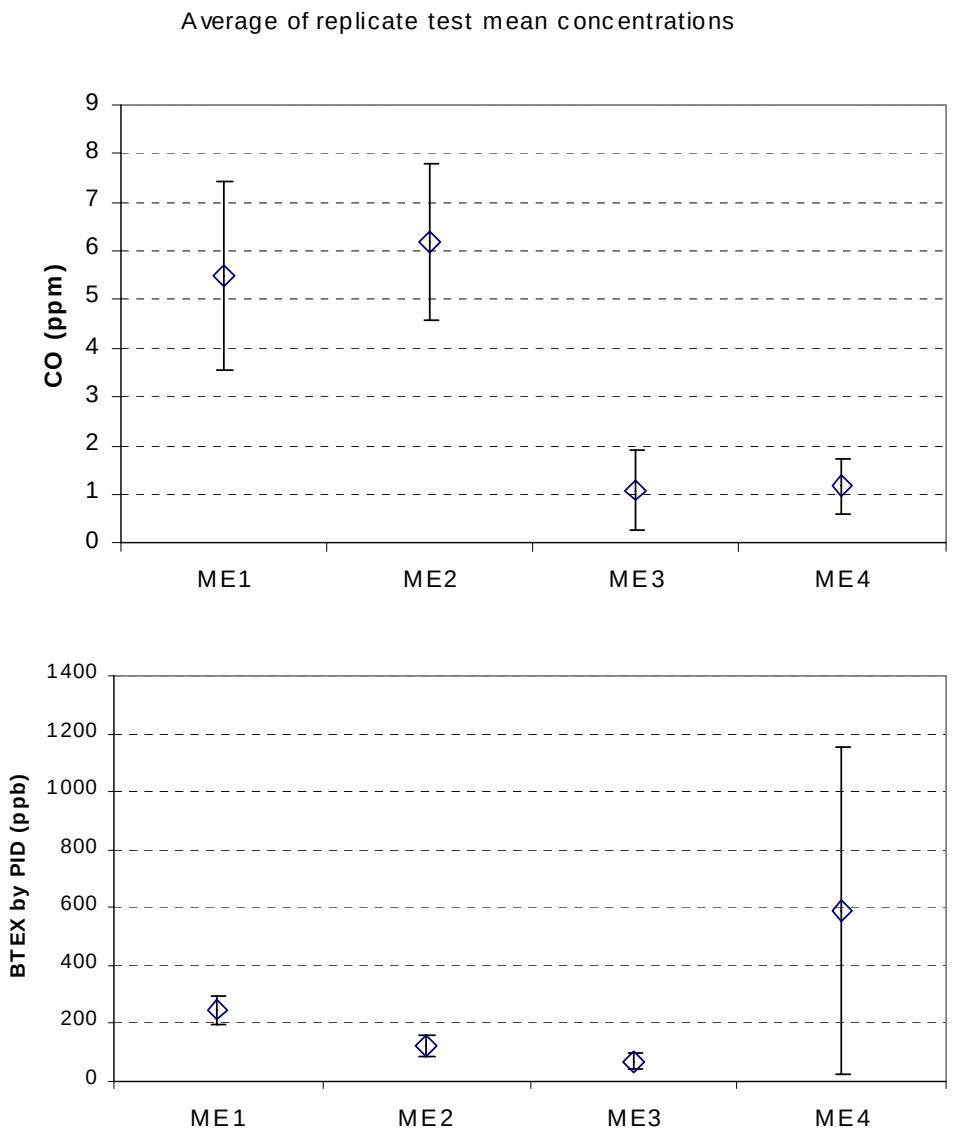


Figure 3.6-3. Range and variability of mean CO and mean BTEX by PID concentration for four microenvironments.

Data summarized are running 1-minute averages (at 10 second intervals) The error bars indicate the standard deviation of the average of five replicate tests. Microenvironments are: freeway driving (ME1), parking garage (ME2), refueling with vapor recovery (ME3), and refueling without vapor recovery (ME4).

4. CONCLUSIONS

Overall, the 2nd Reno Pilot study was a success. Specifically, we completed the stated goal of the study: to demonstrate the proper operation and reliability of analytical instrumentation and comparability of time-integrated, semi-continuous and continuous methods for compounds of interest. In addition, we demonstrated the validity of the method of reconstructing time series for compounds of interest by using surrogate measurements. In this case, we specifically demonstrated the validity of using the PID signal and the canister data to reconstruct the time series for BTEX.

The following conclusions are drawn from the 2nd Reno Pilot Study results:

Modifications to the sampling van and addition of the data acquisition system were significant improvements that allowed for more complete data collection. The new power system does not produce artifacts; however, it is insufficient to power the API CO instrument. Possible alternatives include use of a different brand of NDIR CO or the addition of more battery banks to support the API NDIR CO. Several improvements are still planned to the sampling van including the addition of a continuously logged barometric pressure sensor, direct logging of flow to the integrated samplers, and logging of canister pressure.

Data capture was generally quite good with near 100% data capture for the reference samples, canisters, DNPH and solid adsorbent. The SPME also had excellent data capture, as did the continuous instruments for CO and PID. The MS200 performed well in the beginning of the study however at the end it was not working. The supplemental continuous formaldehyde instrument is not reliable during mobile measurements, and should only be used for stationary measurements. Our environmental monitoring equipment for temperatures, humidity, etc., lost only 14 minutes of data over the entire study.

The MS200 generally performed well against the canister when comparing the average value from the MS to the integrated canister measurement for the same ME. However, there are still concerns with this supplemental measurement system. There appears to be a concentration bias, especially for benzene. The instrument appears to miss very rapid changes in concentration such as those that occur during refueling events. There are still some electrical noises that appear in the van when in motion. We did not detect these in the stationary MEs, and they did not invalidate more than a few spectra in a run. The MS200 did not run during the last day of the study due to several factors relating to the sensitivity of the detector and the filament voltage control. Some of this appears to be electronic related and may be fixed when we send the electronics box back to be upgraded to the new interface. The MS200 is a developing instrument that should provide interesting supplemental data to the study.

The continuous formaldehyde analyzer worked well for two of the five garage sampling microenvironments (ME2-4 and ME2-5) but did not work well for the freeway (ME1) or refueling (ME3 and ME4) microenvironments. The sensitivity of the instrument to environmental noise associated with driving while collecting data may limit its utility under any sort of mobile environment. With proper operation and

better characterization of instrument performance, the supplemental continuous formaldehyde analyzer may prove useful for monitoring a stationary environment.

Both an EPA-certified gas-filter correlation NDIR CO analyzer (API model 300) and a portable battery-operated passive electrochemical cell instrument (Langan T15v) agree reasonably well to within about 1 ppm. During low-ventilation (half of the freeway tests) the CO concentrations remain at or decrease toward the lowest level measured during the high-vent phase. This behavior suggests that no in-cabin sources or interferences are present.

In general the continuous PID and CO instruments performed very well. The two PIDs were compared both in controlled tests and collocated during the MEs. In both cases, they tracked each other quite well. Differences appear to be due to an offset in one unit, and a slightly different response speed between the two units. The NDIR CO and electrochemical CO instruments compared favorably, usually within 1 ppm. This was partially attributed to the adaptive filtering of the API NDIR CO as demonstrated when comparing it to another NDIR instrument made by Monitor Labs, Inc. For the purposes of this study, we strongly recommend using an instrument without the adaptive filter since the filter causes changes in concentration to appear less sharp than actual and causes peaks to shift to later times which interferes with intercomparisons among methods and instruments.

Comparison of CO from the continuous instruments to that measured by GC from the canisters showed that the canister CO was generally 8% higher with no consistent bias correlated to any particular ME nor with concentration. The correlation between the CO and PID data was strongest for the garage ME.

SPME samples show overall higher concentrations than MS200 (10-min averaged) concentrations. Also, SPME data averaged over the entire sampling periods are generally higher than canister data, due possibly to inadequate temperature corrections of the SPME data. SPME fibers are very sensitive to temperature changes (they absorb more analytes under cold conditions, as in this pilot study) and they might not be fully equilibrated to ambient temperatures prior to sampling. In the future study, the clean fibers will be stored at ambient temperature in a closed container with activated charcoal.

The procedure for collecting and analyzing breath samples worked well; there was only one invalid sample (based on CO_2 concentration) during this study. The data shows consistently higher BTEX concentrations after the peak exposure and are comparable between the two subjects collecting the samples. One exception is toluene where it appears that one of the subjects has toluene present in the breath samples, regardless of the exposure.

The 5-minute canister samples had lower data recovery (80%). This was partially because the sampler that was used to fill this canister was not optimal for the task. A relatively high flow rate was needed to pressurize a canister in only 5 min and the sampler used was not designed for this much flow. For the final study, we have designed and built a new sampler specifically for this task.

The reconstruction of the benzene and BTEX time series from the PID data showed overall good comparison with the MS200 data. However, some concentration peaks were not reproduced in magnitude and appeared to be time shifted, a consequence of the averaging of the PID data from 10 seconds down to 1 minute. In addition, the MS200 does not integrate samples over the 1-minute period; rather the nature of the flow-through system smears the peaks over a longer period due to the time it takes to diffuse through the inlet system and into the mass analyzer. Because of the flow-through system, very short duration high peaks may not be seen. In summary, for most of the MEs the reconstructed data and the MS200 data agreed reasonably well, suggesting that the reconstruction method works and should provide a method to calculate the peak exposures during sampling at the MEs.

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6.APPENDICIES

6.1 Appendix A: SPME

me	date	strthhmm	stophhmm	an_date	Storage	Tavg	RHavg	benze	tolue	ppb etbz	mp_xyl	o_xyl
ME3	4/29/03	1210	1220	4/29/03	2:40	10.69	28.03	6.66	47.13	10.18	29.32	7.99
ME3	4/29/03	1200	1210	4/29/03	3:15	10.69	28.03	17.21	58.56	11.22	24.76	12.06
ME1	4/29/03	812	822	4/29/03	7:33	20.78	31.90	18.80	114.09	19.42	51.10	15.56
ME1	4/29/03	802	812	4/29/03	8:18	15.80	31.81	12.50	98.24	18.51	51.17	16.44
ME1	4/29/03	752	802	4/29/03	9:08	12.32	31.89	15.69	70.86	15.95	45.05	14.50
ME1	4/29/03	742	751	4/29/03	9:38	11.71	37.73	13.12	66.47	19.61	54.81	17.34
ME2	4/29/03	1652	1702	4/29/03	1:08	10.28	34.59	24.70	66.85	19.49	49.33	14.83
ME2	4/29/03	1702	1712	4/29/03	1:28	10.08	35.88	28.21	90.12	26.36	73.08	25.69
ME2	4/29/03	1642	1652	4/29/03	2:18	10.56	34.60	4.08	12.49	2.48	6.95	1.59
ME4	4/30/03	1211	1221	4/30/03	1:04	27.68	12.82	11.74	65.18	15.12	34.53	7.41
ME4	4/30/03	1201	1211	4/30/03	1:34	29.14	12.21	10.29	38.17	13.10	28.02	7.16
ME3	4/30/03	1045	1055	4/30/03	3:15	8.93	36.59	6.61	24.51	6.31	20.73	5.50
ME3	4/30/03	1055	1105	4/30/03	3:35	8.99	36.32	2.71	16.40	7.55	18.23	4.50
ME1	4/30/03	809	819	4/30/03	6:36	25.54	25.88	20.41	155.78	22.19	66.59	19.90
ME1	4/30/03	759	809	4/30/03	7:11	20.69	28.02	21.92	139.74	30.27	80.99	27.37
ME1	4/30/03	739	749	4/30/03	7:56	9.72	42.59	27.17	113.76	33.86	84.96	27.28
ME1	4/30/03	749	759	4/30/03	8:26	12.98	34.35	26.52	101.84	14.13	59.19	18.05
ME4	4/30/03	921	931	4/30/03	7:39	14.10	27.98	17.04	85.61	15.34	57.68	17.01
ME4	4/30/03	931	941	4/30/03	7:49	14.03	28.33	41.04	140.14	20.70	75.84	22.48
ME2	4/30/03	1645	1655	4/30/03	3:35	32.77	11.59	28.60	89.19	13.52	49.40	16.85
ME2	4/30/03	1655	1705	4/30/03	3:45	32.71	10.84	19.14	69.59	16.89	58.29	19.66
ME2	4/30/03	1705	1715	4/30/03	3:55	33.04	11.07	64.00	173.74	48.88	154.57	58.11
ME1	5/1/03	720	730	5/1/03	2:30	11.32	43.40	49.70	152.00	36.87	104.52	34.61
ME1	5/1/03	750	800	5/1/03	2:30	21.41	33.72	29.58	195.04	24.92	81.88	26.47
ME1	5/1/03	730	740	5/1/03	3:10	15.96	30.60	29.78	130.20	26.21	87.38	28.80
ME1	5/1/03	740	750	5/1/03	3:30	19.82	30.06	21.32	110.07	19.09	63.33	23.26
ME4	5/1/03	1116	1126	5/1/03	2:44	13.72	21.79	8.05	54.91	14.50	44.03	12.10
ME4	5/1/03	1106	1116	5/1/03	3:24	14.50	22.27	5.55	43.57	14.64	35.20	8.71
ME3	5/1/03	1225	1235	5/1/03	2:20	13.54	24.52	5.61	17.02	4.60	13.58	3.23
ME2	5/1/03	1647	1656	5/1/03	1:13	14.92	24.64	6.53	38.15	8.80	23.63	6.48
ME2	5/1/03	1707	1717	5/1/03	1:13	16.18	35.42	24.17	83.75	16.99	56.15	20.52
ME2	5/1/03	1657	1707	5/1/03	2:03	14.31	25.74	30.28	91.61	15.95	58.19	19.01
ME3	5/2/03	1036	1046	5/2/03	2:39	10.76	52.57	33.56	94.44	16.85	61.89	19.50
ME3	5/2/03	1046	1056	5/2/03	2:59	10.34	53.49	7.32	39.96	7.48	23.74	5.97
ME3	5/2/03	918	928	5/2/03	4:52	10.77	42.35	4.85	27.41	6.35	18.09	4.01
ME3	5/2/03	928	938	5/2/03	5:12	10.48	43.85	84.69	281.09	56.15	167.71	54.37
ME1	5/2/03	735	745	5/2/03	7:40	16.18	35.42	16.85	83.28	20.74	56.96	17.37
ME1	5/2/03	745	755	5/2/03	8:15	19.57	29.39	22.92	121.35	30.46	86.71	27.35
ME1	5/2/03	745	805	5/2/03	8:20	22.74	29.85	28.56	104.73	18.11	55.28	16.95
ME1	5/2/03	805	815	5/2/03	8:35	22.95	33.30	22.15	149.75	29.73	69.31	22.45

ME2	5/2/03	1645	1655	5/2/03	1:30	14.18	47.03	4.21	19.10	5.85	18.00	5.11
ME2	5/2/03	1655	1705	5/2/03	1:40	13.67	47.85	7.92	26.49	5.24	13.67	4.05
ME1	5/5/03	750	800	5/5/03	5:00	14.99	39.76	15.94	75.70	17.13	53.58	16.78
ME1	5/5/03	800	810	5/5/03	5:10	17.22	33.13	15.05	66.46	0.00	0.00	0.00
ME1	5/5/03	820	830	5/5/03	6:20	21.77	38.99	21.32	151.16	12.04	46.64	13.37
ME1	5/5/03	810	820	5/5/03	6:50	19.78	35.90	24.70	138.72	25.47	90.35	30.36
ME4	5/5/03	923	933	5/5/03	5:57	17.46	28.63	1.76	10.36	1.61	5.98	1.23
ME4	5/5/03	933	943	5/5/03	6:07	16.70	29.65	103.75	386.16	34.98	121.64	31.29
ME 3	5/5/03	1045	1055	5/5/03	5:15	12.42	35.10	4.94	14.62	2.06	8.31	1.89
ME 3	5/5/03	1055	1105	5/5/03	5:25	12.31	35.33	6.55	21.64	2.92	11.16	2.29
ME2	5/6/03	1645	1655	5/6/03	1:10	13.70	33.79	4.95	17.18	2.82	9.78	2.06
ME2	5/6/03	1655	1705	5/6/03	1:20	13.49	34.22	1.39	1.26	0.32	1.07	0.23
ME2	5/6/03	1705	1715	5/6/03	1:30	13.59	34.62	12.52	48.73	14.31	51.91	18.25
				avg	4:29	16.54	32.25					
				max	9:38	33.04	53.49					
				min	1:04	8.93	10.84					

6.2 Appendix B: Canisters and Tenax

C2-C12 Hydrocarbons Target List

	Mnemonics	Names	Formula	MW	Group
1	ETHENE	ethene	C2H4	28.05	O
2	ACETYL	acetylene	C2H2	26.04	Y
3	ETHANE	ethane	C2H6	30.07	P
4	PROPE	Propene	C3H6	42.08	O
5	N_PROP	n-propane	C3H8	44.10	P
6	I_BUTA	isobutane	C4H10	58.12	P
7	LIBUTE	isobutene	C4H8	56.11	O
8	LBUT1E	1-butene	C4H8	56.11	O
9	BUDI1,3	1,3-butadiene	C4H6	54.1	O
10	N_BUTA	n-butane	C4H10	58.12	P
11	T2BUTE	t-2-Butene	C4H8	56.11	O
12	C2BUTE	c-2-butene	C4H8	56.11	O
13	IPENTA	isopentane	C5H12	72.15	P
14	PENTE1	1-pentene	C5H10	70.13	O
15	N_PENT	n-pentane	C5H12	72.15	P
16	I_PREN	isoprene	C5H8	68.11	O
17	T2PENE	t-2-Pentene	C5H10	70.13	O
18	C2PENE	c-2-pentene	C5H10	70.13	O
19	BU22DM	2,2-dimethylbutane	C6H14	86.17	P
20	CPENTA	cyclopentane	C5H10	70.13	P
21	BU23DM	2,3-dimethylbutane	C6H14	86.17	P
22	PENA2M	2-methylpentane	C6H14	86.17	P
23	PENA3M	3-methylpentane	C6H14	86.17	P
24	P1E2ME	2-methyl-1-pentene	C6H12	84.16	O
25	N_HEX	n-hexane	C6H14	86.17	P
26	MCYPNA	Methylcyclopentane	C6H12	84.16	P
27	PEN24M	2,4-dimethylpentane	C7H16	100.20	P
28	BENZE	benzene	C6H6	78.11	A
29	CYHEXA	cyclohexane	C6H12	84.16	P
30	HEXA2M	2-methylhexane	C7H16	98.19	P
31	PEN23M	2,3-dimethylpentane	C7H16	100.20	P
32	HEXA3M	3-methylhexane	C7H16	100.20	P
33	PA224M	2,2,4-trimethylpentane	C8H18	114.23	P
34	N_HEPT	n-heptane	C7H16	100.20	P
35	MECYHX	methylcyclohexane	C7H14	98.19	P
36	PA234M	2,3,4-trimethylpentane	C8H18	114.23	P
37	TOLUE	toluene	C7H8	92.14	A
38	HEP2ME	2-methylheptane	C8H18	114.23	P
39	HEP3ME	3-methylheptane	C8H18	114.23	P
40	N_OCT	n-octane	C8H18	114.22	P
41	ETBZ	ethylbenzene	C8H10	106.16	A
42	MP_XYL	mp-xylene	C8H10	106.16	A
43	STYR	styrene	C8H8	104.14	A
44	O_XYL	o-xylene	C8H10	106.17	A
45	N_NON	n-nonane	C9H20	128.26	P

46	IPRBZ	isopropylbenzene	C9H12	120.20	A
47	N_PRBZ	n-propylbenzene	C9H12	120.20	A
48	M_ETOL	m-ethyltoluene	C9H12	120.20	A
49	P_ETOL	p-ethyltoluene	C9H12	120.20	A
50	BZ135M	1,3,5-trimethylbenzene	C9H12	120.20	A
51	O_ETOL	o-ethyltoluene	C9H12	120.20	A
52	BZ124M	1,2,4-trimethylbenzene	C9H12	120.20	A
53	N_DEC	n-decane	C10H22	142.29	P
54	BZ123M	1,2,3-trimethylbenzene	C9H12	120.20	A
55	DETBZ1	m-diethylbenzene	C10H14	134.22	A
56	DETBZ2	p-diethylbenzene	C10H14	134.22	A
57	N_UNDE	n-undecane	C11H24	156.30	P
58	MTBE	methyl t-butyl ether	C5H12O	88.14	E
	TNMHC				

A = aromatic, AL = Aldehyde, O = alkene (olefin), P = parafin, Y = alkyne, K = ketone, E = ether, X = haogenated, OH = alcohol

Concentrations in ppbC, Tenax

site	date	starthhmm	stophhmm	duration (min)	ethoh	mtbe	tolue	etbz	mp_xyl	o_xyl
Freeway	4/29/03	0742	0822	40	0.00	0.00	215.22	43.24	166.08	61.29
Freeway	4/29/03	0742	0822	40	0.00	0.00	229.54	44.83	170.39	62.76
Refueling W/Vapor Re	4/29/03	1200	1220	20	0.00	0.00	82.06	11.65	48.39	14.41
Garage	4/29/03	1642	1712	30	4.24	0.00	105.02	23.08	95.97	32.16
Freeway	4/30/03	0739	0819	41.1	0.00	0.00	342.38	64.43	247.26	89.48
Refueling W/O Vapor	4/30/03	0921	0941	19.92	0.00	0.00	240.68	38.40	165.02	51.89
Refueling W/Vapor Re	4/30/03	1045	1105	20	0.00	0.00	19.61	4.20	17.13	5.91
Refueling W/O Vapor	4/30/03	1205	1225	20	0.00	0.00	49.12	5.20	20.24	6.35
Garage	4/30/03	1645	1715	30	0.00	0.00	187.19	47.86	200.47	72.90
Refueling W/O Vapor	5/1/03	1106	1126	20.43	0.00	0.00	146.48	10.89	45.22	11.69
Refueling W/Vapor Re	5/1/03	1225	1245	21.3	0.00	0.00	35.57	6.67	31.12	10.55
Garage	5/1/03	1647	1717	30	0.00	0.00	222.61	54.49	208.29	74.62
Freeway	5/2/03	0735	0815	40	0.00	0.00	238.47	39.24	152.56	57.05
Refueling W/O Vapor	5/2/03	0918	0938	20	0.00	0.00	330.84	53.26	223.45	71.59
Refueling W/Vapor Re	5/2/03	1036	1056	20	0.00	0.00	51.20	11.93	58.04	17.54
Garage	5/2/03	1645	1715	30	0.00	0.00	137.43	36.88	145.86	49.65
Garage	5/2/03	1645	1715	30	0.00	0.00	159.00	40.65	161.52	56.03
Garage-Blank	5/2/03	1710	1710	0	0.00	0.00	0.19	0.00	0.00	0.00
Freeway	5/5/03	0750	0830	40	0.00	0.00	396.27	81.14	304.94	108.37
Refueling W/O Vapor	5/5/03	0923	0943	20	0.00	0.00	270.81	24.47	94.68	25.35
Refueling W/Vapor Re	5/5/03	1045	1105	20	0.00	0.00	10.47	2.37	9.10	3.62
Garage	5/6/03	1645	1715	30	0.00	0.00	43.20	11.77	52.29	17.47

Canister BTEX, ppbC

site	date	time	Time (min)	an_type	budi13	benze	tolue	etbz	mp_xyl	o_xyl	tnmhc
Freeway	4/29/03	742-822	20	p	10.78	54.57	317.43	59.84	199.34	79.52	2999.48
Refueling W/Vapor Recovery	4/29/03	1200-1205	5	p	8.86	15.35	88.97	14.96	47.74	17.4	1894.91
Refueling W/Vapor Recovery	**4/29/03**	**1200-1205**	**5**	**r**	**8.79**	**15.52**	**91.18**	**15.33**	**50.57**	**18.45**	**2020.37**
Refueling W/Vapor Recovery	4/29/03	1200-1220	20	p	1.15	20.27	69.36	11.46	38.54	14.8	2685.11
Garage	4/29/03	1642-1712	20	p	6.78	33.88	102.67	24.81	84.19	33.6	1234
Refueling W/Vapor Recovery	4/30/03	1045-1105	20	p	0.99	7.74	31.64	7.79	27.97	11.75	649.59
Refueling W/Vapor Recovery	**4/30/03**	**1045-1105**	20	**r**	**0.99**	**7.84**	**31.81**	**7.8**	**28.07**	**11.73**	**631.17**
Refueling W/Vapor Recovery	4/30/03	1055-1100	5	p	0.83	16.7	88.09	17.5	59.12	22.26	1718.23
Refueling W/O Vapor Recovery	4/30/03	1205-1245	20	p	0.53	12.8	54.95	9.17	31.68	12.13	1694.75
Refueling W/O Vapor Recovery	4/30/03	1212-1217	5	p	0.14	6.97	23.5	3.01	9.83	3.65	1171.77
Garage	4/30/03	1645-1715	20	p	11.52	59.62	223.45	55.82	192.46	77.97	2081.38
Freeway	4/30/03	739-819	20	p	12.67	60.04	376.27	69.5	235.83	93.92	3423.75
Refueling W/O Vapor Recovery	4/30/03	921-927	20	p	1.41	247.58	708.8	71.8	223.88	77.16	46526.7
Refueling W/O Vapor Recovery	4/30/03	921-941	20	p	1.08	56.75	239.86	44.01	152.16	58.44	8873.4
Refueling W/O Vapor Recovery	5/1/03	1106-1126	20	p	0.66	14.02	70.68	14.6	51.8	20.04	1967.44
Refueling W/O Vapor Recovery	5/1/03	1117-1123	5	p	0.89	132.77	385.71	37.26	123.09	41.84	25852.97
Refueling W/Vapor Recovery	5/1/03	1225-1245	20	p	1.06	9.66	43.99	9.62	33.67	13.44	1061.07
Garage	5/1/03	1642-1717	20	p	13.18	63.78	239.78	57.81	202.78	78.49	2437.45
Freeway	5/1/03	720-800	20	p	21.38	109.66	534.75	99	323.27	124.46	4797.09
Freeway	**5/1/03**	**720-800**	20	**r**	**20.43**	**107.86**	**523.17**	**97.41**	**318.88**	**122.91**	**4718.69**
Refueling W/Vapor Recovery	5/2/03	1036-1056	20	p	0.6	13.78	64.99	16.76	62.6	24.44	991.98
Refueling W/Vapor Recovery	5/2/03	1046-1051	5	p	0.19	4.97	35.09	16	61.03	25.1	673.83
Garage	5/2/03	1645-1715	20	p	6.93	31.72	119.67	30.29	108.25	42.87	1269.07
Freeway	5/2/03	735-815	20	p	10.22	43.61	215.65	38.17	125.27	48.75	3511.63
Refueling W/O Vapor Recovery	5/2/03	918-938	20	p	49.8	122.93	419.54	65.06	229.57	85.66	21721.07
Refueling W/O Vapor Recovery	5/2/03	929-934	5	p	2.94	458.68	1320.65	199.46	674.97	254.1	91380.02
Refueling W/Vapor Recovery	5/5/03	1045-1105	20	p	0.54	9.3	50.59	11.11	39.64	15.3	699.04
Refueling W/Vapor Recovery	5/5/03	1055-1100	5	p	1.33	14.65	82.79	16.5	51.23	21.15	980.43
Freeway	5/5/03	750-830	20	p	10.66	57.6	312.85	66.46	230.06	90.79	3246.66
Refueling W/O Vapor Recovery	5/5/03	923-943	20	p	1.38	419.62	1093.91	101.8	328.81	109.53	73618.24
Garage	5/6/03	1645-1715	20	p	6.35	29.18	99.13	26	93.97	36.37	1045

Canisters - Full C2-C12 Speciation (ppbC)

site	Refueling W/Vapor Recovery	**Refueling W/Vapor Recovery**	Refueling W/O Vapor Recovery	Refueling W/Vapor Recovery	Refueling W/O Vapor Recovery	Refueling W/O Vapor Recovery	Refueling W/Vapor Recovery	Refueling W/O Vapor Recovery	Refueling W/O Vapor Recovery	Refueling W/Vapor Recovery	Refueling W/Vapor Recovery
date	4/30/03	**4/30/03**	4/30/03	5/5/03	5/5/03	4/30/03	4/29/03	5/2/03	5/1/03	5/1/03	5/2/03
time	1045-1105	**1045-1105**	921-941	1045-1105	923-943	1205-1245	1200-1220	918-938	1106-1126	1225-1245	1036-1056
an_type	p	**r**	p	p	p	p	p	p	p	p	p
canister	C073	**C073**	C095	C136	C186	C085	C046	C153	C227	C076	C010
ethane	5.20	**5.26**	8.83	4.58	34.04	5.38	5.91	14.87	4.60	4.80	5.00
ethene	10.82	**10.93**	6.98	5.70	5.32	5.48	10.96	11.46	4.09	8.25	7.79
acetyl	35.90	**37.30**	13.60	12.67	4.10	14.69	28.90	20.41	5.22	22.16	13.31
prope	4.42	**4.41**	20.39	3.04	555.07	6.25	9.43	84.86	3.66	4.7	4.69
n_prop	3.03	**3.04**	44.31	3.37	654.88	22.07	11.72	138.73	9.06	5.8	4.97
i_buta	8.39	**8.37**	292.11	8.36	3119.11	49.79	76.51	781.1	85.79	35.36	14.52
lbut1e	1.02	**1.02**	14.77	0.64	68.50	2.32	4.04	25.06	10.58	3.81	0.86
libute	1.69	**1.67**	53.12	0.60	335.61	7.86	0.00	127.69	5.55	3.74	2.21
budi13	0.99	**0.99**	1.08	0.54	1.38	0.53	1.15	49.8	0.66	1.06	0.6
n_buta	42.97	**42.25**	1350.13	52.08	15644.09	217.4	398.79	3806.37	354.28	158.6	77.7
t2bute	1.44	**1.5**	49.99	1.13	404.02	9.16	12.28	114.96	17.44	6.29	2.11
c2bute	0.79	**0.83**	31.44	1.58	179.85	4.11	7.23	53.98	11.38	4.07	2.81
ipenta	99.66	**99.21**	3079.3	99.96	25116.14	557.31	812.57	8387.13	474.96	233.46	176.62
pente1	1.31	**1.41**	77.4	4.41	428.6	7.33	14.96	150.06	10.49	5.03	6.71
n_pent	16.7	**16.89**	496.47	17.43	4118.19	83.55	137.59	1229.93	83.29	41.92	27.72
i_pren	0.47	**0.47**	1.43	0.41	3.58	0.85	1	1.35	0.69	0.56	0.45
t2pene	8.53	**8.59**	253.28	9.08	1998.16	42.71	72.47	596.83	45.39	24.85	13.25
c2pene	3.42	**4.02**	100.55	3.73	795.77	16.87	29.41	235.57	18.81	10.71	5.35
bu22dm	2.04	**1.99**	41.61	2.52	370	8.72	11.7	116.55	6.16	3.42	3.66
cpenta	1.91	**1.85**	42.07	2.44	386.01	8.45	11.17	112.46	8.76	4.18	3.03
bu23dm	3.12	**3.16**	73.75	4.58	623.65	12.01	23.03	170.65	14.37	9.99	6.11
pena2m	12.57	**12.62**	265.51	19.01	2433.1	48.16	81.18	653.25	50.35	25.25	22.83
pena3m	7.56	**8.25**	149.77	11.81	1379.42	27.49	46.61	366.92	28.7	14.24	13.94
p1e2me	0.9	**0.9**	12.44	1.52	156.27	2.4	3.8	28.52	3.37	1.55	1.72
n_hex	5.32	**5.37**	89.44	8.95	840.12	17.84	28.87	219.96	16.87	8.72	9.71
mcypna	8.73	**8.85**	142.4	15.07	1332.12	27.19	45.25	352.73	28.59	14.27	16.54
pen24m	0.97	**1**	14.4	1.79	112.79	2.89	4.52	32.78	4.3	3.78	2.13
benze	7.77	**7.79**	57	9.26	419.62	12.8	20.36	123.05	14.03	9.67	13.82

cyhexa	2.38	**2.42**	35.48	4.22	291.39	7.98	10.31	90.55	7.39	0.32	5.59
hexa2m	5.57	**5.48**	62	10.02	467.73	14.18	19.39	145.54	14.93	7.88	11.42
pen23m	2.03	**1.99**	25.29	3.57	171.67	5.37	7.46	54.36	7.46	5.33	4.25
hexa3m	0.3	**0.28**	3.32	0.43	21.31	0.56	0.84	6.21	0.74	0.38	0.44
pa224m	2.19	**2.1**	23.45	3.75	173.5	5.21	7.13	55.49	4.76	3.05	4.2
n_hept	4.25	**4.49**	45.47	8.45	278.39	10.66	13.79	103.51	11.51	6.41	10.54
mecyhx	4.67	**4.72**	47.99	8.5	308.14	10.56	14.49	105.3	12.11	6.45	10.63
pa234m	0.64	**0.67**	5.23	0.9	20.08	1.01	1.9	6.69	2.65	2.33	1.28
tolue	31.64	**31.81**	239.97	50.59	1093.91	54.95	69.39	419.54	70.68	43.98	64.99
hep2me	2.29	**2.34**	17.19	3.64	67.26	3.62	4.91	29.51	4.61	3.02	4.88
hep3me	2.6	**2.58**	17.28	3.86	65.21	3.8	5.51	29.53	5.03	3.21	5.26
n_oct	1.96	**1.96**	11.36	2.57	33.32	2.52	3.77	17.78	2.52	2.23	3.75
etbz	7.91	**7.86**	45.24	11.05	101.8	9.22	11.5	66.14	14.88	9.62	16.9
mp_xyl	28.39	**28.07**	152.26	39.78	328.81	31.72	38.56	229.84	52.43	33.68	62.6
styr	1.41	**1.27**	4.37	1.37	4.23	0.9	1.43	3.81	1.04	1.36	1.49
o_xyl	11.72	**11.75**	58.83	15.37	109.53	12.11	15.65	85.91	20.23	13.38	24.36
n_non	1.09	**1.03**	5.51	1.44	7.09	1.11	1.65	7.48	0.72	1.19	2.08
iprbz	0.69	**0.66**	3.48	0.81	4.19	0.76	0.82	4.34	1.09	0.8	1.29
n_prbz	2.7	**2.62**	11.77	3.06	12.85	2.38	3.05	14.76	4.03	2.77	4.62
m_etol	9.17	**8.76**	34.14	10.41	36.04	3.62	4.45	42.76	13.27	9.54	16.57
p_etol	4.38	**4.12**	16.91	4.68	15.85	7.53	9.41	20.54	6.11	4.52	7.53
bz135m	4.32	**4**	14.92	4.61	13.89	3.53	4.4	18.18	5.98	4.15	7.81
o_etol	4.11	**3.95**	12.9	4.5	14.29	3.51	5.09	16.69	5.57	4.02	6.6
bz124m	13.95	**12.89**	47.24	15.43	40.54	11.14	14.38	52.49	20.08	14.63	25.18
n_dec	1.97	**2.27**	1.72	0.39	1.73	1.18	1.36	3.26	0.46	1.01	0.73
bz123m	3.48	**3.39**	1.09	0.38	7.52	2.55	3.43	0.98	0.65	3.23	5.13
detbz1	0.99	**1.04**	2.25	0.78	1.92	0.74	1.54	2.98	1.09	0.8	1.22
detbz2	3.24	**3.14**	6.54	2.78	5.08	2.01	2.93	7.31	3.28	2.47	4.01
n_unde	1.47	**1.51**	3.53	1.4	2.1	1.05	1.83	3.3	1.11	1.14	1.84
tnmhc	656.76	**646.78**	8908.06	702	72023.3	1690.04	2706.57	21748.67	1976.27	1062.58	996.54

6.3 Appendix C: Breath Samples

Site	Date	Time	CO2, %	bud13	ethoh	mtbe	benze	tolue	etbz	mp_xyl	o_xyl
Refueling W/Vapor Recovery , Pre-Fuel	4/29	1200	5.09	0.27	133.86	0.74	0.87	99.31	0.53	1.36	0.33
Refueling W/Vapor Reco very, Post-Fuel	4/29	1215	4.38	0.10	87.75	0.46	0.89	78.42	0.49	1.20	0.29
Garage, Pre	4/29	1642	5.91	0.21	78.10	0.46	0.81	72.49	0.46	1.09	0.27
Garage, Peak	4/29	1654	6.06	0.04	12.11	0.18	0.23	2.12	0.16	0.61	0.16
Garage, Post	4/29	1715	6.16	0.04	3.26	0.07	0.06	0.45	0.04	0.13	0.03
Freeway, Pre	4/29	731	5.35	0.20	51.26	0.27	0.70	137.39	0.72	1.80	0.43
Freeway, Peak	4/29	800	5.00	2.77	26.90	1.13	4.73	150.46	2.83	9.21	3.06
Freeway, Post	4/29	826	5.44	0.85	26.60	0.36	1.88	125.08	0.99	2.72	0.76
Refueling W/Vapor Recovery , Pre-Fuel	4/30	1047	6.24	0.12	138.93	0.69	1.16	68.79	0.44	1.13	0.27
Refueling W/Vapor Reco very, Post-Fuel	4/30	1059	5.79	0.65	153.24	0.64	2.28	77.75	0.78	2.25	0.62
Refueling W/O Vapor Recover y, Pre-Fuel	4/30	1203	4.93	0.18	54.35	0.40	1.01	50.46	0.44	1.18	0.31
Refueling W/O Vapor Recovery, Post-Fuel	4/30	1216	5.80	0.00	201.01	1.80	5.47	75.04	0.65	1.66	0.41
Garage, Pre	4/30	1643	6.11	1.35	137.30	0.32	1.87	60.47	0.62	1.61	0.43
Garage, Peak	4/30	1707	6.01	3.65	107.43	0.33	5.35	61.73	1.73	5.53	1.80
Garage, Post	4/30	1721	5.83	5.24	123.88	0.57	7.17	63.39	1.68	5.29	1.72
Freeway, Pre	4/30	727	5.64	0.15	86.91	0.48	0.64	87.07	0.57	1.34	0.31
Freeway, Peak	4/30	757	4.71	4.48	51.23	0.75	7.92	102.67	3.49	11.35	3.69
Freeway, Post	4/30	822	4.50	0.69	54.62	0.36	1.81	82.25	0.86	2.32	0.60
Refueling W/O Vapor Recover y, Pre-Fuel	4/30	923	4.92	0.18	65.02	0.46	1.22	75.46	0.69	1.79	0.50
Refueling W/O Vapor Recovery, Post-Fuel	4/30	935	4.74	0.00	64.67	5.04	16.80	99.08	2.14	6.55	1.94
Refueling W/O Vapor Recover y, Pre-Fuel	5/1	1107	6.71	0.05	103.18	0.35	0.97	2.72	0.15	0.43	0.12

Refueling W/O Vapor Recovery, Post-Fuel	5/1	1119	7.74	0.15	176.98	1.22	2.76	4.98	0.27	0.86	0.28
Refueling W/Vapor Recovery , Pre-Fuel	5/1	1227	6.02	0.11	118.30	0.69	1.27	2.63	0.15	0.46	0.13
Refueling W/Vapor Reco very, Post-Fuel	5/1	1238	5.21	0.21	81.07	0.55	1.14	2.61	0.18	0.59	0.18
Garage, Pre	5/1	1648	7.24	0.65	45.68	0.34	1.41	2.90	0.29	0.82	0.26
Garage, Peak	5/1	1703	5.82	3.36	99.74	0.37	3.97	5.92	0.64	1.90	0.61
Garage, Post	5/1	1719	6.30	0.75	60.61	0.33	1.79	3.43	0.28	0.96	0.27
Freeway, Pre	5/1	712	6.33	0.07	36.68	0.24	0.29	0.64	0.04	0.15	0.04
Freeway, Peak	5/1	735	5.05	3.79	36.45	0.67	7.03	19.53	1.93	5.91	2.03
Freeway, Post	5/1	802	5.35	3.58	23.50	0.46	6.14	23.47	1.57	4.80	1.55
Refueling W/Vapor Recovery , Pre-Fuel	5/2	1037	4.82	0.12	42.47	0.45	0.99	30.16	0.25	0.71	0.19
Refueling W/Vapor Reco very, Post-Fuel	5/2	1050	5.70	0.13	28.59	0.47	1.25	35.16	0.52	1.60	0.49
Garage, Pre	5/2	1645	5.25	0.93	72.42	0.00	1.32	29.85	0.34	1.00	0.29
Garage, Peak	5/2	1706	5.25	0.56	69.43	0.18	1.01	27.71	0.26	0.76	0.21
Garage, Post	5/2	1716	6.00	1.45	63.47	0.18	2.72	31.49	0.60	1.81	0.54
Freeway, Pre	5/2	729	5.31	0.19	113.50	0.20	0.49	41.32	0.26	0.72	0.19
Freeway, Peak	5/2	749	4.93	1.96	66.01	0.35	3.65	46.59	1.14	3.47	1.16
Freeway, Post	5/2	816	4.57	2.14	36.27	0.33	3.36	50.42	0.91	2.53	0.75
Refueling W/O Vapor Recover y, Pre-Fuel	5/2	920	5.52	0.42	70.74	0.20	0.72	32.43	0.29	0.74	0.18
Refueling W/O Vapor Recovery, Post-Fuel	5/2	932	6.09	0.00	64.88	5.15	16.07	62.34	1.30	3.80	1.02
Refueling W/Vapor Recovery , Pre-Fuel	5/5	1045	5.99	0.10	92.42	1.09	2.85	5.58	0.29	0.85	0.24
Refueling W/Vapor Reco very, Post-Fuel	5/5	1058	5.59	0.05	33.13	0.86	3.52	7.34	0.36	1.19	0.32
Freeway, Pre	5/5	744	0.98	0.06	17.62	0.27	0.31	0.53	0.05	0.14	0.04
Freeway, Peak	5/5	755	5.89	2.03	17.71	0.48	2.93	4.80	0.50	1.61	0.49
Freeway, Post	5/5	832	5.25	2.17	10.05	0.35	4.29	15.67	1.22	3.79	1.29
Refueling W/O Vapor Recover y, Pre-Fuel	5/5	923	6.30	0.18	88.50	0.23	0.67	1.77	0.13	0.46	0.13
Refueling W/O Vapor Recovery, Post-	5/5	936	6.42	0.00	84.87	16.36	80.68	79.30	2.73	7.74	2.11

Fuel											
Garage, Pre	5/6	1644	6.16	0.49	175.18	0.30	1.42	2.65	0.32	1.00	0.34
Garage, Peak	5/6	1706	5.59	1.37	102.34	0.22	1.97	3.93	0.55	2.00	0.67
Garage, Post	5/6	1718	6.48	0.65	58.69	0.27	1.57	3.05	0.34	0.98	0.27

6.4 Appendix D: DNPH

Site	Date	Start time	Stop time	Duration	V (L)	Vu (L)	formal	formalu	acetal	acetalu	aceto	acetou
Freeway	4/29/03	0742	0822	40	47.1	2.36	17.38	0.95	5.27	0.80	32.18	1.85
Freeway	4/30/03	0739	0819	41	45.2	2.26	19.02	1.04	4.67	0.80	28.35	1.64
Freeway	5/1/03	0720	0800	41.1	45.3	2.27	19.80	1.07	8.22	0.95	57.34	3.24
Freeway	5/2/03	0735	0815	40	44.1	2.21	19.13	1.05	4.84	0.82	20.67	1.23
Freeway	5/5/03	0750	0830	40	44.1	2.21	17.56	0.97	5.24	0.83	61.17	3.45
Garage	4/29/03	1642	1712	30	33.0	1.65	5.59	0.43	2.83	0.99	34.36	2.01
Garage	4/30/03	1645	1715	30	33.0	1.65	7.58	0.52	3.50	1.01	27.38	1.63
Garage	5/1/03	1642	1717	30	33.0	1.65	9.12	0.58	3.76	1.01	20.23	1.27
Garage	5/2/03	1645	1715	30	33.1	1.66	7.35	0.49	2.76	0.99	21.77	1.35
Garage	5/6/03	1645	1715	30	33.1	1.66	5.44	0.42	2.50	0.98	44.91	2.58
Garage-Blank	5/2/03	1706	1706	0	30.6	1.53	0.00	0.23	1.85	0.27	1.68	0.19
Garage-Blank	5/6/03	1612	1612	0	30.6	1.53	0.00	0.23	0.43	0.21	0.87	0.17
Refueling W/O Vapor	4/30/03	0921	0941	19.9	21.9	1.10	3.62	0.52	3.37	1.47	13.31	1.12
Refueling W/O Vapor	4/30/03	1205	1225	20	22.0	1.10	2.12	0.46	2.57	1.46	10.66	1.03
Refueling W/O Vapor	5/5/03	1106	1126	20.4	22.4	1.12	5.52	0.55	2.72	1.43	31.06	1.92
Refueling W/O Vapor	5/2/03	0918	0938	20	22.0	1.10	4.03	0.53	3.26	1.46	5.98	0.89
Refueling W/O Vapor	5/5/03	0923	0943	20	22.0	1.10	5.52	0.56	3.17	1.46	20.10	1.40
Refueling W /Vapor Re	4/29/03	1200	1220	20	22.0	1.10	4.35	0.54	2.97	1.46	20.00	1.39
Refueling W /Vapor Re	5/1/03	1225	1245	21.3	23.4	1.17	3.29	0.49	1.77	1.36	10.01	0.96
Refueling W /Vapor Re	4/30/03	1045	1105	20	22.0	1.10	2.87	0.47	1.38	1.44	12.90	1.11
Refueling W /Vapor Re	5/2/03	1036	1056	20	22.0	1.10	4.67	0.54	2.47	1.46	9.07	0.97
Refueling W /Vapor Re	5/5/03	1045	1105	20	22.0	1.10	3.29	0.52	1.78	1.44	7.94	0.95

formal =Formaldehyde
formalu =Formaldehyde uncertainty
aceto=Acetone
acetou=Acetone uncertainty
acetal = Acetaldehyde
acetalu =Acetaldehyde uncertainty

Appendix F

Evaporative and Tailpipe Emissions Support for S211b Tier 2 Exposure Study
SwRI® Project 03.05383 – Final Report

S O U T H W E S T R E S E A R C H I N S T I T U T E®

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ISO 9001 CERTIFIED
ISO 14001 Certified

July 29, 2005

TO: Desert Research Institute
2215 Raggio Parkway
Reno, NV 89512-1095

ATTN: Dr. Barbara Zielinska

SUBJECT: Final report for SwRI® Project 03.05383, "Evaporative and Tailpipe Emissions Support for S211b Tier 2 Exposure Study"

1.0 INTRODUCTION

This report describes the work performed during the summer of 2002 and the winter of 2004/2005 by the Department of Engine and Emissions Research (DEER) at Southwest Research Institute® (SwRI) in support of Desert Research Institute's (DRI) project entitled "S 211b Tier 2 Exposure Study."

2.0 STATEMENT OF WORK

The objective of this project was to provide DRI with a variety of support activities, test vehicles, a support vehicle, and to perform laboratory testing, all in support of DRI's S211b Tier 2 Exposure Study performed for the American Petroleum Institute. The portion of DRI's study performed in the San Antonio, Texas area consisted of on-road emissions measurements using a trailing vehicle, garage testing of exhaust and evaporative emissions, and laboratory exhaust and evaporative emissions measurements. SwRI provided logistics support to DRI personnel for the on-road and garage testing, but performed no emissions measurements for these tasks. Two test vehicles were procured for the program (a 1993 Toyota Camry V6 and a 1995 Ford F-150 V8), as well as a Dodge Caravan as a trailing vehicle for the on-road work in San Antonio. These vehicles were used for the on-road testing and garage testing, and then were utilized for hot soak evaporative and FTP exhaust emissions testing in the SwRI laboratory. All tests were performed with the vehicles in normal and in a malfunction condition. Tests were performed while operating on summer and winder grade fuels, from Houston, Atlanta, and Chicago. Summer grade fuels were used in 2002 and winter grade fuels were used in 2005. Selected properties of these fuels are presented in Table 1.

TABLE 1. TEST FUEL PROPERTIES

Parameter, method	Summer 2002			Winter 2005		
	Houston GA-4614	Atlanta GA-4637	Chicago GA-4640	Houston GA-5427	Atlanta GA-5437	Chicago GA-5440
ASTM D5845 Petrospec®						
MeOH, wt%	N/A	N/A	N/A	0	0	0
EtOH, wt% (D5599)	N/A	(0)	(10.75)	0	0	10
MTBE, wt% (D5599)	(9.86)	N/A	N/A	10.7	0.4	0.6
ETBE, wt%	N/A	N/A	N/A	0	0	0
TAME, wt%	N/A	N/A	N/A	1.4	0	0
DIPE, wt%	N/A	N/A	N/A	0	0.2	0.5
TBA, wt%	N/A	N/A	N/A	0.3	0	0
O_2 Total wt% (D5599)	(1.81)	(0.01)	(3.73)	2.23	0.1	3.66
Benzene, vol% (D5580)	(0.62)	(1.24)	(0.84)	0.5	1.06	1.03
Aromatic, vol% (D1319)	(19.9)	(38.4)	(17.1)	17.5	21.4	16.3
Olefins, vol%	(17.3)	(10.5)	(9.1)	9.4	6.0	15.2
Saturate, vol%	(52.8)	(51.1)	(70.9)	60.8	72.0	58.0
RON	N/A	N/A	N/A	92.2	90.5	92.3
MON (D2700)	N/A	(81.9)	(83.0)	83.5	82.9	82.8
R+M/2	N/A	N/A	N/A	87.8	86.7	87.5
T50, degF (D86)	(190)	N/A	N/A	184	208	164
T90, deg F (D86)	(327)	N/A	N/A	330	336	319
E200, %	N/A	N/A	N/A	52	40	59
E300, %	N/A	N/A	N/A	82	83	83
RVP, ASTM D5191	7.01	6.29	6.93	10.20	10.87	14.16
API Gravity, ASTM D4052	61.1	55.5	63.7	62.1	60.3	62.8
Specific Gravity, ASTM D4052	0.7347	0.7568	0.7390	0.7308	0.7379	0.7282
Carbon content, wt%, ASTM D5291	84.77	86.76	82.30	83.99	86.28	80.85
Hydrogen content, wt%, ASTM D5291	14.04	13.14	13.71	13.95	13.25	13.64

In some instances, two different methods were utilized to determine fuel properties. In these instances, the second method and corresponding results are presented in parentheses.

SwRI utilized malfunction conditions determined in the 2002 portion of the study to give exhaust hydrocarbon emissions on the order of two grams per mile. These induced malfunctions included removal of the catalysts on both vehicles plus a calibrated manifold air leak on the Toyota Camry. The malfunction for the hot soak portion of the SHED test consisted simply of disconnecting the evaporative canisters from the vehicles.

For the dynamometer FTP exhaust emissions testing, regulated exhaust emissions (total hydrocarbons, THC; non-methane hydrocarbons, NMHC; carbon monoxide, CO; and oxides of nitrogen, NO_x), carbon dioxide, CO_2; and speciated volatile organic compound (VOC) emissions (to include MTBE, ethanol, benzene, toluene, ethylbenzene, xylene, 1, 3-butadiene, formaldehyde, and acetaldehyde) were determined for each test. During hot soak tests, total hydrocarbon and VOC emissions (as above except without aldehyde/ketone measurements) were determined. A sealed housing for evaporative determinations (SHED) was utilized for the hot soak tests. The test plan followed for the laboratory testing is presented in Table 2.

TABLE 2. TEST PLAN

STEP	DESCRIPTION
1	Verify proper mechanical operation of the test vehicle.
2	Remove canister from test vehicle.
3	Purge canister with 300°F "zero" nitrogen at 20L/min for five hours, reattach canister.
4	Drain fuel tank and fill to 40 percent capacity with test fuel.
5	Perform a 2-hour diurnal heat build from 70 to 120°F at a ramp rate of 0.4°F/min.
6	Operate vehicle on chassis dynamometer over one UDDS cycle.
7	Turn engine off for five minutes.
8	Start engine and idle for one minute.
9	Turn engine off for one minute.
10	Start engine and idle for one minute.
11	Remove canister from vehicle and purge canister with "zero" air for 60 minutes.
12	Reattach canister, drain fuel from tank, and fill to 40 percent capacity with chilled test fuel.
13	Conduct one hour DHB (no emission measurements).
14	Operate vehicle on chassis dynamometer over one UDDS.
15	Soak vehicle overnight.
16	Next day prior to the cold-start exhaust portion of the FTP, conduct one-hour Diurnal Heat Build. (DHB).
17	Conduct 3-bag FTP exhaust emission test. Measure regulated gaseous emissions and VOC. emissions.
18	Conduct the Hot Soak segment of the SHED test immediately following the exhaust emissions testing.
19	Switch vehicle to malfunction condition, and disconnect evaporative canister.
20	Repeat Steps 6 through 10 and Steps 14 through 18.
21	Repeat Steps 1 through 20 for each of the remaining two test fuels.
22	Switch to next test vehicle, and repeat Steps 1 through 21.

3.0 TEST PROCEDURES

The exhaust emission portion of the FTP utilizes the Urban Dynamometer Driving Schedule (UDDS), which is 1372 seconds in duration. The UDDS is divided into two segments; the first consisting of 505 seconds, and the second consisting of 867 seconds. A FTP is composed of a 505-second cold-transient (bag 1) portion and an 867-second cold stabilized (bag 2) portion, followed by a ten-minute soak and then a 505-second hot-transient (bag 3) portion. A summary of the cycle duration, driving distance, and average speed is given in Table 3. The FTP driving schedule with the cold- and hot-transient test segments identified is given in Figure 1.

The evaporative emission portion of the FTP as conducted in this study consisted of a one-hour Diurnal Heat Build (DHB) *(40 CFR 86.133-90)* and a one-hour Hot Soak Loss Test (HSL) *(40 CFR 86.138-90).* Total hydrocarbons and VOC emissions were recorded only during the HSL segment of the test. Prior to the cold-start exhaust portion of the FTP, the DHB evaporative segment of the FTP was conducted by fueling the test vehicle to 40 percent of tank capacity with test fuel at a temperature below 55°F. A heating blanket was attached to the outside of the fuel tank, and a thermocouple placed in the fuel inside the fuel tank was connected to the computer controller. The fuel inside the tank was raised to a nominal temperature of 60°F, at which point the DHB segment of the test began. The fuel temperature was raised at a linear rate of 0.4°F per minute for the 60 minute test. The final nominal temperature was 84°F.

The HSL segment of the evaporative emission test was conducted immediately following FTP exhaust emission testing. The vehicle was allowed to "soak" in the enclosure for one hour. Total hydrocarbon and VOC emissions were measured at the beginning and end of the one hour segment to permit calculation of hot soak evaporative emissions. Alcohol measurements were included only for the Chicago fuel.

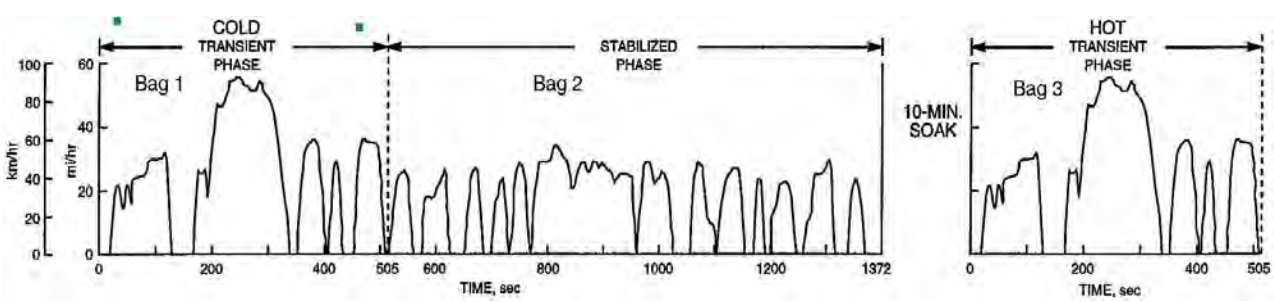

FIGURE 1. FTP DRIVING SCHEDULE

TABLE 3. SUMMARY OF FTP DRIVING SCHEDULE

Segment	Duration, Seconds	Distance, Miles	Average Speed, Miles/Hr.
Transient Phase	505	3.60	25.7
Stabilized Phase	867	3.90	16.2
UDDS	**1372**	**7.50**	**19.7**

The following sections describe the sampling and analytical procedures that were utilized for this study.

3.1 Exhaust Emissions

Emissions of THC, NMHC, CO, NO_x, and CO_2 were quantified in a manner consistent with EPA protocols for light-duty emissions testing as given in the *Code of Federal Regulations, Title 40, Part 86, Subpart B.* Emissions of THC, CO, NO_x, and CO_2 were sampled using proportional exhaust gas samples collected in Tedlar bags. Total hydrocarbon emissions were measured using a flame ionization detector, while CO and CO_2 were determined using non-dispersive infra-red instruments. Emissions of NO_x were measured using a chemiluminescent instrument. Wet absorption techniques were employed to collect alcohol and aldehyde VOC. Alcohol analysis was performed with gas chromatography – flame ionization detection and aldehydes were measured by high performance liquid chromatography with ultra-violet absorbance detection. Values for NMHC were determined by subtracting methane (corrected for FID response factor) from THC.

3.2 Evaporative Emissions

At the beginning and end of each Hot Soak Loss (HSL) segment, total hydrocarbon evaporative emissions were measured according to methods described in *40 CFR 86.138-90.* In addition to total hydrocarbon emissions, bag samples were taken at the beginning and end of each of the evaporative emission test segments to permit hydrocarbon speciation analyses to be performed, and to collect sufficient sample for alcohol analyses (when an alcohol fuel blend was used during testing). Because approximately two minutes were required to adequately fill a bag for analysis, sampling was initiated one minute before the start point and continued until one minute after the stop point.

3.3 Hydrocarbon Speciation Procedures for VOC Determinations

The analytical procedures used for conducting hydrocarbon speciation (C_2 to C_{12} hydrocarbons, aldehydes and ketones, and alcohols) are similar to the CRC Auto/Oil Phase II methods. With these methods, exhaust and evaporative emissions samples are analyzed for the presence of more than 200 different exhaust species. Four GC procedures and one HPCL procedure are used to identify and quantify compounds. In general, all emission "sample" bags

were analyzed before the "background" bags so that reactive exhaust compounds can be analyzed as quickly as possible. A brief description of these procedures is given below.

3.3.1 C_2-C_4 Species

The first GC procedure uses a 15 m x 0.53 mm I.D. DB-WAX (1Fm film) pre-column and a 50 m x 0.53 mm I.D. (10 Fm film) Alumina PLOT/KCI (Carbopack ®) column to permit the separation and determination of exhaust concentrations of C_1-C_4 individual hydrocarbon species, including ethane; ethylene; acetylene; propane; propylene; propadiene; butane; trans-2-butene; 1-butyne; and cis-2-butene. Bag samples were analyzed using a gas chromatograph equipped with a FID. The gas chromatograph system utilizes two analytical columns. The carrier gas is helium. An external multiple component standard in zero air is used to quantify the results. Detection limits for the procedure are on the order of 5 ppbC in dilute exhaust for all compounds.

3.3.2. C_5-C_{12} Species

The second GC procedure uses a 60 m x 0.32 mm I.D. (10 Fm film) DB-1 column to provide separation and exhaust concentrations for more than 100 C_5-C_{12} individual HC compounds. Bag samples are analyzed using a gas chromatograph equipped with a FID. The GC system utilizes a FID, a pneumatically operated and electrically controlled valve, and an analytical column. The carrier gas is helium. An external multiple component standard in zero air is used to quantify the results. Detection limits for the procedure are on the order of 10 ppbC in dilute exhaust for all compounds.

3.3.3 Benzene and Toluene

The third GC procedure uses a separate system configured similarly to the second GC method to determine individual concentrations of benzene and toluene according to CRC Auto/Oil Phase II Protocols. The third GC utilizes a 30 m x 0.25 mm I.D. (0.25 Fm film) DB-5 column instead of a DB-1 column.

3.3.4 Aldehydes and Ketones

A HPLC with a Zorbax ® ODS column was utilized for the analysis of aldehydes and ketones. Samples are collected by bubbling dilute exhaust at a nominal flow rate of 4 L/min through chilled glass impingers containing an acetonitrile solution of 2,4-DNPH and perchloric acid. For analysis, a portion of the acetonitrile solution is injected into a liquid chromatograph equipped with a UV detector. External standards of the aldehyde and ketone DNPH derivatives are used to quantify the results. The aldehydes and ketones that were measured include: formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, crotonaldehyde, n-butyraldehyde, benzaldehyde, isovaleraldehyde, valeraldehyde, *o*-tolualdehyde, *m*+*p*-tolualdehyde (not resolved from each other during normal operating conditions, and so reported together), dimethylbenzaldehyde, and hexanaldehyde. Detection limits for this procedure are on the order of 0.005 ppm aldehyde or ketone in dilute exhaust.

3.3.5 Alcohols

The fourth GC is utilized to analyze alcohols. The collection of ethanol in exhaust and from the SHED was accomplished by bubbling the sample through glass impingers. Each impinger contains 25 mL of deionized water maintained at ice-bath temperature. Exhaust samples were collected continuously during test cycles at a nominal flow rate of 4 L/min through a Teflon sample line held at 102°C (215°F). Evaporative emissions were sampled from Tedlar bags using a system configured similarly to that used for exhaust emissions (except an unheated sample line is used to transfer the sample to impingers).

For analysis, a portion of the liquid sample is injected into a GC equipped with a FID and an analytical column. The analytical column is a 3 m x 0.53 mm I.D. capillary column with a 1-µm film of DB-WAX as the stationary phase. The GC carrier gas is helium with a column head pressure of approximately 4 psi. External standards prepared in deionized water are used to quantify the results. Detection limits for this procedure are on the order of 0.06 ppm in dilute exhaust.

4.0 RESULTS

Regulated emissions results for the Ford F-150 and the Toyota Camry are presented in Tables 4 through 7. Results are presented for the normal and malfunction modes by fuel type. During the Winter 2005 season, for the Ford operating in normal mode on the Chicago fuel, a second exhaust emissions test was performed because the CO result appeared unexpectedly high. The CO result remained relatively high, however.

TABLE 4. REGULATED AND HOT SOAK EMISSIONS FOR FORD F-150, SUMMER 2002

Parameter	Units	Houston Fuel		Atlanta Fuel		Chicago Fuel	
		Normal	Mal-function	Normal	Mal-function	Normal	Mal-function
HC	g/mi	0.397	2.19	0.469	2.45	0.430	2.27
NMHC	g/mi	0.296	2.09	0.366	2.35	0.281	2.17
CO	g/mi	2.19	15.6	1.88	16.89	1.66	15.2
NOx	g/mi	0.989	2.11	1.05	2.13	1.40	2.07
Fuel Economy	mi/gal	14.9	15.0	15.3	15.1	14.5	14.8
Hot Soak HC	g	0.00	2.60	0.07	2.18	0.00	1.95

TABLE 5. REGULATED AND HOT SOAK EMISSIONS FOR FORD F-150, WINTER 2005

Parameter	Units	Houston Fuel		Atlanta Fuel		Chicago Fuel		
		Normal	Mal-function	Normal	Mal-function	Normal	Normal	Mal-function
HC	g/mi	0.570	2.39	0.588	2.63	0.795	0.794	2.41
NMHC	g/mi	0.464	2.23	0.487	2.54	0.637	0.637	2.31
CO	g/mi	2.95	16.3	2.90	17.2	9.32	8.19	16.4
NOx	g/mi	1.04	2.02	1.08	2.20	1.12	1.26	2.27
Fuel Economy	mi/gal	13.6	14.1	14.2	14.0	13.4	13.5	13.8
Hot Soak HC	g	0.21	6.83	0.28	13.9	0.42	N/C*	21.0

*N/C = not conducted

TABLE 6. REGULATED AND HOT SOAK EMISSIONS FOR TOYOTA CAMRY, SUMMER 2002

Parameter	Units	Houston Fuel		Atlanta Fuel		Chicago Fuel	
		Normal	Mal-function	Normal	Mal-function	Normal	Mal-function
HC	g/mi	0.227	4.05	0.288	3.89	0.244	4.21
NMHC	g/mi	0.186	3.55	0.249	3.49	0.208	3.71
CO	g/mi	3.18	64.4	2.64	59.5	2.61	60.4
NOx	g/mi	0.525	2.56	0.581	2.64	0.516	2.44
Fuel Economy	mi/gal	26.8	19.5	22.2	19.9	22.8	19.7
Hot Soak HC	g	0.09	0.77	0.01	0.62	0.05	2.16

TABLE 7. REGULATED AND HOT SOAK EMISSIONS FOR TOYOTA CAMRY FOR TOYOTA CAMRY, WINTER 2005

Parameter	Units	Houston Fuel		Atlanta Fuel		Chicago Fuel	
		Normal	Mal-function	Normal	Mal-function	Normal	Mal-function
HC	g/mi	0.268	3.99	0.384	4.03	0.388	3.75
NMHC	g/mi	0.199	3.47	0.346	3.58	0.276	3.29
CO	g/mi	2.72	64.5	3.78	63.0	3.89	55.0
NOx	g/mi	1.15	1.98	0.877	2.46	0.873	2.76
Fuel Economy	mi/gal	24.3	19.8	23.2	20.1	21.9	19.3
Hot Soak HC	g	0.02	8.02	0.00	4.84	0.11	8.66

The speciated hydrocarbon results are presented in Appendix A for the Ford F-150 and in Appendix B for the Toyota Camry.

5.0 SUMMARY

This report describes a project in which SwRI provided logistic support to DRI for on-road and garage exposure studies, and for laboratory exhaust and evaporative emissions testing. Hot Soak evaporative and FTP tailpipe vehicle emissions were measured for two vehicles operating on six fuels, to include operation in normal and in malfunction conditions.

6.0 CLOSURE

It has been a pleasure to perform this project for DRI. If you have any questions of a technical nature, please contact Patrick Merritt by telephone at (210) 522-5422, by fax at (210) 522-3950, or by e-mail at pmerritt@swri.org.

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APPENDIX A

HYDROCARBON SPECIATION DATA FOR FORD F-150

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FTP Composite Results, Winter 2005, pp. A1-A5
SHED Test Results, Winter 2005, pp. A6-A10
FTP Composite Results, Summer 2002, pp. A11-A15
SHED Test Results, Summer 2002, pp. A16-A20

A blank space in the tables indicates that the compound was not detected during analysis. A "Trace" value indicates that the compound was detected, but computations of mass or mass rate resulted in a value of less than 0.05. An "*" in the table indicates a malfunction of the analytical equipment during sample analysis and that no data are available.

HYDROCARBON SPECIATION DATA:
FTP COMPOSITE
FORD F-150

	FTP Composite, mg/mi					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	F-HOU-N	F-HOU-MF	F-ATL-N	F-ATL-MF	F-CHI-N	F-CHI-MF
COMPOUND	3/16/2005	3/17/2005	3/23/2005	3/24/2005	3/28/2005	3/29/2005
METHANE	101.9	91.2	100.3	95.3	147.5	92.8
ETHANE	29.9	31.9	29.8	34.2	34.8	34.4
ETHYLENE	40.9	261.7	37.4	269.6	78.7	276.7
PROPANE	3.3	2.5	2.5	2.5	3.1	3.3
PROPYLENE	9.3	143.2	11.2	158.2	13.6	145.0
ACETYLENE	6.9	139.3	3.7	147.6	8.0	139.5
PROPADIENE	0.2	9.6	0.3	8.6	0.2	7.7
BUTANE	35.6	39.9	61.0	61.7	96.9	81.1
TRANS-2-BUTENE	1.4	10.9	1.6	11.7	3.6	11.7
1-BUTENE	2.0	25.5	2.0	25.6	3.9	24.7
2-METHYLPROPENE (ISOBUTYLENE)	11.6	104.1	3.8	57.4	5.3	44.6
2,2-DIMETHYLPROPANE (NEOPENTANE)	57.6	87.0	60.6	88.6	78.2	104.7
PROPYNE	0.3	11.6	0.3	10.6	0.2	1.1
1,3-BUTADIENE	0.7	32.9	1.0	33.7	1.1	39.1
2-METHYLPROPANE (ISOBUTANE)	5.0	5.8	5.4	5.5	6.1	5.4
1-BUTYNE						
METHANOL						
CIS-2-BUTENE	0.3	8.3	0.6	8.8	3.3	8.6
3-METHYL-1-BUTENE						
ETHANOL					21.1	120.3
2-METHYLBUTANE (ISOPENTANE)				1.0		10.8
2-BUTYNE						
1-PENTENE	0.9	8.9	0.5	3.2	1.3	2.0
2-METHYL-1-BUTENE	1.0	18.5	1.2	12.2	2.2	16.2
PENTANE	24.4	43.5	32.5	54.8	32.2	47.0
UNIDENTIFIED C5 OLEFINS	Trace	1.7	Trace	0.5		0.3
2-METHYL-1,3-BUTADIENE	0.1	10.8	0.3	10.0	0.3	12.3
TRANS-2-PENTENE	1.4	11.5	1.3	8.1	3.2	14.4
3,3-DIMETHYL-1-BUTENE		0.4	0.1	0.5	Trace	0.5
CIS-2-PENTENE	0.7	6.4	0.6	4.7	1.8	8.5
2-METHYL-2-BUTENE	0.7	13.5	1.2	11.1	3.1	21.7
TERT-BUTANOL						
CYCLOPENTADIENE		2.4		2.4		2.2
2,2-DIMETHYLBUTANE	6.3	10.6	4.9	8.0	2.8	5.4
CYCLOPENTENE	0.4	4.3	0.4	3.2	1.6	6.0
4-METHYL-1-PENTENE	0.3	3.5	1.0	2.3	0.5	3.7
3-METHYL-1-PENTENE						
CYCLOPENTANE	1.4	5.8	1.3	4.4	2.1	4.5
2,3-DIMETHYLBUTANE	4.8	13.3	6.2	12.7	6.0	11.5
MTBE	7.5	83.7	0.1	1.7	0.2	2.4
4-METHYL-CIS-2-PENTENE						
2-METHYLPENTANE	30.0	64.8	18.5	41.6	19.8	40.8
4-METHYL-TRANS-2-PENTENE		3.4	0.2	1.7	0.5	3.4
3-METHYLPENTANE	20.6	44.2	12.5	27.0	12.8	26.6
2-METHYL-1-PENTENE	0.3	3.4	0.4	2.8	0.5	4.0
1-HEXENE	0.3	3.4	0.4	2.8	0.5	4.0
HEXANE	18.3	43.6	11.5	26.4	9.6	21.9
UNIDENTIFIED C6	0.2	12.0	0.7	7.1	0.2	10.7
TRANS-3-HEXENE						
CIS-3-HEXENE	0.4	2.6	0.3	1.4	0.6	3.3
DI-ISOPROPYL ETHER						
TRANS-2-HEXENE	0.5	3.7	0.4	2.7	0.8	5.1

HYDROCARBON SPECIATION DATA:
FTP COMPOSITE
FORD F-150

	FTP Composite, mg/mi					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	F-HOU-N	F-HOU-MF	F-ATL-N	F-ATL-MF	F-CHI-N	F-CHI-MF
COMPOUND	3/16/2005	3/17/2005	3/23/2005	3/24/2005	3/28/2005	3/29/2005
3-METHYL-TRANS-2-PENTENE	0.7	5.7	0.6	3.8	1.6	9.1
2-METHYL-2-PENTENE	0.4	3.4	0.4	2.7	0.9	5.5
3-METHYLCYCLOPENTENE				Trace		
CIS-2-HEXENE	0.2	2.0	0.2	1.0	0.5	2.7
ETBE						
3-METHYL-CIS-2-PENTENE	0.4	3.2	0.4	2.1	1.1	5.8
2,2-DIMETHYLPENTANE, NOTE A	4.6	13.1	3.2	8.9	4.4	12.0
METHYLCYCLOPENTANE, NOTE A	4.5	12.8	3.1	8.7	4.3	11.8
2,4-DIMETHYLPENTANE	2.5	7.4	3.5	9.4	1.9	6.2
2,2,3-TRIMETHYLBUTANE	0.3	1.3	0.4	0.9	0.1	0.8
3,4-DIMETHYL-1-PENTENE		0.4		0.3		0.7
1-METHYLCYCLOPENTENE	1.0	5.6	1.0	4.7	1.2	7.6
BENZENE	6.5	46.5	10.6	81.3	14.8	80.5
3-METHYL-1-HEXENE		1.4		0.3		1.2
3,3-DIMETHYLPENTANE	2.1	3.9	1.4	2.3	0.9	0.5
CYCLOHEXANE	0.4	2.0	1.0	2.7	1.1	5.5
2-METHYLHEXANE						
2,3-DIMETHYLPENTANE	14.4	43.5	12.4	38.7	7.8	23.4
1,1-DIMETHYLCYCLOPENTANE	0.1		Trace	0.5	0.3	1.2
TERT-AMYL METHYL ETHER						
CYCLOHEXENE	0.8	11.1	0.1	1.3	0.2	2.7
3-METHYLHEXANE	12.1	35.6	8.4	26.5	4.9	14.3
CIS-1,3-DIMETHYLCYCLOPENTANE	0.3	4.0	1.0	2.7	2.3	6.4
3-ETHYLPENTANE	1.2	3.3	1.4	5.6	1.5	7.9
TRANS-1,2-DIMETHYLCYCLOPENTANE						
TRANS-1,3-DIMETHYLCYCLOPENTANE	0.9	1.7	1.1	3.4	0.6	5.7
1-HEPTENE						
2,2,4-TRIMETHYLPENTANE	3.8	15.4	21.7	57.4	6.7	17.9
2-METHYL-1-HEXENE						
TRANS-3-HEPTENE		1.0	0.2	1.6	0.5	3.9
HEPTANE	7.5	27.0	6.8	23.1	4.3	14.0
CIS-3-HEPTENE						
UNIDENTIFIED C7	1.0	6.5	0.3	2.9	1.3	6.7
2-METHYL-2-HEXENE		0.5		1.3	0.5	2.9
3-METHYL-TRANS-3-HEXENE						
TRANS-2-HEPTENE	0.2	1.4	0.1	1.2	0.3	2.1
3-ETHYL-CIS-2-PENTENE			Trace			
2,4,4-TRIMETHYL-1-PENTENE	0.2	1.7	0.3	1.5	0.4	2.5
2,3-DIMETHYL-2-PENTENE						
CIS-2-HEPTENE	0.1	1.1		1.0	0.2	1.5
METHYLCYCLOHEXANE	1.8	8.0	2.4	9.4	4.5	16.8
CIS-1,2-DIMETHYLCYCLOPENTANE						
2,2-DIMETHYLHEXANE						
1,1,3-TRIMETHYLCYCLOPENTANE	0.5	2.4	0.5	2.0	0.4	2.1
2,4,4-TRIMETHYL-2-PENTENE	0.1	Trace	0.2	0.1	Trace	0.3
2,2,3-TRIMETHYLPENTANE	0.5	2.6	2.2	9.4	1.1	6.8
2,5-DIMETHYLHEXANE						
ETHYLCYCLOPENTANE						
2,4-DIMETHYLHEXANE	1.4	9.1	2.8	11.9	1.0	6.2
1-TRANS-2-CIS-4-TRIMETHYLCYCLOPENTANE	0.5	2.3	0.3	2.3	0.5	2.1
3,3-DIMETHYLHEXANE						
1-TRANS-2-CIS-3-TRIMETHYLCYCLOPENTANE	0.1	0.8	0.2	0.7	0.3	2.0

HYDROCARBON SPECIATION DATA:
FTP COMPOSITE
FORD F-150

	FTP Composite, mg/mi					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	F-HOU-N	F-HOU-MF	F-ATL-N	F-ATL-MF	F-CHI-N	F-CHI-MF
COMPOUND	3/16/2005	3/17/2005	3/23/2005	3/24/2005	3/28/2005	3/29/2005
2,3,4-TRIMETHYLPENTANE	1.0	4.1	4.8	16.9	2.5	10.0
2,3,3-TRIMETHYLPENTANE	0.9	2.0	2.6	11.4	2.9	9.0
TOLUENE	8.4	85.5	20.7	189.2	14.7	114.8
2,3-DIMETHYLHEXANE	1.2	3.6	1.7	11.9	1.1	7.9
1,1,2-TRIMETHYLCYCLOPENTANE						
2-METHYLHEPTANE		0.2			0.1	1.7
3,4-DIMETHYLHEXANE, NOTE B		1.9		1.6		0.8
4-METHYLHEPTANE	3.2	13.2	3.1	9.9	1.8	7.6
3-METHYLHEPTANE	3.3	12.9	3.1	11.3	1.8	6.6
1-CIS,2-TRANS,3-TRIMETHYLCYCLOPENTANE						
CIS-1,3-DIMETHYLCYCLOHEXANE						
TRANS-1,4-DIMETHYLCYCLOHEXANE						
3-ETHYLHEXANE	0.4	2.7	0.2	2.6	0.7	3.6
2,2,5-TRIMETHYLHEXANE	0.3	1.4	0.8	3.6	1.5	5.6
TRANS-1-METHYL-3-ETHYLCYCLOPENTANE						
CIS-1-METHYL-3-ETHYLCYCLOPENTANE	0.3	2.2	0.2	2.0	0.5	2.1
1,1-DIMETHYLCYCLOHEXANE						
TRANS-1-METHYL-2-ETHYLCYCLOPENTANE						
1-METHYL-1-ETHYL-CYCLOPENTANE						
2,4,4-TRIMETHYLHEXANE	0.1	1.0	0.1	0.7	0.1	1.3
2,2,4-TRIMETHYLHEXANE						
TRANS-1,2-DIMETHYLCYCLOHEXANE	0.1	1.6	0.2	1.0	0.2	2.0
1-OCTENE						
TRANS-4-OCTENE		0.3	0.1	1.9		0.9
OCTANE	1.6	7.7	1.7	7.9	1.2	4.5
UNIDENTIFIED C8	1.2	3.4	0.3	4.2	0.9	4.4
TRANS-2-OCTENE						
TRANS-1,3-DIMETHYLCYCLOHEXANE, NOTE C						
CIS-2-OCTENE	Trace	0.7	0.1	0.5	0.1	0.6
ISOPROPYLCYCLOPENTANE						
2,2-DIMETHYLHEPTANE	Trace					
2,3,5-TRIMETHYLHEXANE	Trace	0.4	0.1	0.8	0.3	1.0
CIS-1-METHYL-2-ETHYLCYCLOPENTANE	0.1	1.0	0.1	0.9	0.1	1.0
2,4-DIMETHYLHEPTANE	0.2	1.0	0.1	1.0	0.2	0.7
4,4-DIMETHYLHEPTANE	0.1	0.5	0.1	0.3	0.1	0.5
CIS-1,2-DIMETHYLCYCLOHEXANE						
ETHYLCYCLOHEXANE						
2,6-DIMETHYLHEPTANE, NOTE D	0.3	1.7	0.3	2.1	0.7	1.7
1,1,3-TRIMETHYLCYCLOHEXANE						
2,5-DIMETHYLHEPTANE, NOTE E	0.2	1.2	0.2	1.2	0.2	1.0
3,3-DIMETHYLHEPTANE						
3,5-DIMETHYLHEPTANE, NOTE E	0.2	1.2	0.2	1.2	0.2	1.0
ETHYLBENZENE	3.1	33.3	4.4	43.7	3.3	22.1
2,3,4-TRIMETHYLHEXANE						
2,3-DIMETHYLHEPTANE						
m-& p-XYLENE	9.6	110.1	12.8	122.9	9.6	65.2
4-METHYLOCTANE						
3,4-DIMETHYLHEPTANE						
4-ETHYLHEPTANE						
2-METHYLOCTANE	1.0	6.5	0.8	5.0	0.6	3.8
3-METHYLOCTANE	0.7	4.2	0.6	3.4	0.4	2.3
STYRENE	0.3	15.5	0.8	19.4	0.3	11.2

HYDROCARBON SPECIATION DATA:
FTP COMPOSITE
FORD F-150

	FTP Composite, mg/mi					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	F-HOU-N	F-HOU-MF	F-ATL-N	F-ATL-MF	F-CHI-N	F-CHI-MF
COMPOUND	3/16/2005	3/17/2005	3/23/2005	3/24/2005	3/28/2005	3/29/2005
o-XYLENE	3.5	42.6	5.0	48.1	3.3	23.5
1-NONENE	0.1	1.1	0.2	1.4	0.1	1.9
TRANS-3-NONENE						
CIS-3-NONENE						
NONANE	0.3	3.0	0.4	2.9	0.4	2.6
TRANS-2-NONENE						
ISOPROPYLBENZENE (CUMENE)		0.5	0.1	0.6	Trace	0.5
2,2-DIMETHYLOCTANE	Trace	0.6	0.1	0.5	0.1	0.9
2,4-DIMETHYLOCTANE	0.1	0.7	0.1	0.3	0.1	1.0
n-PROPYLBENZENE	0.5	9.8	0.8	12.0	0.6	6.7
1-METHYL-3-ETHYLBENZENE	2.3	52.6	3.3	47.0	2.6	31.8
1-METHYL-4-ETHYLBENZENE	0.9	7.9	1.5	21.5	0.8	10.6
1,3,5-TRIMETHYLBENZENE	1.1	19.4	1.7	19.6	0.8	13.2
1-METHYL-2-ETHYLBENZENE	0.8	15.7	1.5	19.8	0.7	10.4
1,2,4-TRIMETHYLBENZENE	1.6	70.5	5.4	77.5	2.5	47.8
TERT-BUTYLBENZENE						
1-DECENE						
DECANE, NOTE F	0.1	1.3	0.3	1.4	Trace	2.4
ISOBUTYLBENZENE, NOTE F	0.1	1.2	0.3	1.3	Trace	2.3
1,3,-DIMETHYL-5-ETHYLBENZENE						
METHYLPROPYLBENZENE (sec butylbenzene)		0.8	0.1	1.4	0.2	0.9
1-METHYL-3-ISOPROPYLBENZENE						Trace
1,2,3-TRIMETHYLBENZENE	0.4	14.2	1.2	18.4	0.4	11.3
1-METHYL-4-ISOPROPYLBENZENE		0.9	0.1	1.0	0.2	0.9
INDAN						
1-METHYL-2-ISOPROPYLBENZENE		6.6	0.4	5.4	0.1	7.6
1,3-DIETHYLBENZENE						
1,4-DIETHYLBENZENE		0.1		0.5	Trace	0.7
1-METHYL-3-N-PROPYLBENZENE	0.1	5.7	0.2	10.3	0.2	6.8
1-METHYL-4-N-PROPYLBENZENE, NOTE G	0.4	14.4	0.8	16.8	0.5	13.4
1,2 DIETHYLBENZENE		0.2		1.0		1.0
1-METHYL-2-N-PROPYLBENZENE		2.3	0.1	4.0		2.4
1,4-DIMETHYL-2-ETHYLBENZENE		5.8	0.7	8.5		6.5
1,3-DIMETHYL-4-ETHYLBENZENE		4.4	0.7	8.8	0.4	5.6
1,2-DIMETHYL-4-ETHYLBENZENE	0.8	1.9		1.7	0.9	1.8
1,3-DIMETHYL-2-ETHYLBENZENE		1.9		1.4		0.9
UNDECANE	Trace	3.7	0.2	4.5	0.1	2.8
1,2-DIMETHYL-3-ETHYLBENZENE						
1,2,4,5-TETRAMETHYLBENZENE		2.7		4.5		5.6
2-METHYLBUTYLBENZENE (sec AMYLBENZENE)						
3,4 DIMETHYLCUMENE						
1,2,3,5-TETRAMETHYLBENZENE	0.3	7.6	0.7	10.4	0.5	2.2
TERT-1-BUT-2-METHYLBENZENE		2.4	Trace	3.6	Trace	4.9
1,2,3,4-TETRAMETHYLBENZENE		4.3		4.8	Trace	4.1
N-PENT-BENZENE		2.0		2.2		2.0
TERT-1-BUT-3,5-DIMETHYLBENZENE						
TERT-1-BUTYL-4-ETHYLBENZENE		5.0		3.3		6.2
NAPHTHALENE						
DODECANE	Trace	2.4	Trace	4.1	0.1	1.0
1,3,5-TRIETHYLBENZENE						
1,2,4-TRIETHYLBENZENE						
HEXYLBENZENE						

HYDROCARBON SPECIATION DATA:
FTP COMPOSITE
FORD F-150

	FTP Composite, mg/mi					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	F-HOU-N	F-HOU-MF	F-ATL-N	F-ATL-MF	F-CHI-N	F-CHI-MF
COMPOUND	3/16/2005	3/17/2005	3/23/2005	3/24/2005	3/28/2005	3/29/2005
UNIDENTIFIED C9-C12+	3.7	76.1	3.6	92.4	5.2	94.8
FORMALDEHYDE	9.3	56.5	5.4	38.7	6.6	34.1
ACETALDEHYDE	2.2	17.3	2.1	16.9	4.9	32.0
ACROLEIN	0.1	4.6	0.2	6.6	0.2	8.2
ACETONE	0.8	7.5	0.3	5.9	0.8	4.4
PROPIONALDEHYDE	Trace	8.2	0.3	5.1	0.3	4.3
CROTONALDEHYDE	0.3	5.4	0.2	4.9	0.2	5.3
ISOBUTYRALDEHYDE, NOTE H	0.1	1.2	Trace	1.0	0.2	1.2
METHYL ETHYL KETONE, NOTE H	0.1	1.2	Trace	1.0	0.2	1.2
BENZALDEHYDE	0.5	10.2	0.6	13.8	0.1	7.8
ISOVALERALDEHYDE	0.2	1.2		0.9	Trace	1.5
VALERALDEHYDE		1.1		0.8		0.8
O-TOLUALDEHYDE		4.0	0.1	4.0	Trace	2.3
M/P-TOLUALDEHYDE	0.2	13.0	0.4	13.6	0.1	8.2
HEXANALDEHYDE		0.2	Trace	0.5	Trace	1.3
DIMETHYLBENZALDEHYDE	0.1	4.1	Trace	5.2	0.1	3.7

A - 2,2-Dimethylpentane and methylcyclopentane
B - 3-Methyl-3-ethyl-pentane co-elutes with reported compound. Not reported separately.
C - Cis-1,4-Dimethylcyclohexane co-elutes with reported compound. Not reported separately.
D - Propylcyclopentane co-elutes with reported compound. Not reported separately.
E - 2,5-Dimethylheptane and 3,5-dimethylheptane co-elute. GC peak area split equally between the two compounds.
F - Decane and isobutylbenzene co-elute. GC peak area split equally between the two compounds.
G - n-Butylbenzene co-elutes with reported compound. Not reported separately.
H - Isobutyraldehyde and methyl ethyl ketone co-elute. LC peak area split equally between the two compounds.

HYDROCARBON SPECIATION DATA
SHED TEST
FORD F-150

	SHED results, mg					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	F-HOU-N	F-HOU-MF	F-ATL-N	F-ATL-MF	F-CHI-N	F-CHI-MF
COMPOUND	3/16/2005	3/17/2005	3/23/2005	3/24/2005	3/28/2005	3/29/2005
METHANE	--	--	--	--	--	--
ETHANE	1.5	3.3	0.9	4.6	5.6	6.7
ETHYLENE	0.3	0.4	0.3	0.6		0.2
PROPANE	1.1	40.5	1.5	82.6	57.1	145.8
PROPYLENE	0.2	5.7	0.6	15.6	7.4	22.5
ACETYLENE						
PROPADIENE						
BUTANE	53.8	2311.0	106.2	3837.5	494.4	4161.4
TRANS-2-BUTENE	2.1	50.2	2.8	117.8	7.7	211.3
1-BUTENE	0.7	27.8	0.9	61.2	6.1	115.1
2-METHYLPROPENE (ISOBUTYLENE)	1.2	33.2	1.3	70.8	7.3	134.3
2,2-DIMETHYLPROPANE (NEOPENTANE)	43.9	1183.5	61.9	2925.1	151.9	4437.8
PROPYNE						
1,3-BUTADIENE		1.2		2.4		7.9
2-METHYLPROPANE (ISOBUTANE)	5.7	199.7	10.4	481.5	68.0	792.8
1-BUTYNE						
METHANOL						
CIS-2-BUTENE		38.9		96.4	5.7	162.6
3-METHYL-1-BUTENE						
ETHANOL					227.0	3370.0
2-METHYLBUTANE (ISOPENTANE)						
2-BUTYNE						
1-PENTENE		56.0	1.0	104.5	6.4	234.0
2-METHYL-1-BUTENE		125.1	2.7	238.4	14.1	500.5
PENTANE	21.0	506.3	25.7	1109.7	65.4	1711.8
UNIDENTIFIED C5 OLEFINS						
2-METHYL-1,3-BUTADIENE	1.6	4.9		7.9		35.9
TRANS-2-PENTENE	5.2	129.2	2.4	245.5	5.4	530.8
3,3-DIMETHYL-1-BUTENE				2.6		14.2
CIS-2-PENTENE	2.9	73.9	1.1	134.6	2.1	291.7
2-METHYL-2-BUTENE	9.8	220.7	6.4	414.3	30.7	883.9
TERT-BUTANOL						
CYCLOPENTADIENE	1.5	4.3		4.7		15.3
2,2-DIMETHYLBUTANE	2.6	27.8	1.8	59.8	2.8	96.4
CYCLOPENTENE		24.6		44.7	4.0	96.2
4-METHYL-1-PENTENE	0.4	12.6	2.4	23.4	1.2	49.6
3-METHYL-1-PENTENE						
CYCLOPENTANE		28.1		55.3	4.2	96.2
2,3-DIMETHYLBUTANE	5.5	58.6	3.3	118.7	6.9	200.6
MTBE		170.1		46.9	1.1	78.2
4-METHYL-CIS-2-PENTENE						
2-METHYLPENTANE	30.1	219.1	15.5	389.8	25.9	673.2
4-METHYL-TRANS-2-PENTENE				20.0	2.0	44.3
3-METHYLPENTANE	9.1	118.0	7.2	222.2	15.1	384.3
2-METHYL-1-PENTENE	1.1	12.1	0.6	22.7	2.0	50.0
1-HEXENE	1.1	12.1	0.6	22.7	2.0	50.0
HEXANE	8.7	90.4	7.5	167.0	13.6	279.1
UNIDENTIFIED C6	0.7	6.7	1.0	5.8	13.7	28.3
TRANS-3-HEXENE						
CIS-3-HEXENE	1.7	10.7	0.8	20.9		46.9
DI-ISOPROPYL ETHER						
TRANS-2-HEXENE		14.3	1.4	30.0	3.5	66.6

HYDROCARBON SPECIATION DATA
SHED TEST
FORD F-150

	SHED results, mg					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	F-HOU-N	F-HOU-MF	F-ATL-N	F-ATL-MF	F-CHI-N	F-CHI-MF
COMPOUND	3/16/2005	3/17/2005	3/23/2005	3/24/2005	3/28/2005	3/29/2005
3-METHYL-TRANS-2-PENTENE	4.2	29.1	1.7	51.9	4.8	116.1
2-METHYL-2-PENTENE	1.5	17.8	1.8	30.7	3.6	66.8
3-METHYLCYCLOPENTENE						
CIS-2-HEXENE	1.0	9.1		16.0	1.7	36.3
ETBE						
3-METHYL-CIS-2-PENTENE	2.0	18.7	1.0	34.2	2.1	77.1
2,2-DIMETHYLPENTANE, NOTE A	3.5	38.5	2.5	68.2	6.7	132.1
METHYLCYCLOPENTANE, NOTE A	3.4	37.6	2.5	66.8	6.5	129.4
2,4-DIMETHYLPENTANE	1.9	17.3	1.6	35.5	2.7	59.2
2,2,3-TRIMETHYLBUTANE		2.4		1.7		7.0
3,4-DIMETHYL-1-PENTENE		0.8		1.4		3.7
1-METHYLCYCLOPENTENE	1.8	17.5	1.9	34.0		83.1
BENZENE	6.7	27.2	7.3	65.6	0.2	133.8
3-METHYL-1-HEXENE				2.1		5.0
3,3-DIMETHYLPENTANE		4.0	1.6	3.8	5.2	3.0
CYCLOHEXANE	1.3	11.6		20.0		44.8
2-METHYLHEXANE						
2,3-DIMETHYLPENTANE	7.0	44.4	5.3	84.0	8.4	120.0
1,1-DIMETHYLCYCLOPENTANE		1.6		2.8		6.3
TERT-AMYL METHYL ETHER						
CYCLOHEXENE		2.2		3.3	0.5	7.7
3-METHYLHEXANE	5.8	33.1	3.9	52.8	5.1	73.2
CIS-1,3-DIMETHYLCYCLOPENTANE	1.3	9.5	0.8	17.3	2.1	35.0
3-ETHYLPENTANE	1.2	10.4	0.9	24.4	2.0	43.4
TRANS-1,2-DIMETHYLCYCLOPENTANE						
TRANS-1,3-DIMETHYLCYCLOPENTANE	1.3	7.8	0.6	15.0	1.6	28.8
1-HEPTENE						
2,2,4-TRIMETHYLPENTANE	2.7	21.4	4.0	59.6	4.0	65.7
2-METHYL-1-HEXENE						
TRANS-3-HEPTENE	0.5	4.0	0.4	7.3	0.9	15.8
HEPTANE	5.5	21.4	4.1	39.7	5.0	60.2
CIS-3-HEPTENE						
UNIDENTIFIED C7	0.4	3.4		17.1	0.5	42.4
2-METHYL-2-HEXENE						18.4
3-METHYL-TRANS-3-HEXENE					1.6	
TRANS-2-HEPTENE	0.2	2.3	0.2	3.0	0.5	5.5
3-ETHYL-CIS-2-PENTENE						3.1
2,4,4-TRIMETHYL-1-PENTENE	0.6	3.6	0.4	6.3	1.0	14.1
2,3-DIMETHYL-2-PENTENE						
CIS-2-HEPTENE		1.5	0.2	2.8	0.4	6.0
METHYLCYCLOHEXANE	2.7	18.1	2.2	32.8	4.8	66.4
CIS-1,2-DIMETHYLCYCLOPENTANE						
2,2-DIMETHYLHEXANE						
1,1,3-TRIMETHYLCYCLOPENTANE		1.3	0.2	2.5	0.3	5.1
2,4,4-TRIMETHYL-2-PENTENE			0.9	0.2		
2,2,3-TRIMETHYLPENTANE	1.6	3.7	0.9	8.1	1.7	23.6
2,5-DIMETHYLHEXANE						
ETHYLCYCLOPENTANE						
2,4-DIMETHYLHEXANE	1.8	11.0	0.5	8.9	2.0	13.5
1-TRANS-2-CIS-4-TRIMETHYLCYCLOPENTANE			0.2	3.4	0.4	6.3
3,3-DIMETHYLHEXANE						
1-TRANS-2-CIS-3-TRIMETHYLCYCLOPENTANE				1.7	0.2	5.2

HYDROCARBON SPECIATION DATA
SHED TEST
FORD F-150

	SHED results, mg					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	F-HOU-N	F-HOU-MF	F-ATL-N	F-ATL-MF	F-CHI-N	F-CHI-MF
COMPOUND	3/16/2005	3/17/2005	3/23/2005	3/24/2005	3/28/2005	3/29/2005
2,3,4-TRIMETHYLPENTANE	2.4	11.2	1.6	17.7	2.4	29.2
2,3,3-TRIMETHYLPENTANE	1.0	7.8	1.3	12.9		22.4
TOLUENE	12.8	37.6	15.1	82.5		125.9
2,3-DIMETHYLHEXANE		4.1		7.8		15.9
1,1,2-TRIMETHYLCYCLOPENTANE						
2-METHYLHEPTANE		1.1			0.2	3.8
3,4-DIMETHYLHEXANE, NOTE B						
4-METHYLHEPTANE	1.6	6.9	1.3	10.2	1.6	15.8
3-METHYLHEPTANE	1.7	7.0	1.3	11.4	1.9	11.6
1-CIS,2-TRANS,3-TRIMETHYLCYCLOPENTANE						
CIS-1,3-DIMETHYLCYCLOHEXANE						
TRANS-1,4-DIMETHYLCYCLOHEXANE						
3-ETHYLHEXANE	0.3	0.8				7.1
2,2,5-TRIMETHYLHEXANE	0.6	3.3	0.5	4.2	0.8	7.8
TRANS-1-METHYL-3-ETHYLCYCLOPENTANE						
CIS-1-METHYL-3-ETHYLCYCLOPENTANE	0.6	1.5	0.1	1.2	0.2	1.8
1,1-DIMETHYLCYCLOHEXANE						
TRANS-1-METHYL-2-ETHYLCYCLOPENTANE						
1-METHYL-1-ETHYL-CYCLOPENTANE						
2,4,4-TRIMETHYLHEXANE		0.2				
2,2,4-TRIMETHYLHEXANE						
TRANS-1,2-DIMETHYLCYCLOHEXANE	0.4	0.6		0.2	0.1	3.0
1-OCTENE						
TRANS-4-OCTENE		0.6				1.7
OCTANE	1.2	2.8	0.9	3.4	1.2	7.0
UNIDENTIFIED C8		6.0		18.1	0.3	9.8
TRANS-2-OCTENE	0.4	0.7		0.8		2.6
TRANS-1,3-DIMETHYLCYCLOHEXANE, NOTE C						
CIS-2-OCTENE						0.9
ISOPROPYLCYCLOPENTANE						
2,2-DIMETHYLHEPTANE						
2,3,5-TRIMETHYLHEXANE		0.3		0.3		0.9
CIS-1-METHYL-2-ETHYLCYCLOPENTANE		0.3		0.3		0.9
2,4-DIMETHYLHEPTANE	0.2	0.5		0.1	0.1	0.3
4,4-DIMETHYLHEPTANE				0.1		0.6
CIS-1,2-DIMETHYLCYCLOHEXANE						
ETHYLCYCLOHEXANE						
2,6-DIMETHYLHEPTANE, NOTE D	0.4	1.0	0.2	1.5	0.3	3.3
1,1,3-TRIMETHYLCYCLOHEXANE						
2,5-DIMETHYLHEPTANE, NOTE E	0.1	0.3		0.4	0.1	0.9
3,3-DIMETHYLHEPTANE						
3,5-DIMETHYLHEPTANE, NOTE E	0.1	0.3		0.4	0.1	0.9
ETHYLBENZENE	3.0	5.2	2.8	9.4	3.3	10.8
2,3,4-TRIMETHYLHEXANE						
2,3-DIMETHYLHEPTANE						
m-& p-XYLENE	7.4	12.6	6.0	25.7	7.6	31.8
4-METHYLOCTANE						
3,4-DIMETHYLHEPTANE						
4-ETHYLHEPTANE						
2-METHYLOCTANE				1.4	0.1	2.5
3-METHYLOCTANE				1.1		1.6
STYRENE						

HYDROCARBON SPECIATION DATA
SHED TEST
FORD F-150

	SHED results, mg					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	F-HOU-N	F-HOU-MF	F-ATL-N	F-ATL-MF	F-CHI-N	F-CHI-MF
COMPOUND	3/16/2005	3/17/2005	3/23/2005	3/24/2005	3/28/2005	3/29/2005
o-XYLENE	1.5	2.6	0.9	8.6	1.3	10.0
1-NONENE		0.3		0.4	0.1	0.4
TRANS-3-NONENE						
CIS-3-NONENE						
NONANE				0.1		0.5
TRANS-2-NONENE						
ISOPROPYLBENZENE (CUMENE)				0.1		0.2
2,2-DIMETHYLOCTANE						0.2
2,4-DIMETHYLOCTANE				0.1		
n-PROPYLBENZENE				0.1		0.2
1-METHYL-3-ETHYLBENZENE						
1-METHYL-4-ETHYLBENZENE						
1,3,5-TRIMETHYLBENZENE						
1-METHYL-2-ETHYLBENZENE						0.3
1,2,4-TRIMETHYLBENZENE						2.0
TERT-BUTYLBENZENE						
1-DECENE						
DECANE, NOTE F						
ISOBUTYLBENZENE, NOTE F						
1,3,-DIMETHYL-5-ETHYLBENZENE						
METHYLPROPYLBENZENE (sec butylbenzene)						
1-METHYL-3-ISOPROPYLBENZENE			0.5			
1,2,3-TRIMETHYLBENZENE				0.3		0.3
1-METHYL-4-ISOPROPYLBENZENE						
INDAN						
1-METHYL-2-ISOPROPYLBENZENE						
1,3-DIETHYLBENZENE						
1,4-DIETHYLBENZENE						
1-METHYL-3-N-PROPYLBENZENE						
1-METHYL-4-N-PROPYLBENZENE, NOTE G						
1,2 DIETHYLBENZENE						
1-METHYL-2-N-PROPYLBENZENE						
1,4-DIMETHYL-2-ETHYLBENZENE						
1,3-DIMETHYL-4-ETHYLBENZENE						
1,2-DIMETHYL-4-ETHYLBENZENE						
1,3-DIMETHYL-2-ETHYLBENZENE						
UNDECANE						
1,2-DIMETHYL-3-ETHYLBENZENE						
1,2,4,5-TETRAMETHYLBENZENE						
2-METHYLBUTYLBENZENE (sec AMYLBENZENE)						
3,4 DIMETHYLCUMENE						
1,2,3,5-TETRAMETHYLBENZENE						
TERT-1-BUT-2-METHYLBENZENE						
1,2,3,4-TETRAMETHYLBENZENE						
N-PENT-BENZENE						
TERT-1-BUT-3,5-DIMETHYLBENZENE						
TERT-1-BUTYL-4-ETHYLBENZENE						
NAPHTHALENE						
DODECANE					0.1	
1,3,5-TRIETHYLBENZENE						
1,2,4-TRIETHYLBENZENE						
HEXYLBENZENE						

HYDROCARBON SPECIATION DATA
SHED TEST
FORD F-150

	SHED results, mg					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	F-HOU-N	F-HOU-MF	F-ATL-N	F-ATL-MF	F-CHI-N	F-CHI-MF
COMPOUND	3/16/2005	3/17/2005	3/23/2005	3/24/2005	3/28/2005	3/29/2005
UNIDENTIFIED C9-C12+	0.2	1.6		2.2	1.1	8.4

A - 2,2-Dimethylpentane and methylcyclopentane co-elute. GC peak area split equally between the two compounds.
B - 3-Methyl-3-ethyl-pentane co-elutes with reported compound. Not reported separately.
C - Cis-1,4-Dimethylcyclohexane co-elutes with reported compound. Not reported separately.
D - Propylcyclopentane co-elutes with reported compound. Not reported separately.
E - 2,5-Dimethylheptane and 3,5-dimethylheptane co-elute. GC peak area split equally between the two compounds.
F - Decane and isobutylbenzene co-elute. GC peak area split equally between the two compounds.
G - n-Butylbenzene co-elutes with reported compound. Not reported separately.

HYDROCARBON SPECIATION DATA
FTP COMPOSITE
FORD F-150

	FTP Composite, mg/mi					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	FT-4614-S	FT-4614-M	FT-4637-S	FT-4637-M	FT-4640-S	FT-4640-M
COMPOUND	7/17/2002	7/19/2002	7/24/2002	7/23/2002	7/26/2002	7/29/2002
METHANE	97.4	100.8	101.5	104.5	94.3	95.0
ETHANE	32.7	37.0	27.0	35.9	35.3	34.9
ETHYLENE	27.7	245.4	30.1	255.5	25.0	232.7
PROPANE	3.8	3.6	4.1	3.8	2.9	6.4
PROPYLENE	7.2	108.8	12.2	132.7	7.4	124.7
ACETYLENE	3.4	121.1	5.3	102.1	1.9	70.1
PROPADIENE						
BUTANE	3.8	9.1	7.5	12.6	3.2	4.3
TRANS-2-BUTENE	1.0	7.3	2.0	6.6	5.2	17.6
1-BUTENE	2.3	19.2	1.6	18.6	1.2	
2-METHYLPROPENE (ISOBUTYLENE)	8.8	100.9	4.2	60.4	3.4	64.4
2,2-DIMETHYLPROPANE (NEOPENTANE)	0.4	2.0	0.6	2.0	0.2	1.0
PROPYNE						
1,3-BUTADIENE	1.5	37.6	1.2	48.9	0.3	32.9
2-METHYLPROPANE (ISOBUTANE)	0.2	8.6	3.8	9.3	0.2	6.9
1-BUTYNE						
METHANOL						
CIS-2-BUTENE	1.3	6.0		9.1	0.4	6.3
3-METHYL-1-BUTENE						
ETHANOL					12.1	182.6
2-METHYLBUTANE (ISOPENTANE)	23.1	49.3	13.7	59.4	29.6	46.9
2-BUTYNE						
1-PENTENE	0.4	7.8	0.8	1.2	0.4	6.8
2-METHYL-1-BUTENE	0.7	13.6	0.6	11.2	0.5	12.5
PENTANE	10.9	27.6	12.6	33.5	4.3	10.9
UNIDENTIFIED C5 OLEFINS	0.1	0.5		2.0	0.7	12.3
2-METHYL-1,3-BUTADIENE	0.2	6.6		10.3	0.2	11.9
TRANS-2-PENTENE	0.8	10.9	0.4	8.2	0.7	7.6
3,3-DIMETHYL-1-BUTENE		0.4	0.7	0.4	Trace	1.0
CIS-2-PENTENE	0.4	6.2	Trace	4.6	2.4	4.5
2-METHYL-2-BUTENE	1.1	14.9	1.1	12.1	1.3	16.8
TERT-BUTANOL						
CYCLOPENTADIENE	0.1	2.8		8.4	0.1	7.4
2,2-DIMETHYLBUTANE	1.8	4.6	2.1	6.2	2.6	7.0
CYCLOPENTENE	0.3	4.0	0.3	2.9	0.2	3.4
4-METHYL-1-PENTENE	0.1	2.0	0.2	2.0	0.1	2.8
3-METHYL-1-PENTENE						
CYCLOPENTANE	0.9	3.2	0.6	3.4	0.7	2.7
2,3-DIMETHYLBUTANE	3.6	11.1	2.3	9.2	5.6	17.0
MTBE	0.9	41.9				
4-METHYL-CIS-2-PENTENE						
2-METHYLPENTANE	11.7	39.4	7.9	31.2	7.8	26.5
4-METHYL-TRANS-2-PENTENE						
3-METHYLPENTANE	8.9	32.2	5.3	20.9	5.7	20.6
2-METHYL-1-PENTENE	0.1	2.5	0.1	2.5	0.1	2.0
1-HEXENE	0.2	2.8	0.1	2.5	0.1	2.0
HEXANE	8.7	31.2	5.2	19.3	4.6	14.4
UNIDENTIFIED C6	0.1	6.2	2.0	7.3	0.5	9.5
TRANS-3-HEXENE						
CIS-3-HEXENE	0.1	1.6	0.1	1.0	0.1	0.9
DI-ISOPROPYL ETHER						
TRANS-2-HEXENE	0.2	2.4	0.1	1.9	0.1	1.8

HYDROCARBON SPECIATION DATA
FTP COMPOSITE
FORD F-150

	FTP Composite, mg/mi					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	FT-4614-S	FT-4614-M	FT-4637-S	FT-4637-M	FT-4640-S	FT-4640-M
COMPOUND	7/17/2002	7/19/2002	7/24/2002	7/23/2002	7/26/2002	7/29/2002
3-METHYL-TRANS-2-PENTENE	0.3	4.1	0.3	3.2	0.2	3.5
2-METHYL-2-PENTENE	0.2	2.9	0.1	2.1	0.1	2.5
3-METHYLCYCLOPENTENE						
CIS-2-HEXENE	0.1	1.5	0.1	0.9	0.1	0.8
ETBE						
3-METHYL-CIS-2-PENTENE	0.3	2.7	0.2	1.9	0.5	1.7
2,2-DIMETHYLPENTANE, NOTE A	1.6	7.3	1.4	7.2	2.1	9.5
METHYLCYCLOPENTANE, NOTE A	1.6	7.1	1.4	7.0	2.0	9.3
2,4-DIMETHYLPENTANE	1.7	5.5	1.6	5.6	3.5	11.7
2,2,3-TRIMETHYLBUTANE	0.3	3.0	Trace	0.4	0.2	0.4
3,4-DIMETHYL-1-PENTENE						0.3
1-METHYLCYCLOPENTENE	0.7	2.9		2.6		3.1
BENZENE	6.1	60.5	14.2	103.6	6.0	62.0
3-METHYL-1-HEXENE						
3,3-DIMETHYLPENTANE	0.6	1.4	0.5	1.2	0.2	0.8
CYCLOHEXANE	0.4	2.8	0.8	5.3	1.9	10.7
2-METHYLHEXANE						
2,3-DIMETHYLPENTANE	6.4	20.9	6.0	22.9	10.2	32.8
1,1-DIMETHYLCYCLOPENTANE						1.3
TERT-AMYL METHYL ETHER						
CYCLOHEXENE	Trace	1.0		1.2	Trace	1.8
3-METHYLHEXANE	4.6	15.4	4.4	15.8	5.0	16.7
CIS-1,3-DIMETHYLCYCLOPENTANE	0.3	2.1	0.3	2.0	0.6	3.3
3-ETHYLPENTANE	0.3	2.6			0.4	1.2
TRANS-1,2-DIMETHYLCYCLOPENTANE						
TRANS-1,3-DIMETHYLCYCLOPENTANE	0.4	2.1	0.4	2.0	0.8	3.2
1-HEPTENE						
2,2,4-TRIMETHYLPENTANE	10.4	26.2	13.9	41.0	15.5	43.2
2-METHYL-1-HEXENE						
TRANS-3-HEPTENE	0.1	1.7		1.1		0.2
HEPTANE	2.9	10.1	4.6	16.2	5.3	14.9
CIS-3-HEPTENE						
UNIDENTIFIED C7	0.2	1.3	0.2	2.9	0.1	1.9
2-METHYL-2-HEXENE		1.3				
3-METHYL-TRANS-3-HEXENE						
TRANS-2-HEPTENE	0.1	1.1	Trace	0.7	Trace	0.7
3-ETHYL-CIS-2-PENTENE						
2,4,4-TRIMETHYL-1-PENTENE	0.2	1.4	0.1	0.6	0.1	0.8
2,3-DIMETHYL-2-PENTENE						
CIS-2-HEPTENE	0.1	1.1	0.1	0.8	0.1	1.0
METHYLCYCLOHEXANE	0.9	4.5	1.4	7.6	2.1	11.1
CIS-1,2-DIMETHYLCYCLOPENTANE						
2,2-DIMETHYLHEXANE						
1,1,3-TRIMETHYLCYCLOPENTANE	0.2	0.8	0.3	1.1	0.4	1.4
2,4,4-TRIMETHYL-2-PENTENE						
2,2,3-TRIMETHYLPENTANE	2.0	6.0	1.3	6.1	2.6	9.9
2,5-DIMETHYLHEXANE						
ETHYLCYCLOPENTANE						
2,4-DIMETHYLHEXANE	1.2	6.4	1.5	8.3	1.7	8.3
1-TRANS-2-CIS-4-TRIMETHYLCYCLOPENTANE	0.2	1.4	0.5	1.1	0.3	1.9
3,3-DIMETHYLHEXANE						
1-TRANS-2-CIS-3-TRIMETHYLCYCLOPENTANE	0.1	0.3	0.1	0.4	0.1	0.7

HYDROCARBON SPECIATION DATA
FTP COMPOSITE
FORD F-150

	FTP Composite, mg/mi					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	FT-4614-S	FT-4614-M	FT-4637-S	FT-4637-M	FT-4640-S	FT-4640-M
COMPOUND	7/17/2002	7/19/2002	7/24/2002	7/23/2002	7/26/2002	7/29/2002
2,3,4-TRIMETHYLPENTANE	3.8	12.2	3.8	11.3	5.7	18.5
2,3,3-TRIMETHYLPENTANE	3.6	21.6	3.0	13.4	6.6	31.8
TOLUENE	6.5	87.5	27.1	232.4	8.0	102.1
2,3-DIMETHYLHEXANE	1.8	16.0	3.2	20.1	3.0	20.0
1,1,2-TRIMETHYLCYCLOPENTANE						
2-METHYLHEPTANE		6.7	1.8	7.3		
3,4-DIMETHYLHEXANE, NOTE B		0.1	0.1	1.6		1.1
4-METHYLHEPTANE	2.2	1.1	0.2	1.5	2.8	9.8
3-METHYLHEPTANE	2.2	7.7	1.8	7.8	2.3	8.8
1-CIS,2-TRANS,3-TRIMETHYLCYCLOPENTANE			0.1			
CIS-1,3-DIMETHYLCYCLOHEXANE						
TRANS-1,4-DIMETHYLCYCLOHEXANE						
3-ETHYLHEXANE	Trace	1.8	0.2	1.7	0.4	2.0
2,2,5-TRIMETHYLHEXANE	1.0	3.8	1.2	5.4	2.7	10.6
TRANS-1-METHYL-3-ETHYLCYCLOPENTANE						
CIS-1-METHYL-3-ETHYLCYCLOPENTANE	0.2	1.9	0.1	2.5	0.2	2.0
1,1-DIMETHYLCYCLOHEXANE						
TRANS-1-METHYL-2-ETHYLCYCLOPENTANE						
1-METHYL-1-ETHYL-CYCLOPENTANE						
2,4,4-TRIMETHYLHEXANE	0.1	0.8	Trace	0.8	Trace	0.6
2,2,4-TRIMETHYLHEXANE						
TRANS-1,2-DIMETHYLCYCLOHEXANE	Trace	1.0	0.1	0.8	0.1	0.7
1-OCTENE						
TRANS-4-OCTENE						
OCTANE	1.1	4.4	1.6	6.5	1.7	6.7
UNIDENTIFIED C8	0.2	3.6	0.3	1.2	4.9	1.1
TRANS-2-OCTENE	0.1	1.2	0.1	0.7	Trace	0.5
TRANS-1,3-DIMETHYLCYCLOHEXANE, NOTE C						
CIS-2-OCTENE	0.1	0.7	Trace	0.3		0.3
ISOPROPYLCYCLOPENTANE						
2,2-DIMETHYLHEPTANE						
2,3,5-TRIMETHYLHEXANE	0.1	0.7	0.1	1.0	0.3	1.9
CIS-1-METHYL-2-ETHYLCYCLOPENTANE	0.1	0.7	0.1	0.6	Trace	0.7
2,4-DIMETHYLHEPTANE	0.1	0.3	0.2	0.9	2.6	1.0
4,4-DIMETHYLHEPTANE	Trace	1.2		0.2	0.1	0.2
CIS-1,2-DIMETHYLCYCLOHEXANE						
ETHYLCYCLOHEXANE						
2,6-DIMETHYLHEPTANE, NOTE D	0.4	0.6	0.2	1.6	0.5	2.2
1,1,3-TRIMETHYLCYCLOHEXANE						
2,5-DIMETHYLHEPTANE, NOTE E	0.4	1.6	0.6	2.1	0.6	2.7
3,3-DIMETHYLHEPTANE						
3,5-DIMETHYLHEPTANE, NOTE E						
ETHYLBENZENE	2.6	22.1	5.2	37.8	1.9	17.8
2,3,4-TRIMETHYLHEXANE						
2,3-DIMETHYLHEPTANE						
m-& p-XYLENE	6.9	61.5	18.0	120.0	5.7	57.6
4-METHYLOCTANE						
3,4-DIMETHYLHEPTANE						
4-ETHYLHEPTANE						
2-METHYLOCTANE	0.8	5.4	1.2	6.8	0.8	6.4
3-METHYLOCTANE	0.6	3.0	0.7	3.3	0.6	4.9
STYRENE	0.4	11.8	1.4	20.6	0.3	12.6

HYDROCARBON SPECIATION DATA
FTP COMPOSITE
FORD F-150

	FTP Composite, mg/mi					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	FT-4614-S	FT-4614-M	FT-4637-S	FT-4637-M	FT-4640-S	FT-4640-M
COMPOUND	7/17/2002	7/19/2002	7/24/2002	7/23/2002	7/26/2002	7/29/2002
o-XYLENE	2.9	27.8	7.6	48.6	2.4	27.1
1-NONENE	0.1	2.3	0.2	3.1	0.3	3.8
TRANS-3-NONENE						
CIS-3-NONENE						
NONANE	0.5	3.1	1.2	3.6	0.8	4.7
TRANS-2-NONENE						
ISOPROPYLBENZENE (CUMENE)	0.9	1.4	0.2	3.4	0.1	1.8
2,2-DIMETHYLOCTANE	0.1	0.4	0.1	Trace	0.2	
2,4-DIMETHYLOCTANE	Trace	0.3	0.1	0.3	Trace	0.3
n-PROPYLBENZENE	0.5	6.4	1.5	13.4	0.4	6.1
1-METHYL-3-ETHYLBENZENE	2.7	32.2	6.8	12.6	1.9	26.0
1-METHYL-4-ETHYLBENZENE	1.0	13.6	3.1	50.5	0.6	10.3
1,3,5-TRIMETHYLBENZENE	1.0	11.3	3.1	24.6	0.7	10.9
1-METHYL-2-ETHYLBENZENE	1.0	12.2	2.9	22.0	0.7	7.4
1,2,4-TRIMETHYLBENZENE	3.0	46.6	11.2	96.2	2.4	44.3
TERT-BUTYLBENZENE						
1-DECENE						
DECANE, NOTE F	0.1	1.1	0.3	2.3	0.1	1.1
ISOBUTYLBENZENE, NOTE F	0.1	1.0	0.3	2.1	0.1	1.0
1,3,-DIMETHYL-5-ETHYLBENZENE						
METHYLPROPYLBENZENE (sec butylbenzene)						
1-METHYL-3-ISOPROPYLBENZENE				1.9		
1,2,3-TRIMETHYLBENZENE	0.6	10.8	2.7	23.2	0.5	9.1
1-METHYL-4-ISOPROPYLBENZENE						0.4
INDAN						
1-METHYL-2-ISOPROPYLBENZENE						1.8
1,3-DIETHYLBENZENE						
1,4-DIETHYLBENZENE						Trace
1-METHYL-3-N-PROPYLBENZENE	0.1	5.5	1.0	7.7	0.3	7.4
1-METHYL-4-N-PROPYLBENZENE, NOTE G	0.5	13.0	1.9	21.8	0.3	11.7
1,2 DIETHYLBENZENE					0.1	0.2
1-METHYL-2-N-PROPYLBENZENE	0.2	2.0	0.1	2.9	0.2	2.1
1,4-DIMETHYL-2-ETHYLBENZENE						6.1
1,3-DIMETHYL-4-ETHYLBENZENE	0.4	16.3	1.1	18.9	0.3	5.3
1,2-DIMETHYL-4-ETHYLBENZENE	0.1	10.9	1.4	9.5	0.4	1.8
1,3-DIMETHYL-2-ETHYLBENZENE						3.9
UNDECANE	Trace	2.3	0.5	6.3	0.1	2.3
1,2-DIMETHYL-3-ETHYLBENZENE						0.7
1,2,4,5-TETRAMETHYLBENZENE	Trace	3.7	0.6	9.9	0.1	4.0
2-METHYLBUTYLBENZENE (sec AMYLBENZENE)						
3,4 DIMETHYLCUMENE						
1,2,3,5-TETRAMETHYLBENZENE						
TERT-1-BUT-2-METHYLBENZENE						5.7
1,2,3,4-TETRAMETHYLBENZENE						
N-PENT-BENZENE						1.9
TERT-1-BUT-3,5-DIMETHYLBENZENE	0.1	0.8	0.2	2.6		17.1
TERT-1-BUTYL-4-ETHYLBENZENE						
NAPHTHALENE						0.3
DODECANE	0.1	0.3	0.8	5.8		1.6
1,3,5-TRIETHYLBENZENE						
1,2,4-TRIETHYLBENZENE						
HEXYLBENZENE						

HYDROCARBON SPECIATION DATA
FTP COMPOSITE
FORD F-150

	FTP Composite, mg/mi					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	FT-4614-S	FT-4614-M	FT-4637-S	FT-4637-M	FT-4640-S	FT-4640-M
COMPOUND	7/17/2002	7/19/2002	7/24/2002	7/23/2002	7/26/2002	7/29/2002
UNIDENTIFIED C9-C12+	3.0	81.0	18.8	238.9	4.6	105.3
FORMALDEHYDE	9.4	94.0	14.6	75.5	12.7	85.2
ACETALDEHYDE	4.6	22.6	4.3	21.1	5.7	36.2
ACROLEIN	1.2	11.0	0.9	13.4	0.3	11.6
ACETONE	5.6	12.5	4.3	7.4	4.1	7.3
PROPIONALDEHYDE	0.5	8.9	0.5	4.7	0.5	6.5
CROTONALDEHYDE	2.0	9.9	0.8	6.4	1.1	7.6
ISOBUTYRALDEHYDE, NOTE H	0.8	3.0	0.6	2.2	0.4	2.1
METHYL ETHYL KETONE, NOTE H	0.8	3.0	0.6	2.2	0.4	2.1
BENZALDEHYDE	0.1	10.5	0.7	19.5	0.3	10.9
ISOVALERALDEHYDE	0.3	2.1	0.1	1.7	0.1	1.4
VALERALDEHYDE	0.2	1.1	0.3	1.6	0.2	0.3
O-TOLUALDEHYDE	0.3	4.0		5.6		3.2
M/P-TOLUALDEHYDE	0.3	11.8	0.8	18.9	0.3	11.0
HEXANALDEHYDE		0.3				
DIMETHYLBENZALDEHYDE	0.4	4.0	0.2	6.9	0.4	3.9

A - 2,2-Dimethylpentane and methylcyclopentane co-elute. GC peak area split equally between the two compounds.
B - 3-Methyl-3-ethyl-pentane co-elutes with reported compound. Not reported separately.
C - Cis-1,4-Dimethylcyclohexane co-elutes with reported compound. Not reported separately.
D - Propylcyclopentane co-elutes with reported compound. Not reported separately.
E - 2,5-Dimethylheptane and 3,5-dimethylheptane co-elute. GC peak area split equally between the two compounds.
F - Decane and isobutylbenzene co-elute. GC peak area split equally between the two compounds.
G - n-Butylbenzene co-elutes with reported compound. Not reported separately.
H - Isobutyraldehyde and methyl ethyl ketone co-elute. LC peak area split equally between the two compounds.

HYDROCARBON SPECIATION DATA
SHED TEST
FORD F-150

	SHED results, mg					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	FT-4614-S	FT-4614-M	FT-4637-S	FT-4637-M	FT-4640-S	FT-4640-M
COMPOUND	7/17/2002	7/19/2002	7/24/2002	7/23/2002	7/26/2002	7/29/2002
METHANE						
ETHANE		7.2		Trace		0.6
ETHYLENE			7.3	2.8		
PROPANE		0.4		6.0		4.3
PROPYLENE			1.2	0.6		
ACETYLENE						
PROPADIENE						
BUTANE	2.0	123.7	3.1	94.8	2.3	70.5
TRANS-2-BUTENE						3.8
1-BUTENE				2.8		
2-METHYLPROPENE (ISOBUTYLENE)		3.4		2.1		6.0
2,2-DIMETHYLPROPANE (NEOPENTANE)		2.8		3.0	0.7	
PROPYNE						
1,3-BUTADIENE						
2-METHYLPROPANE (ISOBUTANE)	0.6	22.7		25.6	1.1	16.2
1-BUTYNE						
METHANOL						
CIS-2-BUTENE						
3-METHYL-1-BUTENE						
ETHANOL					10.6	193.4
2-METHYLBUTANE (ISOPENTANE)		647.3		687.0	5.7	532.7
2-BUTYNE						
1-PENTENE	1.8	27.2		25.3		23.4
2-METHYL-1-BUTENE	1.0	38.4	8.6	38.4		36.9
PENTANE	3.2	105.9	0.7	118.6	0.8	87.0
UNIDENTIFIED C5 OLEFINS						
2-METHYL-1,3-BUTADIENE		1.4	2.7	1.1	2.5	1.1
TRANS-2-PENTENE	1.2	43.6	0.9	39.5		37.6
3,3-DIMETHYL-1-BUTENE		0.4		0.3	1.1	0.4
CIS-2-PENTENE	0.5	24.0	0.5	21.9	0.5	21.1
2-METHYL-2-BUTENE	2.4	59.0	2.4	56.4	2.2	54.2
TERT-BUTANOL						
CYCLOPENTADIENE		0.8		0.5		0.5
2,2-DIMETHYLBUTANE	0.5	21.3	0.4	23.3	0.5	23.1
CYCLOPENTENE		7.6	0.3	7.5	0.4	6.7
4-METHYL-1-PENTENE		3.5		2.6		3.1
3-METHYL-1-PENTENE						
CYCLOPENTANE	0.6	12.2	0.6	13.7	0.5	12.1
2,3-DIMETHYLBUTANE	1.7	47.4	1.3	48.3	1.6	51.3
MTBE		97.0				
4-METHYL-CIS-2-PENTENE						
2-METHYLPENTANE	6.7	77.1	6.6	86.6	6.9	81.1
4-METHYL-TRANS-2-PENTENE						
3-METHYLPENTANE	3.4	57.7	2.8	52.5	2.9	50.4
2-METHYL-1-PENTENE	0.2	2.9	0.3	2.8	0.4	2.5
1-HEXENE	0.2	2.9	0.3	2.8	0.4	2.5
HEXANE	3.6	40.1	2.9	35.7	3.4	33.1
UNIDENTIFIED C6	1.9	4.6		12.4		11.3
TRANS-3-HEXENE						

HYDROCARBON SPECIATION DATA
SHED TEST
FORD F-150

	SHED results, mg					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	FT-4614-S	FT-4614-M	FT-4637-S	FT-4637-M	FT-4640-S	FT-4640-M
COMPOUND	7/17/2002	7/19/2002	7/24/2002	7/23/2002	7/26/2002	7/29/2002
CIS-3-HEXENE		2.5		2.1		2.1
DI-ISOPROPYL ETHER						
TRANS-2-HEXENE	0.4	4.0		3.2		3.3
3-METHYL-TRANS-2-PENTENE		5.9	0.3	6.1		5.5
2-METHYL-2-PENTENE	0.3	3.7	0.4	3.4	0.4	3.1
3-METHYLCYCLOPENTENE						
CIS-2-HEXENE		2.5	0.3	5.6	0.3	2.5
ETBE						
3-METHYL-CIS-2-PENTENE		4.6	0.6	4.2	0.5	4.0
2,2-DIMETHYLPENTANE, NOTE A	1.9	16.8	1.1	17.5	1.3	18.7
METHYLCYCLOPENTANE, NOTE A	1.9	16.4	1.1	17.1	1.2	18.4
2,4-DIMETHYLPENTANE	1.5	13.5	1.2	15.2	1.5	17.1
2,2,3-TRIMETHYLBUTANE		1.1		0.9		1.0
3,4-DIMETHYL-1-PENTENE						
1-METHYLCYCLOPENTENE	0.9	13.9	2.1	9.1	0.9	8.5
BENZENE	3.8	23.1	5.6	25.2	5.6	21.4
3-METHYL-1-HEXENE						
3,3-DIMETHYLPENTANE		0.4	0.8	1.9	1.1	
CYCLOHEXANE		16.9		16.3		21.3
2-METHYLHEXANE						
2,3-DIMETHYLPENTANE	5.1	32.2	4.1	34.7	4.5	38.0
1,1-DIMETHYLCYCLOPENTANE						
TERT-AMYL METHYL ETHER						
CYCLOHEXENE		0.4		0.5		0.3
3-METHYLHEXANE	3.0	17.3	2.7	18.5	3.0	18.1
CIS-1,3-DIMETHYLCYCLOPENTANE	0.6	3.0	0.5	3.3	0.5	4.1
3-ETHYLPENTANE	0.6		0.5		0.6	6.6
TRANS-1,2-DIMETHYLCYCLOPENTANE						
TRANS-1,3-DIMETHYLCYCLOPENTANE	0.4	2.4	0.3	3.1	0.4	3.2
1-HEPTENE						
2,2,4-TRIMETHYLPENTANE	4.2	34.8	3.6	38.2	4.2	31.8
2-METHYL-1-HEXENE						
TRANS-3-HEPTENE		1.2		1.1		
HEPTANE	4.2	15.5	4.0	17.8	4.6	17.2
CIS-3-HEPTENE						
UNIDENTIFIED C7		1.4		3.3		0.5
2-METHYL-2-HEXENE						
3-METHYL-TRANS-3-HEXENE						
TRANS-2-HEPTENE		1.4		0.7		0.7
3-ETHYL-CIS-2-PENTENE						
2,4,4-TRIMETHYL-1-PENTENE	0.3	1.9	0.3	1.0		1.2
2,3-DIMETHYL-2-PENTENE						
CIS-2-HEPTENE		1.1		0.5		0.6
METHYLCYCLOHEXANE	1.7	6.0	1.5	7.4	1.7	9.5
CIS-1,2-DIMETHYLCYCLOPENTANE						
2,2-DIMETHYLHEXANE						
1,1,3-TRIMETHYLCYCLOPENTANE		1.0		1.0		1.2
2,4,4-TRIMETHYL-2-PENTENE					0.3	
2,2,3-TRIMETHYLPENTANE	1.3	6.9	0.4	6.3		9.0

HYDROCARBON SPECIATION DATA
SHED TEST
FORD F-150

	SHED results, mg					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	FT-4614-S	FT-4614-M	FT-4637-S	FT-4637-M	FT-4640-S	FT-4640-M
COMPOUND	7/17/2002	7/19/2002	7/24/2002	7/23/2002	7/26/2002	7/29/2002
2,5-DIMETHYLHEXANE						
ETHYLCYCLOPENTANE						
2,4-DIMETHYLHEXANE	0.8	5.9	0.3	1.4	0.6	3.5
1-TRANS-2-CIS-4-TRIMETHYLCYCLOPENTANE	0.3	1.5	0.3	1.3		1.6
3,3-DIMETHYLHEXANE						
1-TRANS-2-CIS-3-TRIMETHYLCYCLOPENTANE		0.6		0.5		0.6
2,3,4-TRIMETHYLPENTANE	2.7	13.8	2.6	10.8	2.9	13.9
2,3,3-TRIMETHYLPENTANE	2.1	17.5	1.9	10.6	2.4	19.3
TOLUENE	10.2	31.4	14.8	44.4	15.7	32.3
2,3-DIMETHYLHEXANE		10.2		8.3		9.5
1,1,2-TRIMETHYLCYCLOPENTANE						
2-METHYLHEPTANE			1.7			
3,4-DIMETHYLHEXANE, NOTE B						
4-METHYLHEPTANE	1.5	7.9		6.6	1.9	8.0
3-METHYLHEPTANE	1.7	8.4	1.4	4.7	1.9	8.0
1-CIS,2-TRANS,3-TRIMETHYLCYCLOPENTANE						
CIS-1,3-DIMETHYLCYCLOHEXANE						
TRANS-1,4-DIMETHYLCYCLOHEXANE						
3-ETHYLHEXANE						
2,2,5-TRIMETHYLHEXANE	0.8	3.7	0.6	3.8	1.1	5.3
TRANS-1-METHYL-3-ETHYLCYCLOPENTANE						
CIS-1-METHYL-3-ETHYLCYCLOPENTANE		0.7		0.5		0.6
1,1-DIMETHYLCYCLOHEXANE						
TRANS-1-METHYL-2-ETHYLCYCLOPENTANE						
1-METHYL-1-ETHYL-CYCLOPENTANE						
2,4,4-TRIMETHYLHEXANE				0.4		
2,2,4-TRIMETHYLHEXANE						
TRANS-1,2-DIMETHYLCYCLOHEXANE		0.3				0.4
1-OCTENE						
TRANS-4-OCTENE						
OCTANE	1.3	4.1	1.5	4.0	1.5	4.8
UNIDENTIFIED C8	0.3			1.1		1.7
TRANS-2-OCTENE		0.4				
TRANS-1,3-DIMETHYLCYCLOHEXANE, NOTE C						
CIS-2-OCTENE						
ISOPROPYLCYCLOPENTANE						
2,2-DIMETHYLHEPTANE						
2,3,5-TRIMETHYLHEXANE		0.3		0.3	0.3	0.7
CIS-1-METHYL-2-ETHYLCYCLOPENTANE				0.3		
2,4-DIMETHYLHEPTANE				0.6		0.7
4,4-DIMETHYLHEPTANE						
CIS-1,2-DIMETHYLCYCLOHEXANE						
ETHYLCYCLOHEXANE						
2,6-DIMETHYLHEPTANE, NOTE D	0.3	1.1	0.5	1.0	0.5	1.5
1,1,3-TRIMETHYLCYCLOHEXANE						
2,5-DIMETHYLHEPTANE, NOTE E	0.3	0.9	0.4	1.0	0.5	1.5
3,3-DIMETHYLHEPTANE						
3,5-DIMETHYLHEPTANE, NOTE E						
ETHYLBENZENE	2.9	6.0	4.4	7.3	3.8	6.4

HYDROCARBON SPECIATION DATA
SHED TEST
FORD F-150

	SHED results, mg					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	FT-4614-S	FT-4614-M	FT-4637-S	FT-4637-M	FT-4640-S	FT-4640-M
COMPOUND	7/17/2002	7/19/2002	7/24/2002	7/23/2002	7/26/2002	7/29/2002
2,3,4-TRIMETHYLHEXANE						
2,3-DIMETHYLHEPTANE						
m-& p-XYLENE	7.7	14.3	13.8	23.1	10.9	18.4
4-METHYLOCTANE						
3,4-DIMETHYLHEPTANE						
4-ETHYLHEPTANE						
2-METHYLOCTANE	0.4	1.4	0.7	2.3	0.6	1.6
3-METHYLOCTANE	0.3	1.0		1.1		1.3
STYRENE						
o-XYLENE	0.5	5.1	1.6	8.0	10.2	8.7
1-NONENE			7.0	1.3		
TRANS-3-NONENE						
CIS-3-NONENE						
NONANE		2.5	0.6	0.9	0.6	1.1
TRANS-2-NONENE						
ISOPROPYLBENZENE (CUMENE)			0.5	1.8		0.5
2,2-DIMETHYLOCTANE	0.9					
2,4-DIMETHYLOCTANE						
n-PROPYLBENZENE			1.3	1.3	0.5	0.4
1-METHYL-3-ETHYLBENZENE			3.5	3.4	0.9	
1-METHYL-4-ETHYLBENZENE			0.5	0.9		0.3
1,3,5-TRIMETHYLBENZENE			2.5	1.8		0.3
1-METHYL-2-ETHYLBENZENE			1.8		0.4	0.6
1,2,4-TRIMETHYLBENZENE						
TERT-BUTYLBENZENE						
1-DECENE						
DECANE, NOTE F	1.4	2.3				
ISOBUTYLBENZENE, NOTE F	1.3	2.1				
1,3,-DIMETHYL-5-ETHYLBENZENE						
METHYLPROPYLBENZENE (sec butylbenzene)						
1-METHYL-3-ISOPROPYLBENZENE						
1,2,3-TRIMETHYLBENZENE			2.2	0.7		
1-METHYL-4-ISOPROPYLBENZENE					1.0	1.1
INDAN						
1-METHYL-2-ISOPROPYLBENZENE						0.3
1,3-DIETHYLBENZENE						
1,4-DIETHYLBENZENE						
1-METHYL-3-N-PROPYLBENZENE			0.3		0.3	
1-METHYL-4-N-PROPYLBENZENE, NOTE G			1.8			
1,2 DIETHYLBENZENE					1.8	
1-METHYL-2-N-PROPYLBENZENE			0.5			
1,4-DIMETHYL-2-ETHYLBENZENE						0.7
1,3-DIMETHYL-4-ETHYLBENZENE	0.4	1.1	1.5	0.6		
1,2-DIMETHYL-4-ETHYLBENZENE						
1,3-DIMETHYL-2-ETHYLBENZENE						
UNDECANE			0.4			
1,2-DIMETHYL-3-ETHYLBENZENE						
1,2,4,5-TETRAMETHYLBENZENE						
2-METHYLBUTYLBENZENE (sec AMYLBENZENE)						

HYDROCARBON SPECIATION DATA
SHED TEST
FORD F-150

	SHED results, mg					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	FT-4614-S	FT-4614-M	FT-4637-S	FT-4637-M	FT-4640-S	FT-4640-M
COMPOUND	7/17/2002	7/19/2002	7/24/2002	7/23/2002	7/26/2002	7/29/2002
3,4 DIMETHYLCUMENE						
1,2,3,5-TETRAMETHYLBENZENE						
TERT-1-BUT-2-METHYLBENZENE						
1,2,3,4-TETRAMETHYLBENZENE						
N-PENT-BENZENE		0.3				
TERT-1-BUT-3,5-DIMETHYLBENZENE				0.1		
TERT-1-BUTYL-4-ETHYLBENZENE						1.3
NAPHTHALENE						
DODECANE			0.8			
1,3,5-TRIETHYLBENZENE						
1,2,4-TRIETHYLBENZENE						
HEXYLBENZENE						
UNIDENTIFIED C9-C12+	7.5	3.3	15.8	16.7	4.5	8.6

A - 2,2-Dimethylpentane and methylcyclopentane co-elute. GC peak area split equally between the two compounds.
B - 3-Methyl-3-ethyl-pentane co-elutes with reported compound. Not reported separately.
C - Cis-1,4-Dimethylcyclohexane co-elutes with reported compound. Not reported separately.
D - Propylcyclopentane co-elutes with reported compound. Not reported separately.
E - 2,5-Dimethylheptane and 3,5-dimethylheptane co-elute. GC peak area split equally between the two compounds.
F - Decane and isobutylbenzene co-elute. GC peak area split equally between the two compounds.
G - n-Butylbenzene co-elutes with reported compound. Not reported separately.

APPENDIX B

HYDROCARBON SPECIATION DATA FOR TOYOTA CAMRY

TABLE OF CONTENTS FOR APPENDIX B

FTP Composite Results, Winter 2005, pp. B1-B5
SHED Test Results, Winter 2005, pp. B6-B10
FTP Composite Results, Summer 2002, pp. B11-B15
SHED Test Results, Summer 2002, pp. B16-20

A blank space in the tables indicates that the compound was not detected during analysis. A "Trace" value indicates that the compound was detected, but computations of mass or mass rate resulted in a value of less than 0.05. An "*" in the table indicates a malfunction of the analytical equipment during sample analysis and that no data are available.

HYDROCARBON SPECIATION DATA
FTP COMPOSITE
TOYOTA CAMRY

	FTP Composite, mg/mi					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	C-HOU-N	C-HOU-MF	C-ATL-N	C-ATL-MF	C-CHI-N	C-CHI-MF
COMPOUND	3/31/2005	4/1/2005	4/5/2005	4/6/2005	4/12/2005	4/13/2005
METHANE	67.0	497.2	37.8	441.0	104.6	422.3
ETHANE	6.0	29.1	7.6	31.1	8.5	29.8
ETHYLENE	19.7	317.6	27.6	323.9	29.0	309.1
PROPANE	0.4	2.4	1.0	2.6	1.2	2.6
PROPYLENE	11.0	127.8	16.5	148.6	15.8	123.1
ACETYLENE	8.5	772.5	10.7	736.3	9.9	621.4
PROPADIENE	0.6	11.5	0.8	10.7		8.8
BUTANE	5.5	58.8	10.3	82.0	16.5	95.5
TRANS-2-BUTENE	0.9	9.2	1.3	10.3	1.4	9.2
1-BUTENE	2.2	21.7	2.9	22.6	3.1	20.8
2-METHYLPROPENE (ISOBUTYLENE)	8.7	80.1	6.1	49.9	5.1	38.2
2,2-DIMETHYLPROPANE (NEOPENTANE)	9.4	131.9	11.6	115.4	17.9	128.1
PROPYNE	0.1	1.0	0.1			1.1
1,3-BUTADIENE	2.7	32.0	3.7	34.3	4.3	36.7
2-METHYLPROPANE (ISOBUTANE)	0.8	9.4	1.0	7.0	1.1	7.1
1-BUTYNE						
METHANOL						
CIS-2-BUTENE	0.7	7.4	0.9	8.1	1.0	6.9
3-METHYL-1-BUTENE						
ETHANOL					15.0	165.2
2-METHYLBUTANE (ISOPENTANE)	0.6	14.5	0.7	1.2	0.9	11.9
2-BUTYNE						
1-PENTENE	0.7	10.7	0.7	6.3	1.4	8.0
2-METHYL-1-BUTENE	1.3	18.5	0.8	11.3	1.6	15.6
PENTANE	4.0	65.4	6.6	70.1	7.4	51.7
UNIDENTIFIED C5 OLEFINS	0.8	2.5	Trace	0.7		0.6
2-METHYL-1,3-BUTADIENE	0.5	9.5	0.8	8.6	1.3	9.0
TRANS-2-PENTENE	0.8	14.7	0.7	8.7	1.7	14.8
3,3-DIMETHYL-1-BUTENE	0.1	0.5	Trace	0.4	Trace	0.4
CIS-2-PENTENE	0.4	7.9	0.4	5.0	0.9	6.9
2-METHYL-2-BUTENE	0.5	21.2	0.8	11.6	2.5	22.9
TERT-BUTANOL						
CYCLOPENTADIENE		3.4	0.1	1.9	0.1	1.6
2,2-DIMETHYLBUTANE	1.0	13.8	1.0	9.5	0.8	5.1
CYCLOPENTENE	0.3	4.5	0.3	3.1	0.6	5.3
4-METHYL-1-PENTENE	0.3	3.2	0.3	2.0	0.5	3.0
3-METHYL-1-PENTENE						
CYCLOPENTANE	0.4	8.1	0.4	5.4	0.6	4.5
2,3-DIMETHYLBUTANE	1.5	19.4	1.6	15.9	1.8	12.1
MTBE	3.8	149.5		1.9	0.2	2.5
4-METHYL-CIS-2-PENTENE						
2-METHYLPENTANE	7.2	98.2	5.5	53.7	6.5	44.5
4-METHYL-TRANS-2-PENTENE	1.4	1.7	0.1	1.6	0.2	3.1
3-METHYLPENTANE	4.8	66.8	3.7	34.7	4.4	28.8
2-METHYL-1-PENTENE	0.3	4.5	0.3	3.1	0.6	4.0
1-HEXENE	0.3	4.5	0.3	3.1	0.6	4.0
HEXANE	4.7	68.9	3.5	35.6	3.6	24.7
UNIDENTIFIED C6	0.9	9.5	0.6	5.5	0.7	5.4
TRANS-3-HEXENE						
CIS-3-HEXENE	0.2	3.7	0.1	1.8	0.4	3.8
DI-ISOPROPYL ETHER					0.1	
TRANS-2-HEXENE	0.3	5.9	0.2	3.0	0.7	5.7

HYDROCARBON SPECIATION DATA
FTP COMPOSITE
TOYOTA CAMRY

	FTP Composite, mg/mi					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	C-HOU-N	C-HOU-MF	C-ATL-N	C-ATL-MF	C-CHI-N	C-CHI-MF
COMPOUND	3/31/2005	4/1/2005	4/5/2005	4/6/2005	4/12/2005	4/13/2005
3-METHYL-TRANS-2-PENTENE	0.3	7.1	0.3	4.4	1.0	9.3
2-METHYL-2-PENTENE	0.2	5.8	0.2	2.7	0.6	5.8
3-METHYLCYCLOPENTENE			0.1			Trace
CIS-2-HEXENE	0.1	1.7	Trace	1.6	0.3	3.1
ETBE						
3-METHYL-CIS-2-PENTENE	0.6	5.0	0.7	2.9	0.7	6.7
2,2-DIMETHYLPENTANE, NOTE A	1.2	20.6	0.9	11.9	1.9	13.6
METHYLCYCLOPENTANE, NOTE A	1.2	20.2	0.9	11.7	1.9	13.4
2,4-DIMETHYLPENTANE	0.8	10.8	1.3	11.9	1.0	6.3
2,2,3-TRIMETHYLBUTANE	0.1	1.5	0.1	0.9	Trace	0.4
3,4-DIMETHYL-1-PENTENE	Trace	0.4	Trace	0.4	0.1	0.5
1-METHYLCYCLOPENTENE	0.3	6.4	0.5	4.5	0.6	4.8
BENZENE	5.0	78.4	9.9	116.0	8.3	84.6
3-METHYL-1-HEXENE	0.1	0.6		1.3		1.2
3,3-DIMETHYLPENTANE	0.6	5.9	0.4	3.3	0.4	0.4
CYCLOHEXANE	0.2	2.8	0.3	3.7	0.6	6.3
2-METHYLHEXANE						
2,3-DIMETHYLPENTANE	5.0	69.0	5.5	51.6	3.8	26.2
1,1-DIMETHYLCYCLOPENTANE	0.1		0.1	0.8	0.1	1.1
TERT-AMYL METHYL ETHER						
CYCLOHEXENE	0.6	20.4	0.1	1.2	0.3	2.2
3-METHYLHEXANE	4.4	57.2	3.8	36.1	2.4	16.2
CIS-1,3-DIMETHYLCYCLOPENTANE	0.5	7.0	0.5	4.9	1.0	7.7
3-ETHYLPENTANE	0.8	11.5	0.8	7.8	1.2	8.8
TRANS-1,2-DIMETHYLCYCLOPENTANE						
TRANS-1,3-DIMETHYLCYCLOPENTANE	0.4	6.1	0.5	4.7	0.9	7.1
1-HEPTENE						
2,2,4-TRIMETHYLPENTANE	1.2	14.3	8.2	72.9	2.9	19.9
2-METHYL-1-HEXENE						
TRANS-3-HEPTENE	0.2	2.1	0.1	1.8	0.4	4.1
HEPTANE	3.1	41.0	3.5	34.0	2.6	17.4
CIS-3-HEPTENE						
UNIDENTIFIED C7	0.3	6.6	0.1	2.3	0.6	5.0
2-METHYL-2-HEXENE		1.9		0.6		3.8
3-METHYL-TRANS-3-HEXENE						
TRANS-2-HEPTENE	0.1	2.6	0.1	1.7	0.2	2.5
3-ETHYL-CIS-2-PENTENE						
2,4,4-TRIMETHYL-1-PENTENE	0.1	3.0	0.1	1.6	0.3	3.2
2,3-DIMETHYL-2-PENTENE						
CIS-2-HEPTENE	0.1	1.6	0.1	1.2	0.2	1.7
METHYLCYCLOHEXANE	1.0	13.4	1.5	14.1	2.9	20.7
CIS-1,2-DIMETHYLCYCLOPENTANE						
2,2-DIMETHYLHEXANE						
1,1,3-TRIMETHYLCYCLOPENTANE	0.1	2.4	0.3	2.6	0.3	1.9
2,4,4-TRIMETHYL-2-PENTENE	0.1	0.1	0.1	0.1		0.1
2,2,3-TRIMETHYLPENTANE	0.6	7.5	1.2	13.5	0.9	7.2
2,5-DIMETHYLHEXANE						
ETHYLCYCLOPENTANE						
2,4-DIMETHYLHEXANE	0.7	9.0	1.4	15.6	1.0	5.9
1-TRANS-2-CIS-4-TRIMETHYLCYCLOPENTANE	0.2	4.2	0.2	3.2	0.4	2.7
3,3-DIMETHYLHEXANE						
1-TRANS-2-CIS-3-TRIMETHYLCYCLOPENTANE	0.1	1.6	0.1	1.3	0.2	2.4

HYDROCARBON SPECIATION DATA
FTP COMPOSITE
TOYOTA CAMRY

	FTP Composite, mg/mi					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	C-HOU-N	C-HOU-MF	C-ATL-N	C-ATL-MF	C-CHI-N	C-CHI-MF
COMPOUND	3/31/2005	4/1/2005	4/5/2005	4/6/2005	4/12/2005	4/13/2005
2,3,4-TRIMETHYLPENTANE	0.5	7.0	1.9	24.0	1.8	12.1
2,3,3-TRIMETHYLPENTANE	0.2	3.1	2.1	19.8	0.8	9.8
TOLUENE	8.4	121.2	21.8	242.4	9.9	107.2
2,3-DIMETHYLHEXANE	1.0	10.9	1.4	20.4	0.5	9.4
1,1,2-TRIMETHYLCYCLOPENTANE						
2-METHYLHEPTANE			1.0		0.2	1.6
3,4-DIMETHYLHEXANE, NOTE B	0.4	4.7	0.7	3.0	0.1	0.3
4-METHYLHEPTANE	1.5	18.6	1.0	16.4	1.4	10.1
3-METHYLHEPTANE	1.8	22.5	0.1	18.6	1.2	8.1
1-CIS,2-TRANS,3-TRIMETHYLCYCLOPENTANE			0.3	0.4		
CIS-1,3-DIMETHYLCYCLOHEXANE						
TRANS-1,4-DIMETHYLCYCLOHEXANE						
3-ETHYLHEXANE		4.9	1.6	3.6	0.7	6.0
2,2,5-TRIMETHYLHEXANE	0.2	2.3	0.6	5.2	1.0	6.8
TRANS-1-METHYL-3-ETHYLCYCLOPENTANE			Trace			
CIS-1-METHYL-3-ETHYLCYCLOPENTANE	0.2	3.2	0.2	2.1	0.6	3.6
1,1-DIMETHYLCYCLOHEXANE						
TRANS-1-METHYL-2-ETHYLCYCLOPENTANE						
1-METHYL-1-ETHYL-CYCLOPENTANE						
2,4,4-TRIMETHYLHEXANE	0.1	2.0	0.1	1.1	0.1	
2,2,4-TRIMETHYLHEXANE						
TRANS-1,2-DIMETHYLCYCLOHEXANE	0.1	2.5	0.1	1.6	0.2	2.6
1-OCTENE						
TRANS-4-OCTENE	0.1	2.3	Trace	1.0		1.0
OCTANE	1.1	14.3	1.4	12.4	0.9	6.1
UNIDENTIFIED C8	0.9	10.9	0.3	3.7	0.4	4.2
TRANS-2-OCTENE				2.0		1.6
TRANS-1,3-DIMETHYLCYCLOHEXANE, NOTE C						
CIS-2-OCTENE	0.1	1.1	0.1	0.7	0.1	0.8
ISOPROPYLCYCLOPENTANE						
2,2-DIMETHYLHEPTANE						
2,3,5-TRIMETHYLHEXANE	0.1	0.6	0.1	1.0	0.1	1.3
CIS-1-METHYL-2-ETHYLCYCLOPENTANE		1.7	0.1	1.2	0.1	1.2
2,4-DIMETHYLHEPTANE	0.2	1.6	0.1	1.4	0.1	0.9
4,4-DIMETHYLHEPTANE	0.1	1.0	0.1	0.6	0.1	0.7
CIS-1,2-DIMETHYLCYCLOHEXANE						
ETHYLCYCLOHEXANE					0.2	
2,6-DIMETHYLHEPTANE, NOTE D	0.3	3.2	0.3	2.7	0.4	2.8
1,1,3-TRIMETHYLCYCLOHEXANE						
2,5-DIMETHYLHEPTANE, NOTE E	0.2	2.4	0.2	2.0	0.2	1.2
3,3-DIMETHYLHEPTANE						
3,5-DIMETHYLHEPTANE, NOTE E	0.2	2.4	0.2	2.0	0.2	1.2
ETHYLBENZENE	3.7	45.8	6.2	54.5	3.5	23.3
2,3,4-TRIMETHYLHEXANE						
2,3-DIMETHYLHEPTANE						
m-& p-XYLENE	13.2	165.9	19.2	170.4	10.9	75.3
4-METHYLOCTANE						
3,4-DIMETHYLHEPTANE						
4-ETHYLHEPTANE						
2-METHYLOCTANE	0.9	12.2	0.9	8.6	0.6	5.0
3-METHYLOCTANE	0.6	8.1	0.7	5.7	0.4	3.2
STYRENE	1.1	16.1	1.8	19.7		9.2

HYDROCARBON SPECIATION DATA
FTP COMPOSITE
TOYOTA CAMRY

	FTP Composite, mg/mi					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	C-HOU-N	C-HOU-MF	C-ATL-N	C-ATL-MF	C-CHI-N	C-CHI-MF
COMPOUND	3/31/2005	4/1/2005	4/5/2005	4/6/2005	4/12/2005	4/13/2005
o-XYLENE	5.3	64.1	7.7	66.7	3.9	27.3
1-NONENE	0.2	2.0	0.2	2.4	0.3	2.6
TRANS-3-NONENE						
CIS-3-NONENE						
NONANE	0.4	5.9	0.5	4.9	0.4	3.6
TRANS-2-NONENE						
ISOPROPYLBENZENE (CUMENE)	Trace	0.8	Trace	0.6	Trace	0.4
2,2-DIMETHYLOCTANE	0.1	1.4	0.1	0.9	0.1	1.3
2,4-DIMETHYLOCTANE	0.1	1.4	0.1	0.7	0.2	1.6
n-PROPYLBENZENE	1.0	16.1	1.6	17.5	0.9	8.3
1-METHYL-3-ETHYLBENZENE	4.5	66.5	7.1	69.6	3.7	34.2
1-METHYL-4-ETHYLBENZENE	1.9	27.3	2.7	27.7	1.5	12.5
1,3,5-TRIMETHYLBENZENE	2.3	32.6	2.8	30.4	2.3	17.9
1-METHYL-2-ETHYLBENZENE	1.9	23.6	2.6	26.9	1.8	12.2
1,2,4-TRIMETHYLBENZENE	7.2	105.3	10.8	114.8	6.6	58.7
TERT-BUTYLBENZENE						
1-DECENE						
DECANE, NOTE F	0.2	2.5	Trace	1.8	0.8	3.3
ISOBUTYLBENZENE, NOTE F	0.2	2.4	Trace	1.7	0.7	3.1
1,3,-DIMETHYL-5-ETHYLBENZENE						
METHYLPROPYLBENZENE (sec butylbenzene)	0.1	1.3	0.3	2.0	0.1	1.2
1-METHYL-3-ISOPROPYLBENZENE						
1,2,3-TRIMETHYLBENZENE	1.6	23.9	2.5	28.0	1.9	14.4
1-METHYL-4-ISOPROPYLBENZENE	0.1	1.3	0.1	1.4	0.1	1.2
INDAN						
1-METHYL-2-ISOPROPYLBENZENE	0.8	11.3	1.3	9.0	1.1	10.0
1,3-DIETHYLBENZENE						
1,4-DIETHYLBENZENE	Trace	0.3				
1-METHYL-3-N-PROPYLBENZENE	0.5	11.0	2.4	19.4	0.9	9.0
1-METHYL-4-N-PROPYLBENZENE, NOTE G	1.2	17.7	1.9	24.7	1.8	15.5
1,2 DIETHYLBENZENE		1.8	0.1	1.4	0.2	
1-METHYL-2-N-PROPYLBENZENE	0.2	2.3	0.5	6.9	0.3	1.3
1,4-DIMETHYL-2-ETHYLBENZENE	1.3	11.1	1.1	7.9		
1,3-DIMETHYL-4-ETHYLBENZENE	1.3	13.3	1.3	7.4	1.9	9.5
1,2-DIMETHYL-4-ETHYLBENZENE			2.1			
1,3-DIMETHYL-2-ETHYLBENZENE		1.6	0.1	2.9	0.2	1.3
UNDECANE	0.2	4.9	0.7	7.3	0.7	3.7
1,2-DIMETHYL-3-ETHYLBENZENE					0.4	5.3
1,2,4,5-TETRAMETHYLBENZENE	0.1	7.2	0.7	9.3	1.0	9.7
2-METHYLBUTYLBENZENE (sec AMYLBENZENE)						
3,4 DIMETHYLCUMENE					0.1	
1,2,3,5-TETRAMETHYLBENZENE	1.0	11.8	1.4	17.4		0.9
TERT-1-BUT-2-METHYLBENZENE	0.2	7.1	0.6	8.0	1.2	7.1
1,2,3,4-TETRAMETHYLBENZENE	0.1	10.7	0.8	8.6		
N-PENT-BENZENE	0.3	7.0	0.5	7.8	0.1	3.0
TERT-1-BUT-3,5-DIMETHYLBENZENE						
TERT-1-BUTYL-4-ETHYLBENZENE	Trace	8.0	0.3	5.8	0.2	2.6
NAPHTHALENE		2.5		1.3		
DODECANE	0.2	5.1	0.2	4.3	0.1	1.5
1,3,5-TRIETHYLBENZENE						
1,2,4-TRIETHYLBENZENE						
HEXYLBENZENE						

HYDROCARBON SPECIATION DATA
FTP COMPOSITE
TOYOTA CAMRY

	FTP Composite, mg/mi					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	C-HOU-N	C-HOU-MF	C-ATL-N	C-ATL-MF	C-CHI-N	C-CHI-MF
COMPOUND	3/31/2005	4/1/2005	4/5/2005	4/6/2005	4/12/2005	4/13/2005
UNIDENTIFIED C9-C12+	6.3	136.7	9.4	120.6	13.9	144.1
FORMALDEHYDE	4.8	36.2	4.0	48.7	3.6	49.6
ACETALDEHYDE	1.1	9.3	1.3	9.1	3.0	18.7
ACROLEIN	0.4	3.8	0.3	4.4	0.1	2.5
ACETONE	0.8	5.5	0.4	2.1	0.4	1.7
PROPIONALDEHYDE	0.2	4.2	0.2	2.9	0.5	4.7
CROTONALDEHYDE	0.3	4.0	0.3	2.8	0.5	2.9
ISOBUTYRALDEHYDE, NOTE H	Trace	0.8	0.2	0.8	0.2	0.7
METHYL ETHYL KETONE, NOTE H	Trace	0.8	0.2	0.8	0.2	0.7
BENZALDEHYDE	0.4	5.4	0.9	8.1	0.6	4.6
ISOVALERALDEHYDE	Trace	0.6	0.1	0.7	0.1	0.8
VALERALDEHYDE		0.5	0.1	0.6	0.1	0.6
O-TOLUALDEHYDE	0.1	1.7	0.2	0.9	0.1	1.5
M/P-TOLUALDEHYDE	0.9	7.4	1.2	7.7	0.7	4.3
HEXANALDEHYDE	0.1	0.1	0.1	0.1	0.1	0.1
DIMETHYLBENZALDEHYDE	0.2	3.5	0.5	3.3	0.4	2.1

A - 2,2-Dimethylpentane and methylcyclopentane co-elute. GC peak area split equally between the two compounds.
B - 3-Methyl-3-ethyl-pentane co-elutes with reported compound. Not reported separately.
C - Cis-1,4-Dimethylcyclohexane co-elutes with reported compound. Not reported separately.
D - Propylcyclopentane co-elutes with reported compound. Not reported separately.
E - 2,5-Dimethylheptane and 3,5-dimethylheptane co-elute. GC peak area split equally between the two compounds.
F - Decane and isobutylbenzene co-elute. GC peak area split equally between the two compounds.
G - n-Butylbenzene co-elutes with reported compound. Not reported separately.
H - Isobutyraldehyde and methyl ethyl ketone co-elute. LC peak area split equally between the two compounds.

HYDROCARBON SPECIATION DATA
SHED TEST
TOYOTA CAMRY

	SHED results, mg					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	C-HOU-N	C-HOU-MF	C-ATL-N	C-ATL-MF	C-CHI-N	C-CHI-MF
COMPOUND	3/31/2005	4/1/2005	4/5/2005	4/6/2005	4/12/2005	4/13/2005
METHANE	--	--	--	--	--	--
ETHANE	0.2	6.8		1.6	0.1	3.3
ETHYLENE		1.0		0.4		0.4
PROPANE		34.4		22.8	0.1	55.6
PROPYLENE	0.2	9.3		11.2	0.2	7.7
ACETYLENE						
PROPADIENE						
BUTANE	4.9	2046.6	8.8	1982.4	22.2	2917.3
TRANS-2-BUTENE	0.6	80.8	0.5	43.9	0.9	69.3
1-BUTENE		49.3		19.3	0.2	38.3
2-METHYLPROPENE (ISOBUTYLENE)	0.4	39.5	0.2	18.5	0.4	45.2
2,2-DIMETHYLPROPANE (NEOPENTANE)	7.5	1790.2	6.9	1065.8	14.3	1695.8
PROPYNE						
1,3-BUTADIENE		3.7		0.5		1.6
2-METHYLPROPANE (ISOBUTANE)		356.6	0.4	225.1	1.0	266.1
1-BUTYNE						
METHANOL						
CIS-2-BUTENE	0.4	74.1	0.2	42.7	0.6	53.2
3-METHYL-1-BUTENE						
ETHANOL					44.7	1301.8
2-METHYLBUTANE (ISOPENTANE)						
2-BUTYNE						
1-PENTENE	0.4	73.7	3.3	20.6	0.7	67.6
2-METHYL-1-BUTENE	0.9	95.6	1.1	42.6	1.6	163.0
PENTANE	2.8	675.1	5.8	480.1	8.9	611.6
UNIDENTIFIED C5 OLEFINS						
2-METHYL-1,3-BUTADIENE		9.6		0.7		7.0
TRANS-2-PENTENE	1.2	128.2	0.9	41.9	2.9	169.2
3,3-DIMETHYL-1-BUTENE		4.0				2.6
CIS-2-PENTENE	0.7	67.2	0.4	21.5	1.3	93.2
2-METHYL-2-BUTENE	2.8	140.4	1.8	63.6	4.6	292.2
TERT-BUTANOL						
CYCLOPENTADIENE		3.6				3.3
2,2-DIMETHYLBUTANE	0.3	76.3	0.3	33.7	0.4	27.9
CYCLOPENTENE		22.1		6.8	0.7	32.2
4-METHYL-1-PENTENE	0.8	12.8	0.5	3.7		16.0
3-METHYL-1-PENTENE						
CYCLOPENTANE		48.4		20.7	0.9	32.2
2,3-DIMETHYLBUTANE	0.6	96.9	0.8	48.9	1.1	65.5
MTBE		1529.3		6.3		25.2
4-METHYL-CIS-2-PENTENE						
2-METHYLPENTANE	3.2	414.3	8.6	152.5	4.6	218.8
4-METHYL-TRANS-2-PENTENE	2.1	25.5		7.6	1.9	15.0
3-METHYLPENTANE	2.0	252.0	2.3	85.2	2.8	124.8
2-METHYL-1-PENTENE	0.4		0.2	3.5	0.4	16.0
1-HEXENE	0.4		0.2	3.5	0.4	16.0
HEXANE	3.4	208.1	3.3	67.5	3.5	90.1
UNIDENTIFIED C6	0.4	39.2	0.3			4.2
TRANS-3-HEXENE						
CIS-3-HEXENE		12.2		4.0	0.6	14.6
DI-ISOPROPYL ETHER						21.4
TRANS-2-HEXENE	0.4	15.8	0.4	5.3	0.8	37.2

HYDROCARBON SPECIATION DATA
SHED TEST
TOYOTA CAMRY

	SHED results, mg					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	C-HOU-N	C-HOU-MF	C-ATL-N	C-ATL-MF	C-CHI-N	C-CHI-MF
COMPOUND	3/31/2005	4/1/2005	4/5/2005	4/6/2005	4/12/2005	4/13/2005
3-METHYL-TRANS-2-PENTENE	1.3	25.8	0.6	8.8	1.3	21.7
2-METHYL-2-PENTENE	0.5	16.8	0.3	5.4	0.5	
3-METHYLCYCLOPENTENE			0.2			
CIS-2-HEXENE	0.3	10.4		3.3	0.4	11.2
ETBE						
3-METHYL-CIS-2-PENTENE	0.4	15.5	0.4	5.3	0.5	23.4
2,2-DIMETHYLPENTANE, NOTE A	1.2	54.8	0.9	19.9	1.4	42.8
METHYLCYCLOPENTANE, NOTE A	1.2	53.6	0.9	19.5	1.4	41.9
2,4-DIMETHYLPENTANE		24.1	0.3	15.8	0.1	18.1
2,2,3-TRIMETHYLBUTANE	0.2	3.5		1.2	0.5	2.2
3,4-DIMETHYL-1-PENTENE		1.2				1.0
1-METHYLCYCLOPENTENE	0.9	11.5	1.0	6.2	1.1	24.2
BENZENE	3.1	23.8	2.6	28.2	5.4	41.4
3-METHYL-1-HEXENE						
3,3-DIMETHYLPENTANE		10.0	0.6	3.9	1.0	2.1
CYCLOHEXANE		6.9				14.3
2-METHYLHEXANE						
2,3-DIMETHYLPENTANE	1.8	91.1	2.0	42.5	2.7	40.9
1,1-DIMETHYLCYCLOPENTANE						1.6
TERT-AMYL METHYL ETHER						2.6
CYCLOHEXENE		21.9		0.5		
3-METHYLHEXANE	1.3	79.2	1.8	27.2	1.8	23.1
CIS-1,3-DIMETHYLCYCLOPENTANE	0.4	11.5	0.2	4.4	0.4	11.1
3-ETHYLPENTANE	0.4	13.4	0.3	6.0	0.5	12.1
TRANS-1,2-DIMETHYLCYCLOPENTANE						
TRANS-1,3-DIMETHYLCYCLOPENTANE	0.3	7.7	0.2	3.7	0.3	9.6
1-HEPTENE						
2,2,4-TRIMETHYLPENTANE	0.6	13.6	0.5	39.7	1.4	20.7
2-METHYL-1-HEXENE						
TRANS-3-HEPTENE	0.2	1.4		0.4		5.0
HEPTANE	1.6	36.4	1.9	20.2	2.4	19.8
CIS-3-HEPTENE						
UNIDENTIFIED C7	0.8	6.6		0.6	0.3	6.0
2-METHYL-2-HEXENE		3.9				5.4
3-METHYL-TRANS-3-HEXENE						
TRANS-2-HEPTENE		2.7		0.8		2.4
3-ETHYL-CIS-2-PENTENE						
2,4,4-TRIMETHYL-1-PENTENE	0.2	3.4		1.2	0.2	4.2
2,3-DIMETHYL-2-PENTENE						
CIS-2-HEPTENE		1.7		0.6		1.8
METHYLCYCLOHEXANE	1.1	12.2	0.7	7.7	1.3	21.7
CIS-1,2-DIMETHYLCYCLOPENTANE						
2,2-DIMETHYLHEXANE						
1,1,3-TRIMETHYLCYCLOPENTANE	0.7	1.9		1.0		1.3
2,4,4-TRIMETHYL-2-PENTENE		3.3	0.5	1.7	0.3	
2,2,3-TRIMETHYLPENTANE		3.3		4.3	0.4	3.7
2,5-DIMETHYLHEXANE						
ETHYLCYCLOPENTANE						
2,4-DIMETHYLHEXANE	0.3	4.3	0.3	4.3	0.3	7.0
1-TRANS-2-CIS-4-TRIMETHYLCYCLOPENTANE		1.5		0.8		1.8
3,3-DIMETHYLHEXANE						
1-TRANS-2-CIS-3-TRIMETHYLCYCLOPENTANE				0.5		1.4

HYDROCARBON SPECIATION DATA
SHED TEST
TOYOTA CAMRY

	SHED results, mg					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	C-HOU-N	C-HOU-MF	C-ATL-N	C-ATL-MF	C-CHI-N	C-CHI-MF
COMPOUND	3/31/2005	4/1/2005	4/5/2005	4/6/2005	4/12/2005	4/13/2005
2,3,4-TRIMETHYLPENTANE	0.5	5.9	0.4	8.4	1.0	9.5
2,3,3-TRIMETHYLPENTANE	0.3	1.4	0.4	4.7	0.4	5.7
TOLUENE	4.8	31.3	8.2	48.9	11.8	43.5
2,3-DIMETHYLHEXANE		4.1			1.7	2.4
1,1,2-TRIMETHYLCYCLOPENTANE						
2-METHYLHEPTANE						1.2
3,4-DIMETHYLHEXANE, NOTE B		0.6				0.4
4-METHYLHEPTANE		8.8	0.5	5.1	0.9	5.1
3-METHYLHEPTANE	0.6	9.2	0.5	4.8	0.9	5.9
1-CIS,2-TRANS,3-TRIMETHYLCYCLOPENTANE						
CIS-1,3-DIMETHYLCYCLOHEXANE						
TRANS-1,4-DIMETHYLCYCLOHEXANE						
3-ETHYLHEXANE						
2,2,5-TRIMETHYLHEXANE		1.6	0.1	1.3	0.3	3.1
TRANS-1-METHYL-3-ETHYLCYCLOPENTANE						
CIS-1-METHYL-3-ETHYLCYCLOPENTANE		1.2		0.4	0.2	1.1
1,1-DIMETHYLCYCLOHEXANE						
TRANS-1-METHYL-2-ETHYLCYCLOPENTANE						
1-METHYL-1-ETHYL-CYCLOPENTANE						
2,4,4-TRIMETHYLHEXANE		0.2				
2,2,4-TRIMETHYLHEXANE						
TRANS-1,2-DIMETHYLCYCLOHEXANE		1.1				
1-OCTENE						
TRANS-4-OCTENE				0.2		0.6
OCTANE	0.4	4.2	0.5	2.2	0.5	2.8
UNIDENTIFIED C8	0.8	2.3		0.3		0.2
TRANS-2-OCTENE		0.8		0.2		0.5
TRANS-1,3-DIMETHYLCYCLOHEXANE, NOTE C						
CIS-2-OCTENE		0.2				
ISOPROPYLCYCLOPENTANE						
2,2-DIMETHYLHEPTANE						
2,3,5-TRIMETHYLHEXANE						0.5
CIS-1-METHYL-2-ETHYLCYCLOPENTANE		0.3		0.2		
2,4-DIMETHYLHEPTANE		0.1		0.2		0.4
4,4-DIMETHYLHEPTANE		0.4				
CIS-1,2-DIMETHYLCYCLOHEXANE						
ETHYLCYCLOHEXANE						
2,6-DIMETHYLHEPTANE, NOTE D		0.7		0.4		0.9
1,1,3-TRIMETHYLCYCLOHEXANE						
2,5-DIMETHYLHEPTANE, NOTE E		0.3		0.1		0.2
3,3-DIMETHYLHEPTANE						
3,5-DIMETHYLHEPTANE, NOTE E		0.3		0.1		0.2
ETHYLBENZENE	1.6	5.2	2.0	4.4	2.2	5.2
2,3,4-TRIMETHYLHEXANE						
2,3-DIMETHYLHEPTANE						
m-& p-XYLENE	3.3	11.4	4.3	10.0	3.0	11.9
4-METHYLOCTANE						
3,4-DIMETHYLHEPTANE						
4-ETHYLHEPTANE						
2-METHYLOCTANE	0.6					
3-METHYLOCTANE						
STYRENE						

HYDROCARBON SPECIATION DATA
SHED TEST
TOYOTA CAMRY

	SHED results, mg					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	C-HOU-N	C-HOU-MF	C-ATL-N	C-ATL-MF	C-CHI-N	C-CHI-MF
COMPOUND	3/31/2005	4/1/2005	4/5/2005	4/6/2005	4/12/2005	4/13/2005
o-XYLENE		1.8	0.7	2.2	0.2	2.2
1-NONENE						0.2
TRANS-3-NONENE						
CIS-3-NONENE						
NONANE						0.3
TRANS-2-NONENE						
ISOPROPYLBENZENE (CUMENE)						
2,2-DIMETHYLOCTANE						
2,4-DIMETHYLOCTANE						
n-PROPYLBENZENE						
1-METHYL-3-ETHYLBENZENE						
1-METHYL-4-ETHYLBENZENE						
1,3,5-TRIMETHYLBENZENE						
1-METHYL-2-ETHYLBENZENE						
1,2,4-TRIMETHYLBENZENE				0.2		0.3
TERT-BUTYLBENZENE						
1-DECENE						
DECANE, NOTE F						
ISOBUTYLBENZENE, NOTE F						
1,3,-DIMETHYL-5-ETHYLBENZENE						
METHYLPROPYLBENZENE (sec butylbenzene)						
1-METHYL-3-ISOPROPYLBENZENE						
1,2,3-TRIMETHYLBENZENE						
1-METHYL-4-ISOPROPYLBENZENE						
INDAN						
1-METHYL-2-ISOPROPYLBENZENE						
1,3-DIETHYLBENZENE						
1,4-DIETHYLBENZENE						
1-METHYL-3-N-PROPYLBENZENE						
1-METHYL-4-N-PROPYLBENZENE, NOTE G						
1,2 DIETHYLBENZENE						
1-METHYL-2-N-PROPYLBENZENE						
1,4-DIMETHYL-2-ETHYLBENZENE						
1,3-DIMETHYL-4-ETHYLBENZENE						
1,2-DIMETHYL-4-ETHYLBENZENE						
1,3-DIMETHYL-2-ETHYLBENZENE						
UNDECANE						
1,2-DIMETHYL-3-ETHYLBENZENE						
1,2,4,5-TETRAMETHYLBENZENE						
2-METHYLBUTYLBENZENE (sec AMYLBENZENE)						
3,4 DIMETHYLCUMENE						
1,2,3,5-TETRAMETHYLBENZENE						
TERT-1-BUT-2-METHYLBENZENE						
1,2,3,4-TETRAMETHYLBENZENE						
N-PENT-BENZENE						0.2
TERT-1-BUT-3,5-DIMETHYLBENZENE						
TERT-1-BUTYL-4-ETHYLBENZENE						
NAPHTHALENE						
DODECANE						
1,3,5-TRIETHYLBENZENE						
1,2,4-TRIETHYLBENZENE						
HEXYLBENZENE						

HYDROCARBON SPECIATION DATA
SHED TEST
TOYOTA CAMRY

	SHED results, mg					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	C-HOU-N	C-HOU-MF	C-ATL-N	C-ATL-MF	C-CHI-N	C-CHI-MF
COMPOUND	3/31/2005	4/1/2005	4/5/2005	4/6/2005	4/12/2005	4/13/2005
UNIDENTIFIED C9-C12+		1.3	0.4		0.3	

A - 2,2-Dimethylpentane and methylcyclopentane co-elute. GC peak area split equally between the two compounds.
B - 3-Methyl-3-ethyl-pentane co-elutes with reported compound. Not reported separately.
C - Cis-1,4-Dimethylcyclohexane co-elutes with reported compound. Not reported separately.
D - Propylcyclopentane co-elutes with reported compound. Not reported separately.
E - 2,5-Dimethylheptane and 3,5-dimethylheptane co-elute. GC peak area split equally between the two compounds.
F - Decane and isobutylbenzene co-elute. GC peak area split equally between the two compounds.
G - n-Butylbenzene co-elutes with reported compound. Not reported separately.

HYDROCARBON SPECIATION DATA
FTP COMPOSITE
TOYOTA CAMRY

	FTP Composite, mg/mi					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	TC-4614-S	TC-4614-M	TC-4637-S	TC-4637-M	TC-4640-S	TC-4640-M
COMPOUND	7/18/2002	8/20/2002	8/2/2002	8/9/2002	8/14/2002	8/15/2002
METHANE	39.8	482.9	39.0	395.1	34.7	480.9
ETHANE	5.2	*	8.2	27.6	*	38.8
ETHYLENE	11.4	*	19.9	344.8	*	337.8
PROPANE		*	0.3	3.0	*	6.4
PROPYLENE	0.2	*			*	
ACETYLENE	3.9	*	4.9	528.6	*	530.1
PROPADIENE		*			*	
BUTANE	1.3	*	1.2	14.4	*	8.8
TRANS-2-BUTENE		*	0.6	6.9	*	1.9
1-BUTENE	1.0	*	2.0	22.4	*	2.4
2-METHYLPROPENE (ISOBUTYLENE)	6.0	*	4.2	56.5	*	6.1
2,2-DIMETHYLPROPANE (NEOPENTANE)	0.3	*		0.7	*	
PROPYNE		*			*	
1,3-BUTADIENE		*	0.3	7.7	*	
2-METHYLPROPANE (ISOBUTANE)		*		166.5	*	
1-BUTYNE		*			*	
METHANOL		*			*	
CIS-2-BUTENE		*	0.1	16.0	*	
3-METHYL-1-BUTENE		*			*	
ETHANOL		*			7.2	256.2
2-METHYLBUTANE (ISOPENTANE)	3.5	*	0.6	11.0	*	71.7
2-BUTYNE						
1-PENTENE	0.4	9.0		6.2	0.4	2.1
2-METHYL-1-BUTENE	0.6	14.5	0.4	10.7	0.5	13.5
PENTANE	2.4	40.6	1.1	42.8	1.0	17.5
UNIDENTIFIED C5 OLEFINS	0.2	6.3	0.3	2.9		9.0
2-METHYL-1,3-BUTADIENE	0.5	9.1	2.4	8.3	0.6	11.2
TRANS-2-PENTENE	0.7	14.2	0.7	9.1	0.6	11.4
3,3-DIMETHYL-1-BUTENE		0.3	0.4	0.3		4.8
CIS-2-PENTENE	0.4	8.3	0.3	5.0	0.3	6.0
2-METHYL-2-BUTENE	1.1	20.4	0.9	13.5	1.2	19.9
TERT-BUTANOL						
CYCLOPENTADIENE	0.2	7.3		5.3	0.3	6.3
2,2-DIMETHYLBUTANE	0.5	6.4	0.5	7.2	0.6	9.7
CYCLOPENTENE	1.2	4.8	0.2	3.2	0.2	4.1
4-METHYL-1-PENTENE	0.2	2.8	0.2	2.6	0.1	1.8
3-METHYL-1-PENTENE						1.7
CYCLOPENTANE	0.3	4.9	0.2	4.4	0.3	2.4
2,3-DIMETHYLBUTANE	0.9	16.8	0.8	11.8	1.5	24.7
MTBE	1.3	54.8				
4-METHYL-CIS-2-PENTENE						
2-METHYLPENTANE	2.6	62.7	2.5	40.0	2.6	44.5
4-METHYL-TRANS-2-PENTENE	0.2	2.2	Trace	0.9		
3-METHYLPENTANE	2.5	47.5	1.8	26.9	1.6	32.1
2-METHYL-1-PENTENE	0.2	4.1	0.2	2.5	0.1	2.4
1-HEXENE	0.2	3.5	0.2	2.5	0.1	2.5
HEXANE	2.8	50.8	1.8	26.8	1.3	27.4
UNIDENTIFIED C6	0.4	61.2	0.5	7.9	0.3	6.6
TRANS-3-HEXENE						
CIS-3-HEXENE		2.8	0.1	1.3		1.6
DI-ISOPROPYL ETHER						
TRANS-2-HEXENE	0.1	4.5	0.1	2.1	0.1	2.5

HYDROCARBON SPECIATION DATA
FTP COMPOSITE
TOYOTA CAMRY

	FTP Composite, mg/mi					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	TC-4614-S	TC-4614-M	TC-4637-S	TC-4637-M	TC-4640-S	TC-4640-M
COMPOUND	7/18/2002	8/20/2002	8/2/2002	8/9/2002	8/14/2002	8/15/2002
3-METHYL-TRANS-2-PENTENE	0.2	6.6	0.2	16.6	0.2	4.4
2-METHYL-2-PENTENE	0.3	4.3	0.1	2.4	0.1	3.1
3-METHYLCYCLOPENTENE	0.2					
CIS-2-HEXENE	0.2	2.5	0.1	1.2		1.4
ETBE						
3-METHYL-CIS-2-PENTENE	0.4	5.2	0.3	2.6	0.2	3.5
2,2-DIMETHYLPENTANE, NOTE A	0.6	11.5	0.5	9.6	0.8	16.5
METHYLCYCLOPENTANE, NOTE A	0.6	11.3	0.5	9.4	0.8	16.2
2,4-DIMETHYLPENTANE	0.7	9.2	0.7	8.0	1.3	20.3
2,2,3-TRIMETHYLBUTANE		0.9		0.5		1.1
3,4-DIMETHYL-1-PENTENE				0.1		
1-METHYLCYCLOPENTENE	0.4	8.2	0.2	6.5	0.3	6.2
BENZENE	3.8	95.9	9.0	138.3	42.9	99.3
3-METHYL-1-HEXENE		Trace				
3,3-DIMETHYLPENTANE	0.3	2.1	0.1	1.4		1.6
CYCLOHEXANE	0.2	3.4	0.4	5.6	0.9	11.9
2-METHYLHEXANE						
2,3-DIMETHYLPENTANE	2.7	33.0	2.8	30.5	4.3	56.6
1,1-DIMETHYLCYCLOPENTANE				0.6		1.3
TERT-AMYL METHYL ETHER						
CYCLOHEXENE	0.1	1.2	0.1	1.0		1.3
3-METHYLHEXANE	2.4	23.2	2.0	21.7	2.3	28.8
CIS-1,3-DIMETHYLCYCLOPENTANE	0.2	3.6	0.2	2.9	0.3	6.3
3-ETHYLPENTANE	0.1	3.9				3.3
TRANS-1,2-DIMETHYLCYCLOPENTANE						
TRANS-1,3-DIMETHYLCYCLOPENTANE	0.1	3.4	0.2	2.6	0.4	6.3
1-HEPTENE						
2,2,4-TRIMETHYLPENTANE	3.4	38.1	5.4	51.8	5.9	66.5
2-METHYL-1-HEXENE						
TRANS-3-HEPTENE	0.1	2.6	0.1	1.0		0.6
HEPTANE	0.8	15.7	0.5	21.9	2.8	32.7
CIS-3-HEPTENE						
UNIDENTIFIED C7	0.2	2.4		1.1		1.7
2-METHYL-2-HEXENE		2.6				
3-METHYL-TRANS-3-HEXENE						
TRANS-2-HEPTENE	0.1	1.9	Trace	0.8		0.8
3-ETHYL-CIS-2-PENTENE						
2,4,4-TRIMETHYL-1-PENTENE	0.1	2.3	0.1	1.2		1.4
2,3-DIMETHYL-2-PENTENE						
CIS-2-HEPTENE	0.1	1.6	0.1	0.9	0.1	1.1
METHYLCYCLOHEXANE	0.6	7.6	0.8	11.2	1.4	20.6
CIS-1,2-DIMETHYLCYCLOPENTANE						
2,2-DIMETHYLHEXANE						
1,1,3-TRIMETHYLCYCLOPENTANE	0.1	1.2	0.1	1.5	0.1	2.3
2,4,4-TRIMETHYL-2-PENTENE						
2,2,3-TRIMETHYLPENTANE	0.5	9.3	0.9	6.6		16.6
2,5-DIMETHYLHEXANE						
ETHYLCYCLOPENTANE						
2,4-DIMETHYLHEXANE	0.3	9.2	0.8	8.5	2.3	12.2
1-TRANS-2-CIS-4-TRIMETHYLCYCLOPENTANE	0.2	2.2	0.2	2.0	0.2	3.3
3,3-DIMETHYLHEXANE						
1-TRANS-2-CIS-3-TRIMETHYLCYCLOPENTANE	0.0	0.9	Trace	0.5		1.4

HYDROCARBON SPECIATION DATA
FTP COMPOSITE
TOYOTA CAMRY

	FTP Composite, mg/mi					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	TC-4614-S	TC-4614-M	TC-4637-S	TC-4637-M	TC-4640-S	TC-4640-M
COMPOUND	7/18/2002	8/20/2002	8/2/2002	8/9/2002	8/14/2002	8/15/2002
2,3,4-TRIMETHYLPENTANE	1.8	19.3	1.6	15.0	2.8	30.7
2,3,3-TRIMETHYLPENTANE	2.3	34.8	1.5	18.2	2.9	52.4
TOLUENE	7.9	142.2	24.6	309.2	9.2	154.3
2,3-DIMETHYLHEXANE	1.3	18.0	1.7	2.5		29.1
1,1,2-TRIMETHYLCYCLOPENTANE						
2-METHYLHEPTANE	0.9					
3,4-DIMETHYLHEXANE, NOTE B		1.1	0.1	0.8	0.1	1.7
4-METHYLHEPTANE	0.3	12.2	1.4	12.1	1.5	17.1
3-METHYLHEPTANE	1.0	12.4	0.9	10.3	1.3	14.1
1-CIS,2-TRANS,3-TRIMETHYLCYCLOPENTANE				0.7		
CIS-1,3-DIMETHYLCYCLOHEXANE						
TRANS-1,4-DIMETHYLCYCLOHEXANE						
3-ETHYLHEXANE	0.1	3.0	0.3	2.0	0.4	4.3
2,2,5-TRIMETHYLHEXANE	0.4	5.8	0.6	7.0	1.7	17.3
TRANS-1-METHYL-3-ETHYLCYCLOPENTANE						
CIS-1-METHYL-3-ETHYLCYCLOPENTANE	1.0	3.1	0.3	2.0	0.3	3.3
1,1-DIMETHYLCYCLOHEXANE						
TRANS-1-METHYL-2-ETHYLCYCLOPENTANE						
1-METHYL-1-ETHYL-CYCLOPENTANE						
2,4,4-TRIMETHYLHEXANE	0.1	1.5	0.1	0.9		0.9
2,2,4-TRIMETHYLHEXANE						
TRANS-1,2-DIMETHYLCYCLOHEXANE	0.1	2.0	0.1	1.0	0.1	1.2
1-OCTENE						
TRANS-4-OCTENE						
OCTANE	0.7	8.4	1.0	9.6	1.0	11.8
UNIDENTIFIED C8	0.2	3.8		0.7	0.1	1.7
TRANS-2-OCTENE	0.1	2.4		0.9		0.3
TRANS-1,3-DIMETHYLCYCLOHEXANE, NOTE C						
CIS-2-OCTENE	0.1	1.1	Trace	0.4	0.2	0.3
ISOPROPYLCYCLOPENTANE						
2,2-DIMETHYLHEPTANE						
2,3,5-TRIMETHYLHEXANE	0.1	1.1	0.1	1.3	0.3	3.0
CIS-1-METHYL-2-ETHYLCYCLOPENTANE	0.1	1.1	0.1	0.9		1.0
2,4-DIMETHYLHEPTANE	0.1	1.0	0.1	1.3	0.2	1.5
4,4-DIMETHYLHEPTANE	Trace	0.5	Trace	0.3		0.5
CIS-1,2-DIMETHYLCYCLOHEXANE						
ETHYLCYCLOHEXANE		0.3	0.1			
2,6-DIMETHYLHEPTANE, NOTE D	0.1	1.8	0.2	1.7	0.5	3.7
1,1,3-TRIMETHYLCYCLOHEXANE						
2,5-DIMETHYLHEPTANE, NOTE E	0.2	2.4	0.4	3.4	0.5	4.9
3,3-DIMETHYLHEPTANE						
3,5-DIMETHYLHEPTANE, NOTE E						
ETHYLBENZENE	2.4	28.5	4.3	42.5	2.3	23.4
2,3,4-TRIMETHYLHEXANE						
2,3-DIMETHYLHEPTANE						
m-& p-XYLENE	7.7	82.8	15.1	147.7	8.3	78.8
4-METHYLOCTANE						
3,4-DIMETHYLHEPTANE						
4-ETHYLHEPTANE						
2-METHYLOCTANE	0.7	8.1	1.1	7.1	0.9	9.0
3-METHYLOCTANE	0.5	4.6	0.5	4.6	0.6	6.1
STYRENE	0.7	12.0	1.2	16.1	0.7	9.7

HYDROCARBON SPECIATION DATA
FTP COMPOSITE
TOYOTA CAMRY

	FTP Composite, mg/mi					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	TC-4614-S	TC-4614-M	TC-4637-S	TC-4637-M	TC-4640-S	TC-4640-M
COMPOUND	7/18/2002	8/20/2002	8/2/2002	8/9/2002	8/14/2002	8/15/2002
o-XYLENE	3.6	35.3	6.1	57.3	3.7	33.0
1-NONENE	0.2	2.7	0.2	2.0	0.4	4.3
TRANS-3-NONENE						
CIS-3-NONENE						
NONANE	0.4	3.1	0.7	5.3	0.9	8.0
TRANS-2-NONENE						
ISOPROPYLBENZENE (CUMENE)	0.1	0.2		0.3	0.3	0.8
2,2-DIMETHYLOCTANE	0.1	0.4	0.1	0.8		
2,4-DIMETHYLOCTANE	0.3	0.7	0.1	0.5		0.7
n-PROPYLBENZENE	0.8	8.6	1.7	15.6	0.7	8.5
1-METHYL-3-ETHYLBENZENE	2.9	42.6	7.1	53.4	4.6	39.3
1-METHYL-4-ETHYLBENZENE	0.8	19.5	3.4	19.4		12.2
1,3,5-TRIMETHYLBENZENE	1.5	19.5	3.8	29.7	1.5	14.4
1-METHYL-2-ETHYLBENZENE	1.3	16.2	3.1	24.4	0.9	12.5
1,2,4-TRIMETHYLBENZENE	7.0	76.8	14.8	79.5	6.1	70.2
TERT-BUTYLBENZENE						
1-DECENE						
DECANE, NOTE F	0.3	0.5	1.0	3.6	0.3	2.0
ISOBUTYLBENZENE, NOTE F	0.3	0.4	0.9	3.4	0.2	1.9
1,3,-DIMETHYL-5-ETHYLBENZENE						
METHYLPROPYLBENZENE (sec butylbenzene)			0.3	2.2		0.7
1-METHYL-3-ISOPROPYLBENZENE		19.2				
1,2,3-TRIMETHYLBENZENE	1.3	0.5	3.5	30.6	1.2	15.6
1-METHYL-4-ISOPROPYLBENZENE			0.2	1.7		
INDAN						
1-METHYL-2-ISOPROPYLBENZENE		14.7	0.2	1.6	0.2	3.9
1,3-DIETHYLBENZENE						
1,4-DIETHYLBENZENE		6.3	1.0	0.5		1.2
1-METHYL-3-N-PROPYLBENZENE	0.6		1.9	21.1	0.9	14.7
1-METHYL-4-N-PROPYLBENZENE, NOTE G	1.6	0.6	0.1	39.2	1.4	0.2
1,2 DIETHYLBENZENE			0.1	1.2		
1-METHYL-2-N-PROPYLBENZENE	0.2	1.2	0.2	1.5	0.2	4.5
1,4-DIMETHYL-2-ETHYLBENZENE		29.2	2.0	13.8	1.8	12.3
1,3-DIMETHYL-4-ETHYLBENZENE	2.1	3.2		13.0		3.3
1,2-DIMETHYL-4-ETHYLBENZENE	1.1	20.9	3.2	28.6		17.6
1,3-DIMETHYL-2-ETHYLBENZENE		2.6	0.3		0.3	
UNDECANE	0.3	2.5	0.3	2.6	0.3	1.6
1,2-DIMETHYL-3-ETHYLBENZENE						
1,2,4,5-TETRAMETHYLBENZENE	0.1	9.0	2.0	17.9	0.4	11.7
2-METHYLBUTYLBENZENE (sec AMYLBENZENE)						
3,4 DIMETHYLCUMENE						
1,2,3,5-TETRAMETHYLBENZENE		2.0	0.2	0.1	0.8	0.4
TERT-1-BUT-2-METHYLBENZENE		10.8	Trace		0.7	
1,2,3,4-TETRAMETHYLBENZENE		6.5	0.2	5.7	0.3	4.0
N-PENT-BENZENE			0.3			
TERT-1-BUT-3,5-DIMETHYLBENZENE	0.1	11.2	1.1	23.2		29.0
TERT-1-BUTYL-4-ETHYLBENZENE						
NAPHTHALENE		0.4	0.2	3.4	0.5	0.6
DODECANE	0.3	3.2	0.4	1.1	0.1	3.0
1,3,5-TRIETHYLBENZENE						
1,2,4-TRIETHYLBENZENE						
HEXYLBENZENE						

HYDROCARBON SPECIATION DATA
FTP COMPOSITE
TOYOTA CAMRY

	FTP Composite, mg/mi					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	TC-4614-S	TC-4614-M	TC-4637-S	TC-4637-M	TC-4640-S	TC-4640-M
COMPOUND	7/18/2002	8/20/2002	8/2/2002	8/9/2002	8/14/2002	8/15/2002
UNIDENTIFIED C9-C12+	8.4	152.9	22.0	175.3	9.9	184.7
FORMALDEHYDE	2.2	59.2	2.6	53.0	2.3	63.6
ACETALDEHYDE	5.0	13.9	1.7	13.5	2.6	34.5
ACROLEIN	1.2	8.2	0.4	6.3	0.4	8.6
ACETONE	6.4	6.1	0.8	4.0	0.6	5.7
PROPIONALDEHYDE	0.8	2.7	0.4	6.4	0.2	3.0
CROTONALDEHYDE	2.9	4.0	0.8	4.8	0.3	3.9
ISOBUTYRALDEHYDE, NOTE H	1.1	2.1	0.2	1.4	0.2	1.5
METHYL ETHYL KETONE, NOTE H	1.1	2.1	0.2	1.4	0.2	1.5
BENZALDEHYDE	0.3	6.6	0.7	11.6	0.2	5.3
ISOVALERALDEHYDE	0.4	1.2	0.1	0.2		1.2
VALERALDEHYDE	0.6	0.8	0.1	1.0	0.1	1.1
O-TOLUALDEHYDE	0.4	2.1	0.3	3.3	0.1	2.1
M/P-TOLUALDEHYDE	0.4	7.0	0.6	11.2	0.2	6.6
HEXANALDEHYDE	Trace	Trace		0.1		Trace
DIMETHYLBENZALDEHYDE			0.2	4.0	Trace	2.4

*C1 - C4 DATA NOT AVAILABLE DUE TO INSTRUMENT MALFUNCTION

A - 2,2-Dimethylpentane and methylcyclopentane co-elute. GC peak area split equally between the two compounds.

B - 3-Methyl-3-ethyl-pentane co-elutes with reported compound. Not reported separately.

C - Cis-1,4-Dimethylcyclohexane co-elutes with reported compound. Not reported separately.

D - Propylcyclopentane co-elutes with reported compound. Not reported separately.

E - 2,5-Dimethylheptane and 3,5-dimethylheptane co-elute. GC peak area split equally between the two compounds.

F - Decane and isobutylbenzene co-elute. GC peak area split equally between the two compounds.

G - n-Butylbenzene co-elutes with reported compound. Not reported separately.

H - Isobutyraldehyde and methyl ethyl ketone co-elute. LC peak area split equally between the two compounds.

HYDROCARBON SPECIATION DATA
SHED TEST
TOYOTA CAMRY

	SHED results, mg					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	TC-4614-S	TC-4614-M	TC-4637-S	TC-4637-M	TC-4640-S	TC-4640-M
COMPOUND	8/19/2002	8/20/2002	8/2/2002	8/9/2002	8/14/2002	8/15/2002
METHANE						
ETHANE	*	*			*	
ETHYLENE	*	*			*	
PROPANE	*	*		6.0	*	9.2
PROPYLENE	*	*			*	
ACETYLENE	*	*			*	
PROPADIENE	*	*			*	
BUTANE	*	*	2.0	81.0	*	76.7
TRANS-2-BUTENE	*	*			*	
1-BUTENE	*	*		1.6	*	
2-METHYLPROPENE (ISOBUTYLENE)	*	*	7.7	13.5	*	
2,2-DIMETHYLPROPANE (NEOPENTANE)	*	*			*	
PROPYNE	*	*			*	
1,3-BUTADIENE	*	*			*	*
2-METHYLPROPANE (ISOBUTANE)	*	*	0.6	29.9	*	34.0
1-BUTYNE	*	*			*	
METHANOL	*	*			*	
CIS-2-BUTENE	*	*	3.5		*	
3-METHYL-1-BUTENE	*	*			*	
ETHANOL	*	*			21.0	301.1
2-METHYLBUTANE (ISOPENTANE)	*	*			*	495.8
2-BUTYNE						
1-PENTENE		7.1		3.5		
2-METHYL-1-BUTENE	1.3	10.6		6.9		18.7
PENTANE	4.1	48.4	0.5	46.1	1.1	38.2
UNIDENTIFIED C5 OLEFINS		11.1		2.2		
2-METHYL-1,3-BUTADIENE	1.7	0.6	2.6	0.3	2.9	76.2
TRANS-2-PENTENE		13.0		7.2	0.6	0.7
3,3-DIMETHYL-1-BUTENE	0.9		1.0			35.5
CIS-2-PENTENE	3.2	7.5	0.4	3.7	0.6	19.2
2-METHYL-2-BUTENE	0.5	18.3	1.2	11.4	1.5	54.7
TERT-BUTANOL						
CYCLOPENTADIENE		0.3				
2,2-DIMETHYLBUTANE		3.0		4.1	1.7	23.4
CYCLOPENTENE	0.7	2.9	0.3	1.6	0.6	6.6
4-METHYL-1-PENTENE	0.7	1.3		0.8		2.7
3-METHYL-1-PENTENE						
CYCLOPENTANE		4.2	0.4	3.4	0.9	11.9
2,3-DIMETHYLBUTANE	1.9	7.5	0.8	6.0	1.4	49.3
MTBE		59.8				
4-METHYL-CIS-2-PENTENE						
2-METHYLPENTANE	10.6	20.2	7.8	20.6	7.6	71.6
4-METHYL-TRANS-2-PENTENE		0.5		0.4		
3-METHYLPENTANE	4.1	18.9	2.4	12.5	2.7	46.8
2-METHYL-1-PENTENE		1.7	0.2	0.7		2.6
1-HEXENE		1.7	0.2	0.7		2.6
HEXANE	4.8	19.4	3.4	10.2	3.5	31.9
UNIDENTIFIED C6				0.3	1.0	
TRANS-3-HEXENE						
CIS-3-HEXENE		1.0		0.4		1.8
DI-ISOPROPYL ETHER						
TRANS-2-HEXENE		1.0		0.3		2.2

HYDROCARBON SPECIATION DATA
SHED TEST
TOYOTA CAMRY

	SHED results, mg					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	TC-4614-S	TC-4614-M	TC-4637-S	TC-4637-M	TC-4640-S	TC-4640-M
COMPOUND	8/19/2002	8/20/2002	8/2/2002	8/9/2002	8/14/2002	8/15/2002
3-METHYL-TRANS-2-PENTENE	0.7	2.3	0.7	1.1		4.6
2-METHYL-2-PENTENE	0.5	1.8		0.9	0.6	3.1
3-METHYLCYCLOPENTENE						
CIS-2-HEXENE	0.5	1.4		0.6		1.9
ETBE						
3-METHYL-CIS-2-PENTENE	0.8	2.4	0.4	0.9	0.5	3.2
2,2-DIMETHYLPENTANE, NOTE A	1.9	4.0	0.7	3.3	1.3	18.2
METHYLCYCLOPENTANE, NOTE A	1.8	3.9	0.7	3.3	1.3	17.8
2,4-DIMETHYLPENTANE	1.8	3.5	0.7	3.0	1.6	17.3
2,2,3-TRIMETHYLBUTANE		0.4				0.9
3,4-DIMETHYL-1-PENTENE						0.5
1-METHYLCYCLOPENTENE		2.5	0.8	2.4	1.1	9.7
BENZENE	7.0	8.2	4.2	12.7	6.6	29.8
3-METHYL-1-HEXENE						
3,3-DIMETHYLPENTANE		0.5	0.3	0.3	1.0	0.7
CYCLOHEXANE	1.6	2.0	0.6	2.6	3.5	16.7
2-METHYLHEXANE						
2,3-DIMETHYLPENTANE	6.8	10.8	2.8	8.8	5.1	34.6
1,1-DIMETHYLCYCLOPENTANE						
TERT-AMYL METHYL ETHER						
CYCLOHEXENE						
3-METHYLHEXANE	3.9	7.2	1.9	5.8	3.4	18.3
CIS-1,3-DIMETHYLCYCLOPENTANE	0.7	1.1		0.7		4.0
3-ETHYLPENTANE	0.8	0.7		0.6		5.9
TRANS-1,2-DIMETHYLCYCLOPENTANE						
TRANS-1,3-DIMETHYLCYCLOPENTANE	0.5	0.7		0.5	0.7	3.4
1-HEPTENE						
2,2,4-TRIMETHYLPENTANE	4.4	8.5	2.2	8.9	3.7	28.2
2-METHYL-1-HEXENE					0.8	
TRANS-3-HEPTENE						
HEPTANE	4.3	5.4	2.7	6.7	4.2	16.6
CIS-3-HEPTENE						
UNIDENTIFIED C7					1.5	0.9
2-METHYL-2-HEXENE						
3-METHYL-TRANS-3-HEXENE						
TRANS-2-HEPTENE	0.3	0.6				0.7
3-ETHYL-CIS-2-PENTENE						
2,4,4-TRIMETHYL-1-PENTENE	0.5	0.8		0.4	0.7	1.2
2,3-DIMETHYL-2-PENTENE						
CIS-2-HEPTENE		0.4				0.4
METHYLCYCLOHEXANE	2.3	2.2	0.9	2.5	1.9	9.6
CIS-1,2-DIMETHYLCYCLOPENTANE						
2,2-DIMETHYLHEXANE						
1,1,3-TRIMETHYLCYCLOPENTANE		0.3		0.3	1.4	0.8
2,4,4-TRIMETHYL-2-PENTENE						
2,2,3-TRIMETHYLPENTANE	0.7	1.0	0.3	0.6		7.1
2,5-DIMETHYLHEXANE						
ETHYLCYCLOPENTANE						
2,4-DIMETHYLHEXANE	0.3			0.6		3.9
1-TRANS-2-CIS-4-TRIMETHYLCYCLOPENTANE	0.5			0.4		0.5
3,3-DIMETHYLHEXANE						
1-TRANS-2-CIS-3-TRIMETHYLCYCLOPENTANE						

HYDROCARBON SPECIATION DATA
SHED TEST
TOYOTA CAMRY

	SHED results, mg					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	TC-4614-S	TC-4614-M	TC-4637-S	TC-4637-M	TC-4640-S	TC-4640-M
COMPOUND	8/19/2002	8/20/2002	8/2/2002	8/9/2002	8/14/2002	8/15/2002
2,3,4-TRIMETHYLPENTANE	3.9	4.9	1.4	3.3	2.2	10.8
2,3,3-TRIMETHYLPENTANE		1.7	0.7	2.4		12.4
TOLUENE	28.7	18.2	17.2	38.9	29.7	51.7
2,3-DIMETHYLHEXANE		5.4				6.3
1,1,2-TRIMETHYLCYCLOPENTANE						
2-METHYLHEPTANE						
3,4-DIMETHYLHEXANE, NOTE B						
4-METHYLHEPTANE	2.1	2.7	1.0	2.5	1.0	6.7
3-METHYLHEPTANE	2.5	2.8	1.1	2.0	1.7	6.7
1-CIS,2-TRANS,3-TRIMETHYLCYCLOPENTANE						
CIS-1,3-DIMETHYLCYCLOHEXANE						
TRANS-1,4-DIMETHYLCYCLOHEXANE						
3-ETHYLHEXANE						
2,2,5-TRIMETHYLHEXANE	1.3	1.3	0.4	0.9	1.0	4.2
TRANS-1-METHYL-3-ETHYLCYCLOPENTANE						
CIS-1-METHYL-3-ETHYLCYCLOPENTANE	0.3	0.3				0.4
1,1-DIMETHYLCYCLOHEXANE						
TRANS-1-METHYL-2-ETHYLCYCLOPENTANE						
1-METHYL-1-ETHYL-CYCLOPENTANE						
2,4,4-TRIMETHYLHEXANE						
2,2,4-TRIMETHYLHEXANE						
TRANS-1,2-DIMETHYLCYCLOHEXANE						
1-OCTENE						
TRANS-4-OCTENE						
OCTANE	1.8	1.7	0.8	1.9	2.1	4.2
UNIDENTIFIED C8		0.4		0.3		1.6
TRANS-2-OCTENE						
TRANS-1,3-DIMETHYLCYCLOHEXANE, NOTE C						
CIS-2-OCTENE					0.9	
ISOPROPYLCYCLOPENTANE						
2,2-DIMETHYLHEPTANE						
2,3,5-TRIMETHYLHEXANE						0.4
CIS-1-METHYL-2-ETHYLCYCLOPENTANE						
2,4-DIMETHYLHEPTANE					1.7	0.4
4,4-DIMETHYLHEPTANE						
CIS-1,2-DIMETHYLCYCLOHEXANE						
ETHYLCYCLOHEXANE						
2,6-DIMETHYLHEPTANE, NOTE D	0.6	0.7		0.3	1.1	1.0
1,1,3-TRIMETHYLCYCLOHEXANE						
2,5-DIMETHYLHEPTANE, NOTE E	0.4	0.4		0.6		0.9
3,3-DIMETHYLHEPTANE						
3,5-DIMETHYLHEPTANE, NOTE E						
ETHYLBENZENE	6.0	5.7	3.6	6.7	6.3	8.0
2,3,4-TRIMETHYLHEXANE						
2,3-DIMETHYLHEPTANE						
m-& p-XYLENE	17.4	14.6	9.6	21.4	18.1	23.7
4-METHYLOCTANE						
3,4-DIMETHYLHEPTANE						
4-ETHYLHEPTANE						
2-METHYLOCTANE	0.7			0.6		0.8
3-METHYLOCTANE	0.7				0.6	0.7
STYRENE						

HYDROCARBON SPECIATION DATA
SHED TEST
TOYOTA CAMRY

	SHED results, mg					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	TC-4614-S	TC-4614-M	TC-4637-S	TC-4637-M	TC-4640-S	TC-4640-M
COMPOUND	8/19/2002	8/20/2002	8/2/2002	8/9/2002	8/14/2002	8/15/2002
o-XYLENE	7.0	5.7	3.1	8.3	6.2	8.5
1-NONENE						
TRANS-3-NONENE	0.7					
CIS-3-NONENE						
NONANE				0.3		0.4
TRANS-2-NONENE						
ISOPROPYLBENZENE (CUMENE)				0.4		
2,2-DIMETHYLOCTANE						
2,4-DIMETHYLOCTANE		0.5				
n-PROPYLBENZENE	0.7					0.3
1-METHYL-3-ETHYLBENZENE	2.6					
1-METHYL-4-ETHYLBENZENE						
1,3,5-TRIMETHYLBENZENE				0.8		
1-METHYL-2-ETHYLBENZENE	0.3		0.3	1.1		0.9
1,2,4-TRIMETHYLBENZENE						
TERT-BUTYLBENZENE						
1-DECENE						
DECANE, NOTE F	0.3	1.6	1.0	0.8		
ISOBUTYLBENZENE, NOTE F	0.3	1.5	0.9	0.7		
1,3,-DIMETHYL-5-ETHYLBENZENE						
METHYLPROPYLBENZENE (sec butylbenzene)						
1-METHYL-3-ISOPROPYLBENZENE					2.6	
1,2,3-TRIMETHYLBENZENE						
1-METHYL-4-ISOPROPYLBENZENE						
INDAN						
1-METHYL-2-ISOPROPYLBENZENE	1.5					
1,3-DIETHYLBENZENE						
1,4-DIETHYLBENZENE						
1-METHYL-3-N-PROPYLBENZENE						
1-METHYL-4-N-PROPYLBENZENE, NOTE G						
1,2 DIETHYLBENZENE						
1-METHYL-2-N-PROPYLBENZENE			2.4	0.6		
1,4-DIMETHYL-2-ETHYLBENZENE						0.3
1,3-DIMETHYL-4-ETHYLBENZENE						
1,2-DIMETHYL-4-ETHYLBENZENE	0.6					
1,3-DIMETHYL-2-ETHYLBENZENE						
UNDECANE						
1,2-DIMETHYL-3-ETHYLBENZENE						
1,2,4,5-TETRAMETHYLBENZENE						
2-METHYLBUTYLBENZENE (sec AMYLBENZENE)						
3,4 DIMETHYLCUMENE						
1,2,3,5-TETRAMETHYLBENZENE						
TERT-1-BUT-2-METHYLBENZENE						
1,2,3,4-TETRAMETHYLBENZENE						
N-PENT-BENZENE					0.5	
TERT-1-BUT-3,5-DIMETHYLBENZENE						
TERT-1-BUTYL-4-ETHYLBENZENE					0.6	
NAPHTHALENE						
DODECANE						
1,3,5-TRIETHYLBENZENE						
1,2,4-TRIETHYLBENZENE						
HEXYLBENZENE						

HYDROCARBON SPECIATION DATA
SHED TEST
TOYOTA CAMRY

	SHED results, mg					
	Houston Fuel		Atlanta Fuel		Chicago Fuel	
	TC-4614-S	TC-4614-M	TC-4637-S	TC-4637-M	TC-4640-S	TC-4640-M
COMPOUND	8/19/2002	8/20/2002	8/2/2002	8/9/2002	8/14/2002	8/15/2002
UNIDENTIFIED C9-C12+	0.4		4.7		4.8	0.5

*C1 - C4 DATA NOT AVAILABLE DUE TO INSTRUMENT MALFUNCTION

A - 2,2-Dimethylpentane and methylcyclopentane co-elute. GC peak area split equally between the two compounds.

B - 3-Methyl-3-ethyl-pentane co-elutes with reported compound. Not reported separately.

C - Cis-1,4-Dimethylcyclohexane co-elutes with reported compound. Not reported separately.

D - Propylcyclopentane co-elutes with reported compound. Not reported separately.

E - 2,5-Dimethylheptane and 3,5-dimethylheptane co-elute. GC peak area split equally between the two compounds.

F - Decane and isobutylbenzene co-elute. GC peak area split equally between the two compounds.

G - n-Butylbenzene co-elutes with reported compound. Not reported separately.

H - Isobutyraldehyde and methyl ethyl ketone co-elute. LC peak area split equally between the two compounds.

Appendix G

API Section 211(B) Tier-2 Exposure Database – Naming Convention

API Section 211(B) Tier-2 Exposure Database

The data have been organized into four data files (API Data_Continuous.xls, API Data_SPME.xls, API Data_Time-integrated.xls and API Data_Reconstructed.xls) containing the continuous, SPME, time-integrated and reconstructed exposure data. All files include data fields describing the sample collection conditions (e.g.; microenvironment, fuel type, test mode) as well as data flags indicating problems with the analytical or sample collection methods. Tables explaining the meaning of each data field are also included with each file. The files are supplied in Excel workbook format for convenience, but have been formatted to be compatible with common database software (the value -99 is used for missing data points, and time is in hhmm text format)

The time-integrated data contains speciation results from canister, DNPH cartridge, and TENAX adsorbent tubes, plus time-averaged values of pollutants and environmental parameters that were measured continuously during the batch sample collection periods. Within the time-integrated data file there are 4 sub-categories that are presented separately due to the differing number of experimental variables for each type: 1) microenvironment exposure measurements from the three cities, 2) breath samples collected from subjects participating in 4 of the microenvironments, 3) residence with attached garage, and 4) trailing vehicle exposure tests.

The SPME data set is assembled in essentially the same manner as the time-integrated data, but contains only the BTEX hydrocarbon compounds and uses some different sample descriptors where necessary to identify which portion of each test the sample was collected. The same sample IDs are used to facilitate comparison of the two sampling methods.

The third data file contains 1-minute averages of the pollutants and environmental parameters that were measured continuously during the microenvironment exposure tests in the 3 cities. Data were typically logged every 10 seconds during testing, but to reduce measurement noise, make the data set more manageable, and reduce the effect of minor timing discrepancies between instruments due to imperfect clock synchronization or differences in sample line residence time, the data was time averaged by minute. Each data record in this file has both a time/date stamp and an identification code that relates it to the corresponding time-integrated sample. Data flags are given to identify any missing or invalid data for each minute. Due to the large size of this file, the various sample descriptors have not been included but these can be derived from the identification code as described in the included key.

The fourth file contains 1-min reconstructed data for benzene, 1,3-butadiane and formaldehyde based on PID and NDIR CO continuous data, as described in Chapter 1 of this report. Both full time canister and DNPH-carbonyl samples and 5-min canister samples collected over a peak exposure in selected MEs are included.

Table G-1 contains the key to the name of the samples collected during this study.

Table G-1. Naming convention for the API data

Experiment	Position						
Type	1st Location	2nd Season	3rd + 4th	5th Mode	6th	7th	8th
ME-Atlanta	A	S-Summer W-winter	ME number (01, etc)	M-main P- 5 min B-breath	Under score	Replicate number	Breath: A-pre; B-peak, C-post
ME-Chicago	C	S-Summer W-winter	ME number	M-main P- 5 min B-breath	Under score	Replicate number	Breath: A-pre; B-peak, C-post
ME-Houston	H	S-Summer W-winter	ME number	M-main P- 5 min B-breath	Under score	Replicate number	Breath: A-pre; B-peak, C-post; NOx denuder: D
trailing Vehicle	V	S-Summer W-winter	Fuel (a,c,h) + vehicle (t-truck, s-sedan)	MalFunction (F) Normal (N)	Under score	High (H), Low (L) vent, or coMbined (m)	Background – A; Main-B; Idle-C
Residence w/attached garage	R	S-Summer W-winter	Fuel (a,c,h) + vehicle (t-truck, s-sedan)	MalFunction (F) Normal (N)	Under score	Kichen (K) or Garage(G) location	Background: A; Main - B

For example: AS02M_1 means Atlanta, summer, ME#2, first replicate. HW11B_3B means Houston, winter, ME#11, breath sample, peak

VWasN_HC means trailing vehicle, winter, Atlanta fuel, sedan, normal mode, high vent, idle. RSctF_KA means garage, summer, Chicago fuel, truck, malfunction, kitchen, background

Appendix H

Measurement Data Quality Objectives

Appendix H. Data Quality

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1.1 Measurement Data Quality Objectives

Data quality objectives, including measures of accuracy, precision, detection limit, time resolution, and known interferences, are summarized in Table H-1. For the two CO instruments and the PID, we use manufacturer's specifications for most data quality parameters.

There are also some limitations that are not covered by the tabular summary. For the T-15 CO (electrochemical detector), we find that although the data system can collect data every 10 sec, the response of this instrument responds to rapid changes in concentration on a longer time frame. This may occur since CO must diffuse across a membrane to be measured. The finite diffusion time means that rapid spikes in concentration may not achieve steady-state values across the membrane and are thus not fully measured. Comparisons among CO methods are good over integration times greater than one minute. There were interferences from batteries (H_2 emissions) that were used to power instruments inside the van that showed up as a rising signal from the T-15 CO unit when the vehicle windows were closed. Under high-ventilation conditions in the vehicle or outdoors, no such interferences were observed. At high humidity near saturation we did observe high T-15 CO readings that we suspect are due to the humidity.

The PID does not have an accuracy measure since this instrument reports the total ion signal, which will differ with the distribution of compounds ionizable at 10.6 eV. However, since we find a good correlation of PID signal with BTEX as measured in the canisters, we feel this measurement provides a reasonable surrogate time series signal for these compounds. This instrument does respond to very high humidity where there is condensation of water on the lamp and other areas of the electrometer that are exposed to air. In addition, we observed some summer instances where the PID readings increased inside the vehicle cabin under low ventilation conditions with no change in any other measurement. This may be a response to off-gassing of plasticizers in cabin materials that are mostly phthalate esters.

Table H-1. Measurement data quality

Instrument	Accuracy	Precision	Det Lim	Time Res.	Artifacts	Specifications	Source
CO-T15	+/- 1 ppm	+/-0.05 ppm	0.1 ppm	10 sec	H2, very high humidity	Electrochemical Detector	Manufacturer literature
CO-NDIR	0.50%	+/-0.02 ppm	0.04 ppm	1 sec	None	NDIR	Manufacturer literature
PID	NA	10%	1 ppb	1 sec	Plasticizers, very high humidity	10.6 eV lamp PID	Manufacturer literature
HCHO (a)	<15%	<5%	1 ppb	1 min	None	Hantzch rxn/fluorescence	DRI Use/intercomparisons
MS-200	<8%	<5%	1-3 ppbv	1 min	None	Mass spectrometer	DRI Use/intercomparisons
SPME	3-50%	2-15%	0.2 ppbv	variable	None	GC/FID & PID	DRI Use/intercomparisons
Canister	<5%	<3%	0.05 ppbC	variable	None	GC/FID	DRI Use/intercomparisons
DNPH	<5%	<3%	0.1 ppbv	variable	None	HPLC/Photodiode array	DRI Use/intercomparisons

(a) HCHO performance parameters based on Battelle instrument performance in the Reno pilot study.

1.2 Quality Control and Assurance

1.2.1 External Performance Audit for the API Section 211(b) Study

A site visit to the mobile laboratory and all twelve microenvironment (ME) sampling sites in Atlanta, GA was conducted during February 23-27, 2004, by the independent auditor, Christine Sexsmith, Sexsmith Consulting Services, LLC. The auditor was on site at the mobile lab or in the sampling van and witnessed measurement in at least one of each of the 12 microenvironments sampled. A technical procedure inspection was conducted to verify that DRI personnel were following the approved exposure protocol and that no special circumstances occurred that could affect the outcome of the study. This audit was followed up by the DRI Organic Analytical Laboratory audit in April 2005. The reports from these two audits are available from the API upon request.

1.2.2 Laboratory Comparison and External Performance Audits

The DRI Organic Analytical Laboratory (OAL) participated in the International Hydrocarbon Intercomparison Experiment, organized by National Center for Atmospheric Research (NCAR). The results of Tasks I, II, and III of this laboratory intercomparison have been published (Apel et al., 1994; 1999). Task I involved analysis of a two-component hydrocarbon mixture of known composition and unknown concentration prepared by NIST. The DRI results were within the acceptable range of ± 5% of the nominal values provided by NIST. In Task II the participating laboratories were asked to identify and quantify 16 components present, in the ppb range, in a mixture prepared by NIST. The agreement between the DRI values and the NCAR values, as well as with nominal values provided by NIST, were within acceptable ranges (± 15%). Task III was more complex, involving the analysis of 60 commonly observed hydrocarbons at low ppbv concentrations in a mixture prepared and analyzed by Scott-Marrin, Inc., NCAR and U.S. EPA laboratory. The next tasks, IV and V, which were carried out in 1996 -1997, involved the analysis of ambient air samples in the ppbv and pptv concentration ranges, respectively. The DRI has successfully completed these tasks with agreement between the DRI values and the NCAR values for Tasks III – V within the acceptable range (± 10%).

In the summers of 1995 and 1996 the DRI OAL participated in the NARSTO-Northeast hydrocarbon intercomparison study, involving the analysis of two ambient air samples by participating laboratories. Participants included Biospheric Research Corporation (BRC), State University of New York at Albany (SUNYA), EPA Region I, DRI, and eight of the PAMS network labs in the northeastern U.S. The DRI laboratory performed best in comparison with all other participants (Fujita et al., 1997). In the summer of 1997, the DRI OAL participated in the SCOS97-NARSTO performance audit and laboratory comparisons involving speciated non-methane hydrocarbons (NMHC), carbonyl compounds, halogenated compounds and biogenic hydrocarbons (Fujita et al., 2003). Again, the agreement between DRI values and nominal values were within the acceptable range (± 10%).

During the last six years, the DRI laboratory participated in non-methane hydrocarbon laboratory performance audits, organized by the Quality Assurance Section, Monitoring and Laboratory Division, CARB. The last intercomparison studies, organized in 1999-2002, involved the analysis of ambient air samples by California district laboratories and the DRI OAL laboratory. The results of these intercomparison studies were always very favorable for OAL.

1.2.3 Time-Integrated Methods

Sample Custody. For our quality assurance plan, a sample is considered in custody when it is received by the DRI Division of Atmospheric Sciences (DAS) receiving department from an official package courier. At this time it is logged into the general receiving department's logbook and the Organic Analytical Laboratory is notified of the package's arrival. A representative of the laboratory signs for the package and returns with it to the laboratory where he opens it. The samples are logged into the Organic Analytical Laboratory's receiving logbook, the chain-of-custody form is updated, and the samples are stored appropriately for the sample type. At this time any unusual situations (damaged shipping container, evidence of damage and/or tampering, etc.) are brought to the attention of the laboratory manager. If necessary, a review will be initiated to determine if the damage compromised the integrity and/or quality of the sample.

Samples are stored in the Organic Analytical Laboratory, inside the DRI Northern Nevada Science Center (2215 Raggio Parkway, Reno, NV). The room is locked when not in use and the building has limited access (i.e., it is locked from 1730 to 0730 weekdays and all weekends to ensure access only to authorized personnel).

When a sample is analyzed, its identification number (sample number) is recorded both in the written log book for each instrument and in the Laboratory Information Management System (LIMS) file created for that analysis. The sample number serves as a tracking number, as does the LIMS file itself. Canisters will not be cleaned until each sample has passed initial validation.

Sampling Systems. The sampling equipment is leak-tested and the electronic flow controllers are calibrated prior to the delivery to the field. The flow controllers are re-calibrated after the program to determine if any significant change in the calibration has occurred. In addition, the flow controllers are checked at least weekly in the field with a Galibrator (an instrumented soap bubble flow meter). The average of the pre- and post-sampling flow rates is used to determine the sample volume.

Sampling systems that have internal surfaces upstream of the collection media (e.g., canister sampler), must be cleaned and certified for cleanliness prior to sampling.

Sampling Media Preparation and Certification. Multibed adsorbent cartridges consisting of Tenax TA, Carbotrap (or Carboxen) and Carbosieve are used for ethanol sample collection. Prior to use, the Tenax-TA solid adsorbent is cleaned by Soxhlet extraction with hexane/acetone mixture (4/1 v/v) overnight, and dried in a vacuum oven at ~ 80 °C. The dry Tenax is packed into Pyrex glass tubes together with Carbotrap and Carbosieve and thermally conditioned for four hours in an oven at 300 °C under nitrogen purge. Approximately 10% of the precleaned cartridges are tested by GC/FID prior to sampling.

After cleaning, the cartridges are sealed using clean Swagelok caps (brass) with graphite/Vespel ferrules, placed in metal containers with activated charcoal, and kept in a clean environment at room temperature until use.

The DNPH impregnated SiO2 cartridges are purchased from Waters, Inc., in batches of 25. One cartridge from each batch is tested for background contamination by the High Performance Liquid Chromatography (HPLC) method prior to sampling.

The canisters are cleaned by repeated evacuation and pressurization with humidified zero air, as described in the EPA document "Technical Assistance Document for Sampling and Analysis of Ozone Precursors" (October 1991, EPA/600-8-91/215). Six sequential cycles of evacuation to ~ 0.5 torr absolute pressure and pressurization with ultra-high-purity (UHP) humid zero air to ~ 20 psig are used. The DRI procedure differs from the EPA method in that canisters are heated to 140 °C during the vacuum cycle in the DRI procedure and more vacuum-pressure cycles are used. According to our experience and that of others (Rasmussen, 1992), heating is essential to achieve the desired canister cleanliness. Also, the canisters are maintained longer under vacuum, about one hour in the DRI method, as opposed to half of an hour in the EPA method.

At the end of the cleaning procedure, one canister out of twelve in a lot is filled with humidified UHP zero air and analyzed by the gas chromatograph/flame ionization detection (GC/FID) method. The canisters are considered clean if the total non-methane organic compound (NMOC) concentration is less than 10 ppbC, and the concentration of any individual targeted compound is less than 0.2 ppbv. Canister cleaning and certification are described in the DRI SOP1-701.4 .

Analytical Systems. Prior to analysis, all analytical systems (i.e., GC/ECD/FID, HPLC, GC/MS, and GC/IRD/MSD) are checked for cleanliness and are certified clean (less than 0.1 ppbv of targeted compound). Quality control in the laboratory includes instrument calibration for each batch of samples analyzed, replicates of standards, and reanalysis of approximately 10% of the samples for estimation of analytical precision, which historically has been better than 6%. In past programs, field blanks have come in at 0.5-1 ppb levels, based on the air volume of the samples. Coefficients of variation (CV) calculated from observed differences between duplicate samples were less than 10%. The data quality in this program was within DRI's historical range.

Standards and Materials. Each primary reference standard is traceable to an NIST Standard Reference Material (SRM). For canister hydrocarbon speciation, we use NIST SRM 1805, which consists of 254 ppb of benzene in nitrogen.

Gas cylinders of helium, nitrogen, hydrogen, and ultra zero air (all UHP grade) — from the best sources available — are used for the GC/FID and GC/MSD. The current inventory of reference samples at DRI's Organic Analytical Laboratory consists of over 250 single- and multi-component reference samples, and includes compounds of interest in this project.

Calibrations. The GC/FID, HPLC, and GC/MS systems are calibrated initially by multipoint calibration (i.e., three levels plus humid zero air), and regularly checked by a one-point calibration, using the appropriate NIST SRM or other standard. A day-to-day

reproducibility of ±10% is acceptable for either standard. Control charts are used for assessing analytical system performance.

Samples that fall outside the calibration range are diluted until bracketed by the calibration curve. Instrument responses to calibration standards for each parameter are analyzed using a least squares linear regression. The calibration must generate a correlation co-efficient (R^2) of 0.99 to be acceptable.

During the course of analysis, calibration standards are routinely analyzed to ensure that the instrument response has not changed. The criterion of an instrument response within 10% of the expected response is used by the analyst to determine whether the instrument must be recalibrated.

Relative Accuracy and Precision of Sampling and Analysis. Accuracy involves the closeness of a measurement to a reference value and reflects elements of both bias and precision. Percent relative accuracy is calculated:

$$\% \text{ Relative Accuracy} = \frac{X - Y}{X} \times 100$$

where:

Y = concentration of the targeted compound, as determined by the analytical instrument, and

X = concentration of the targeted compound in the NIST (or traceable) standard.

If the percent relative accuracy does not fall below 20%, the instrument is recalibrated.

Precision is a measure of the repeatability of the results. The overall precision of sampling and analysis is determined by the analysis of collocated samples. These precision tests depend upon available resources. Historically, we have performed collocated sampling of all samplers, of each type, that were deployed in the measurement program to establish equivalency and overall measurement precision prior to actual field sampling. Overall precision was within 20%.

Removal of Ozone and NOx Interferences. Since the carbonyl compound ambient measurement results are subject to various artifacts due to interaction with ozone, we use either a honeycomb O_3 denuder coated with sodium carbonate/sodium nitrite/glycerol mixture (method developed by Dr. Koutrakis from the Harvard School of Public Health), or a copper tube O_3 denuder coated with KI, as recommended by EPA Method TO-11a. Since ambient NO_2 might react with 1,3 butadiene, we use a honeycomb NO_2 denuder coated with triethanolamine (a method also developed by Dr. Koutrakis).

1.2.4 Semi-Continuous Methods

For SPME fibers, blanks and calibration checks were performed daily in order to determine the performance of the instrument and quality of the data. Fibers were kept in the injector port throughout the sample run in order to guarantee that the entire sample had been desorbed and to aid in conditioning of the fiber. In addition, fibers were cleaned in a fiber conditioner at 300 °C for at least one hour. The fiber conditioner

consisted of a 304 SS container with 5 ports and a Watlow heater/temperature controller capable of maintaining temperatures in the 200-300 °C range. A helium flow was maintained during fiber conditioning. One fiber per batch of 5 was checked for cleanliness after conditioning.

Multi-level calibrations were done initially and throughout the summer field study. Liquid calibration was done by injecting 1 μl of a liquid standard prepared in pentane with benzene, toluene, ethylbenzene, and xylenes (BETX) at different concentrations (1, 5, 10, 20, 40, 50, and 100 ng/μl). Gas calibration was performed with certificated standards at different concentrations (20, 80, 100, 200, and 500 ppbv for each compound). Gas standards were stored in canisters and transferred to 1L Tedlar bags for static exposures of SPME fibers. Gas calibrations were performed for different fiber exposure times.

SPME 75 μm Carboxen-PDMS fibers were used with portable or manual samplers. When manual samplers were used, the tip of the needle was closed with a septum or Teflon tape. Fibers were kept after sampling in sealed Mylar bags inside a cooler with dry ice. Storage stability tests showed that samples were preserved without any loss of analyte up to 5 hours (and reasonably preserved without substantial losses for as long as three days) when stored at dry ice temperature. In Atlanta, SPME samples were analyzed, on average, 10 hours after sampling, with a minimum of 1 hour and a maximum of 26 hours between sampling and analysis; 54% of the samples were analyzed before 10 hours of storage at dry ice temperature).

Detection limits for the BTEX compounds were benzene 0.2 ppbv, toluene 0.3 ppbv, ethylbenzene 0.2 ppbv, m-p-xylene 0.2 ppbv, and o-xylene 0.2 ppbv. Precision was evaluated in the laboratory by comparing replicates and standards reproducibility. Two sets of replicates were placed side by side for 10 minutes inside solvent cabinets. Also, three replicates of 4 different standard concentrations were included in the analysis. Replicates ranged from 2 to 15% error for all species. Accuracy was determined by daily calibration checks that varied within a range of 3-30% for benzene. When the relative accuracy did not fall within the 0-30% range for benzene, the GC was recalibrated.

The agreement between canister and SPME methods during the Atlanta field study was within 3-50%. For comparison, Li *et al*., 2001, shows an agreement between SPME and a charcoal sampling method within a factor of two (100%), with a fiber repeatability of 20-30%, for 75 μm Carboxen/PDMS.

1.2.5 Continuous Methods

<u>The CO instruments</u> were calibrated by standards purchased from Scott Specialty and zero points were established by zero air purchased from Air Gas. Since both the T-15 and NDIR instruments have only zero and span controls, we used a span gas close to our expected concentrations, in this case 10 ppmv. For the T-15 CO instrument, a cap is used to flood the sensor with either zero or span gas. The cap is kept in place until a stable reading is obtained. For the NDIR, the gas was introduced through the sample inlet line.

Instruments were checked weekly and recalibrated as needed. In general the CO instruments were very stable. The PID was calibrated with isobutene as a span gas as recommended by the manufacturer.

The MS-200 is calibrated by a standard containing pentane, isopentane, benzene, toluene, and o-xylene. This standard is mixed at DRI and tested against NIST traceable standards before being used in the field. Although the MS-200 is very stable once calibrated and essentially needs only zero checks before each run with the zero air cylinder carried with the instrument, calibration checks are made every few days to confirm instrument calibration. DRI purchased an Alpha Omega continuous HCHO instrument, the only commercially available instrument of its type, for use in the Atlanta field study. The instrument is, in theory, identical to the Battelle instrument that performed well in our Reno pilot study in February 2002. It uses the same reagents, the same reaction, and the same fluorescence basis for detection. However, there are engineering differences in the air/fluid interface, the pumping system, the mixing of the reagents, the flow through the reactor, and the detectors. Although we have made a number changes to the instrument, it did not performed well in this study.

Precision evaluation of portable PID instruments. A series of tests were performed to evaluate the precision of the estimated VOC concentrations measured by the ppbRAE portable PID instruments. Although it is known that the concentrations recorded by these instruments vary with changes in the composition of the ambient VOC, making the accuracy of the instruments hard to quantify, the precision can be evaluated by comparing the concentrations measured by two identical instruments sampling from the same source. This measure of precision is important if simultaneous measurements of VOC concentration in two locations are to be compared.

In each test, both instruments were connected to the same inlet using a stainless steel 'T' and tubing. After synchronizing the internal clocks, data logging was started and a VOC source was introduced at varying concentrations up to 10 ppm for a period of 20 to 45 minutes. The resulting 1-minute average concentrations from the two units were compared by linear regression to determine the level of correlation and bias. The test was repeated on 4 separate days over a 10-day period. Zero checks and calibrations with 10 ppm isobutylene were made prior to the first test and between the second and third.

In all tests, the correlation was high (R^2 = 0.97 or better) with a zero intercept. Slopes ranged from 0.79 to 1.45, indicating no consistent comparative bias. Since the average concentration in most microenvironments is typically less than 100 ppb, we also evaluated the precision in this range. In two tests following the calibrations, the correlation was good (R^2 = 0.98)with the slope varying from 0.75 to 1.36. For two other tests, correlations were less (R^2 = 0.45 and 0.66) with slopes of 0.73 and 0.55. As earlier, the intercepts were zero. Overall, the test results suggest that instrument sensitivity varies, even with frequent calibration. Averaged ambient data may have a precision of about ± 35% or higher when comparing small numbers of measurements or when at near-background concentrations.

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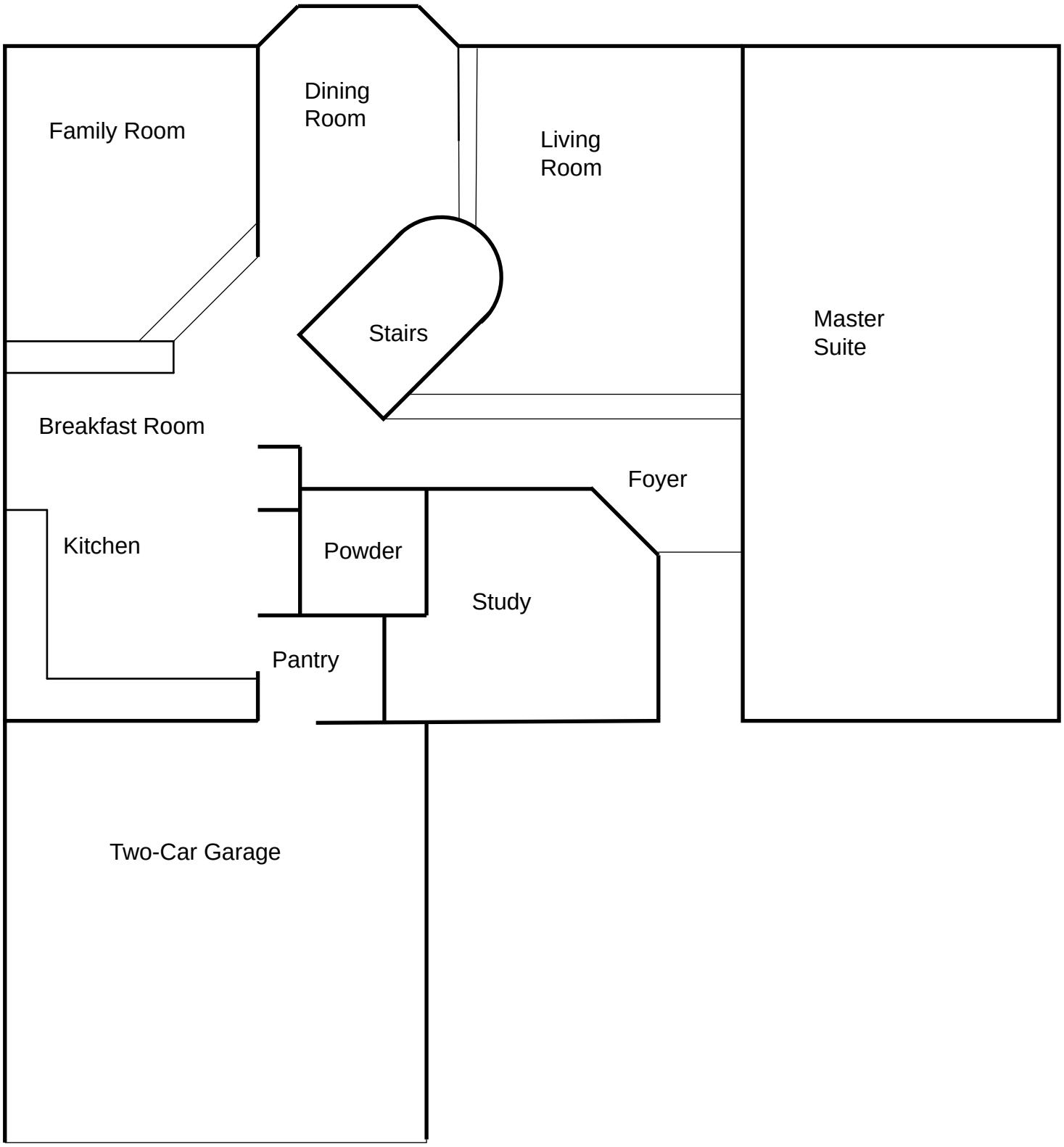
Appendix I

Houston Test House Floor Plan Schematic


Family Room
Dining Room
Living Room
Master Suite
Stairs
Breakfast Room
Foyer
Kitchen
Powder
Study
Pantry
Two-Car Garage